University of Crete Department of Chemistry Laboratory of Bioinorganic Chemistry



Doctoral Thesis

Synthesis and Characterization of Porphyrin Derivatives as Photosensitizers in Solar Energy Harnessing Schemes

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Τμήμα Χημείας

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Σύνθεση και Χαρακτηρισμός Πορφυρινικών Παραγώγων ως Φωτοευαισθητοποιητές σε Συστήματα Αξιοποίησης της Ηλιακής Ενέργειας.

Νικολάου Βασίλειος

Υπεύθυνος Καθηγητής: Αθανάσιος Γ. Κουτσολέλος

Ηράκλειο 2017

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ΠΡΑΚΤΙΚΟ ΕΠΤΑΜΕΛΟΥΣ ΕΞΕΤΑΣΤΙΚΗΣ ΕΠΙΤΡΟΠΗΣ ΓΙΑ ΤΗΝ ΕΞΕΤΑΣΗ ΔΙΔΑΚΤΟΡΙΚΗΣ ΔΙΑΤΡΙΒΗΣ

Η Επταμελής Εξεταστική Επιτροπή της Διδακτορικής Διατριβής του κ. Νικολάου Βασιλείου, η οποία ορίσθηκε στην από 22/03/2016 συνεδρία της Γ.Σ.Ε.Σ., συνεδρίασε σήμερα Παρασκευή 29 Σεπτεμβρίου 2017 να εξετάσει τη διατριβή του υποψήφιου με τίτλο:

«Synthesis and characterization of porphyrin derivatives as photosensitizers in solar energy harnessing schemes »

Τα παρόντα μέλη της Επταμελούς Εξεταστικής Επιτροπής εκφράζουν ομόφωνα την πλήρη ικανοποίησή τους για την υψηλή ποιότητα του περιεχομένου και της υποστήριξης της Διατριβής.

Τα Ερευνητικά αποτελέσματα της εργασίας του κ. Νικολάου Βασιλείου είναι σημαντικά, πρωτότυπα και διευρύνουν το πεδίο της έρευνας στον Τομέα Ανόργανης Χημείας.

Ως εκ τούτου η Επταμελής Εξεταστική Επιτροπή προτείνει ομόφωνα την απονομή του Διδακτορικού Διπλώματος στον κύριο Νικολάου Βασίλειο.

Τα μέλη της Επταμελούς Εξεταστικής Επιτροπής για την Αξιαλόγηση της Διδακτορικής Διατριβής του κυρίου Νικολάου Βασιλείου:

- Κουτσολέλος Αθανάσιος (Επιβλέπων) Καθηγητής Τμήματος Χημείας Πανεπιστημίου Κρήτης
- 2. Δημάδης Κωνσταντίνος Καθηγητής Τμήματος Χημείας Πανεπιστημίου Κρήτης
- Μήλιος Κωνσταντίνος
 Αναπληρωτής Καθηγητής
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- 6. Μητράκη Άννα Καθηγήτρια Τμήματος Επιστήμης και Τεχνολογίας Υλικών Π.Κ
- 7. Αγγαρίδης Παναγιώτης Επίκουρος Καθηγητής Τμήματος Χημείας ΑΠΘ

Dedicated to my loving mother

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The scholarship offered by IKY national institution is greatly acknowledged along with the research program "Perspect-H2O-Supramolecular photocatalytic water splitting" that supported financially my participation in many conferences as well as the short term scientific visits to other universities-institutions throughout the years of my PhD thesis.

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Curriculum Vitae

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Academic Background	
2014-2017	PhD in Chemistry, University of Crete Laboratory of Bioinorganic Chemistry, Chemistry Department, Greece.
	PhD Thesis: Title: "Synthesis and characterization of porphyrin derivatives as photosensitizers in solar energy harnessing schemes."
2012-2014	Master degree in Chemistry, University of Crete Laboratory of Bioinorganic Chemistry, Chemistry Department, Greece (8.77/10)
	<u>Master Thesis:</u> Title: "Click reactions to porphyrin derivatives for the synthesis of new compounds targeting photovoltaic applications." Laboratory of Bioinorganic Chemistry, Chemistry Department, University of Crete, www.chemistry.uoc.gr/coutsolelos
	Courses passed during 1 year: Computational Study of Molecules and Nanomaterials, Chemistry of Macrocyclic Systems, Applications of Spectroscopy in Structure Characterization, Solid State Chemistry, Nuclear Magnetic Resonance (NMR), Contemporary Chemistry.
2008-2012	Bachelor degree in Chemistry, University of Crete, Department of Chemistry, Greece (7.55/10)
	<u>Undergraduate Thesis</u> : Title: "Design and synthesis of a new porphyrin compounds for Dye- sensitized solar cells applications." Laboratory of Bioinorganic Chemistry, Chemistry Department, University of Crete.
	Courses passed during 4 years: Principles of Chemistry, Physics I & II, Mathematics I & II, Introduction to Computer, Qualitative and Quantitative Analysis,

	Organic Chemistry I & II, Inorganic Chemistry I & II, Analytical Chemistry I & II, Physical Chemistry I and II, Biochemistry I & II, Introduction to Biology, Biomolecular Chemistry, Environmental Chemistry, Metal Ions in Medicine, Bioinorganic materials, Bioinorganic Chemistry, Preparatory English I & II.
Work Free avier of	Lab courses passed during 4 years: Organic Chemistry I & II, Inorganic Chemistry I & II, Analytical Chemistry I & II, Physical Chemistry I and II, Biochemistry.
work Experience	
06/2012 -09/2012	Trainee in General Chemical State Laboratory, Rhodes, Greece.
11/2012-09/2016	Participation in scientific research program «Perspect-H2O- Supramolecular photocatalytic water splitting». www.cost.eu/domains_actions/cmst/Actions/CM1202
Research Experience	
01/07/2013 -10/07/2013	Visitor researcher at University of Southampton, England. Bio- organic and Materials Chemistry Lab, School of Chemistry. Professor Eugen Stulz. Purpose of visit: "DNA modification with porphyrins for DNA templated supramolecular multiporphyrin assemblies".
01/12/2015-08/12/2015	Visitor researcher at University of Newcastle, England. Artificial Photosynthesis Team, School of Chemistry. Professor Dr. Elizabeth Gibson. Purpose of visit: "Photocatalytic hydrogen production experiments with metallated porphyrins and corroles as photosensitizers and catalysts".
Funding	
11/2012-10/2014	Participation in scientific research program of the University of Athens entitled "Synthesis of new advanced materials with new generation catalysts by reactions permutation ring opening polymerization (ROMP)".
12/2015-08/2017	Postgraduate Scholarship: Research Projects for Excellence IKY/Siemens.
Teaching Experience	
09/2012-12/2012	Student Practice Inorganic Laboratory assistant: University of Crete, Department of Chemistry in Inorganic Chemistry Laboratory I, supervising by Prof. Vardalachaki E.
09/2013-12/2013	Student Practice Inorganic Laboratory assistant: University of Crete, Department of Chemistry in Inorganic Chemistry Laboratory I, supervising by Prof. Vardalachaki E.

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Foreign Languages	
	Greek: Native language. English: Certificate of Proficiency in English (2009).
Technical Skills	
	Design, Synthesis, purification and characterization of chromophores. Synthesis under anaerobic conditions.
	¹ H and ¹³ C-NMR, UV-Visible, FT-IR, spectroscopies, GC-MS, HPLC, MALDI-TOF MS, Electrochemistry and X-Ray. Fluorescence spectroscopy and Lifetime measurements.
	Windows, Microsoft Office (Word, Excel, PowerPoint, Access, Front page).
	ChemBioOffice, Chem3D, EndNote, Origin, Chemcraft and Avogadro.
	Basic knowledge of density functional theory (DFT) calculations (Gaussian, Unix commands)
Publications	
	1. Zervaki, G.E.; Papastamatakis, E.; Angaridis, P.A.; <u>Nikolaou, V.</u> ; Singh, M.; Kurchania, R.; Kitsopoulos, Th.N.; Sharma, G.D.; Coutsolelos, A.G " <i>A propeller-shaped, triazine-linked porphyrin</i> <i>triad as efficient sensitizer for dye-sensitized solar cells</i> ", <i>Eur. J.</i> <i>Inorg. Chem.</i> 2014 , <i>6</i> , 1020-1033.
	2. Panda, M.K.; Lazarides, T.; Charalambidis, G.; <u>Nikolaou, V.;</u> Coutsolelos, A.G. "Five-coordinate indium(III) porphyrins with hydroxy and carboxy BODIPY as axial ligands: Synthesis, characterization and photophysical studies", Eur. J. Inorg. Chem. 2015, 3, 468-477.
	3. <u>Nikolaou, V.</u> ; Angaridis, P.A.; Charalambidis, G.; Sharma, G.D.; Coutsolelos, A.G "A "click-chemistry" approach for the synthesis of porphyrin dyads as sensitizers for dye-sensitized solar cells", Dalton Trans., 2015, 44, 1734-1747.

<u>Nikolaou, V.</u>; Karikis, K.; Farré, Y.; Charalambidis, G.; Odobel,
 F.; Coutsolelos, A.G. *"Click made porphyrin-corrole dyad: a system for photo-induced charge separation"*, *Dalton Trans.*, 2015, 44, 13473-13479.

5. Zervaki, G.E.; Nikiforou, A.; <u>Nikolaou, V.</u>; Sharma, G.D.; Coutsolelos, A.G. "Scorpion-shaped mono(carboxy)porphyrin-(BODIPY)₂, a novel triazine bridged triad: Synthesis, characterization and dye sensitized solar cell (DSSC) applications", J. Mater. Chem. C, **2015**, 3, 5652-5664.

6. Zervaki, G.E.; Tsaka, V.; Vatikioti, A.; Georgakaki, I.; <u>Nikolaou</u>, <u>V.</u>; Sharma, G.D.; Coutsolelos, A.G. "A triazine di(carboxy)porphyrin dyad versus a triazine di(carboxy)porphyrin triad for sensitizers in DSSCs", Dalton Trans., 2015, 44, 13550-13564.

7. Sharma, G.D.; Angaridis, P.A.; Pipou, S.; Zervaki, G.E.; <u>Nikolaou, V.;</u> Coutsolelos, A.G. *"Efficient co-sensitization of dye-sensitized solar cells by novel porphyrin/triazine dye and tertiary aryl-amine organic dye"*, Org. Electron., 2015, 25, 295–307.

8. Charisiadis, A.; Stangel, C.; <u>Nikolaou, V.</u>; Roy, M.S.; Sharma, G.D.; Coutsolelos, A.G. "A supramolecular assembling of zinc porphyrin with a π -conjugated oligo-(phenylenevinylene) (oPPV) molecular wire for dye sensitized solar cell", RSC Adv., **2015**, *5*, 88508-88519.

9. D. Chriti, A. Grigoropoulos, G. Raptopoulos, G. Charalambidis, <u>V. Nikolaou</u>, A. G. Coutsolelos, M. Pitsikalis, K. Mertis, P. Paraskevopoulou, *"Metathesis polymerization reactions induced by the bimetallic complex (Ph4P)2[W2(μ-Br)3Br6]"*, *Polymers*, **2015**, 7, 2611–2624.

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11. Weber, M.D.;[‡] <u>Nikolaou, V.</u>;[‡] Wittmann, J.E.;[‡] Nikolaou, A.; Angaridis, P.A.; Charalambidis, G.; Stangel, C.; Kahnt, A.; Coutsolelos, A.G.; Costa, R.D. "Benefits of Using BODIPY-Porphyrin Dyads for Developing Deep-Red Lighting Sources", Chem. Commun., 2016, 52, 1602-1605.

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13. Angaridis, P.A.; Ferentinos, E.; Charalambidis, G.; Ladomenou, K.; <u>Nikolaou, V.</u>; Biswas, S.; Sharma, G.D.; Coutsolelos, A.G. "*Pyridyl vs. bipyridyl anchoring groups of porphyrin sensitizers for dye sensitized solar cells*", *RSC Adv.*, 2016, *6*, 22187-22203.

14. Charisiadis, A.; <u>Nikolaou, V.;</u> Karikis, K.; Giatagana, C.; Chalepli, K.; Ladomenou, K.; Biswas, S.; Sharma, G.D.; Coutsolelos, A.G. "*Two new bulky substituted Zn porphyrins bearing carboxylate anchoring groups as promising dyes for DSSCs*", *New J. Chem.*, 2016, 40, 5930-5941.

15. Ladomenou, K.; <u>Nikolaou, V.;</u> Charalambidis, G.; Charisiadis, A.; Coutsolelos, A.G. "*Porphyrin-BODIPY-based hybrid model compounds for artificial photosynthetic reaction centers*", *Comptes Rendus Chimie*, **2016**, *20*, 314-322.

16. Stangel, C.; Charisiadis, A.; Zervaki, G.E.; <u>Nikolaou, V.;</u> Charalambidis, G.; Kahnt, A.; Tagmatarchis, N.; Coutsolelos, A.G. "Case Study for Artificial Photosynthesis: Noncovalent Interactions between C₆₀-Dipyridyl and Zinc Porphyrin Dimer", J. Phys. Chem. C., 2017, 121, 4850-4858.

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19. <u>Nikolaou</u>, V.;[‡] Charisiadis, A.,[‡] Charalampidis, G.; Coutsolelos, A.G.; Odobel, F. **"Recent advances and insights in dye-sensitized NiO photo-cathodes for photovoltaic devices."**, *J. Mater. Chem. A*, **2017**, DOI: 10.1039/C7TA06500K.

V.:‡ S.; 20. Nikolaou, Charisiadis, A.,‡ Chalkiadaki, Alexandropoulos I.; Soman, S.; Panda, M.K.; Coutsolelos, A.G. "Enhancement of the photovoltaic performance in A₃B porphyrin-based DSCs bv incorporating an electron withdrawing triazole spacer", Polyhedron, accepted.

21. Tountas, M.; Polydorou, E.; Verykios, A.; Soultati, A.; Kaltzoglou, A.; Angaridis, P.A.; Papadakis, M.; <u>Nikolaou</u>, V.; Auras, F.; Palilis, L.C.; Tsikritzis, D.; Evangelou, E.K.; Gardelis, E.; Koutsoureli, M.; Papaioannou, G.; Falaras, P.; Davazoglou, D.; Argitis, P.; Kennou, S.; Coutsolelos, A.G.; Vasilopoulou, M. **"Triazine-Functionalized Zinc-Porphyrin of High Dipole Moment as Effective Interfacial Modifier for High-Performance, Air-Stable Solution-Processable Polymers Solar Cells"**, *J. Mater. Chem. A*, submitted.

22. <u>Nikolaou</u>, V.;[‡] Woods, J.;[‡] Charalambidis, G.; Stulz, E.; Coutsolelos, A.G. "*Post-synthetic DNA modification with porphyrins for DNA templated supramolecular multiporphyrin assemblies*", In prog.

23. <u>Nikolaou, V.</u>; Charisiadis A.; Farre, Y.; Charalambidis, G.; Fasoulakis, E.; Odobel, F.; Coutsolelos, A.G.; *"Synthesis of porphyrin derivatives as sensitizers for NiO based dye-sensitized solar cells"*, In prog.

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Conferences

1. "Scientific Conference Greek Medical Students and the 5th International Forum of Medical Students and young doctors of Greece", Hotel Candia, 6-8 May, 2011, Heraklion, Greece.

2. *"Gas chromatography coupled with mass spectrometry"*, Conference. Association of Greek Chemists, April 6, **2013**, Heraklion, **Greece**.

3. *"Bioinspired Material for Solar Energy Utilization"*, Summer School, Department of Chemistry, University of Crete. 20 July-2 August, **2013**, Heraklion, **Greece**.

4. *"Safety Lab"*, Conference in IMBB-ITE. January 21, **2014**, Heraklion, **Greece**.

5. <u>Nikolaou, V</u>. **"Synthesis of new photosensitizers via click chemistry"**, Current Challenges in Supramolecular Artificial Photosynthesis, COST Action CM1202 PERSPECT-H2O, 9-13 March, **2014**, Jena, **Germany**. Oral and poster presentation.

6. <u>Nikolaou, V.</u>; Charalambidis, G.; Coutsolelos, A.G. "Novel Triazine-linked Porphyrin Dyads and Triads as Efficient Sensitization for Dye-Sensitized Solar Cells", Eighth International Conference on Porphyrins and Phthalocyanines (ICPP-8), 22-27 June, **2014**, Istanbul, **Turkey**. Poster presentation.

7. Charisiadis, A.; Stangel, C.; <u>Nikolaou, V.</u>; Sharma G.D; Coutsolelos A.G. "Synthesis, photophysical studies and theoretical calculations of four novel non-covalently linked porphyrin-molecular wire dyads for their application in supramolecular dye-sensitized solar cells", Synthesis of novel ligands for supramolecular photocatalytic active assemblies, COST Action CM1202 PERSPECT-H2O, 15-17 April 2015, Athens, Greece. Poster presentation.

8. <u>Nikolaou, V.;</u> Karikis, K.; Farre, Y.; Charalambidis, G.; Odobel, F.; Coutsolelos, A.G. "Click made porphyrin-corrole dyad: a system for photo-induced charge separation", International Discussion Meeting, Royal Society, "Solar Fuels: Moving from

Materials to Devices", 7-8 July 2015, London, UK. Poster presentation.

9. Charisiadis, A.; <u>Nikolaou, V.</u>; Costa, R.D; Coutsolelos A.G. "Synthesis and characterization of three new porphyrins, that bear four alkoxy chains each at their periphery with increasing length, for their application in LECs", Second European Symposium on Current Challenges in Supramolecular Artificial Photosynthesis of the COST Action CM1202 PERSPECT-H2O, 2-4 September 2015, Gdańsk, Poland. Poster presentation.

10. *"Scientific Writing Workshop"*, EAP Instructor Kallia Katsampoxaki-Hodgetts, Associate Professor Tulpesh Patel, 21 July, 2015, Heraklion, **Greece.**

11. <u>Nikolaou, V.</u> "**BDP-Porphyrin dyads for LEC devices**", 18th Conference of Postgraduate Chemistry students, 26-27 March **2016**, Heraklion, **Greece**. Oral presentation.

12. Charisiadis, A.; <u>Nikolaou, V.</u>; Karikis, K.; Giatagana, C.; Chalepli, K.; Ladomenou, K.; Biswas, S.; Sharma, G.D.; Coutsolelos, A.G. **"Two new bulky substituted Zn porphyrins bearing carboxylate anchoring groups as promising dyes for DSSCs"**, COST Action CM1202 - PERSPECT-H2O - Supramolecular photocatalytic water splitting, 4-6 September **2016**, Milazzo, **Italy**. Poster presentation.

13. Charisiadis, A.; <u>Nikolaou, V.</u>; Karikis, K.; Giatagana, C.; Chalepli, K.; Ladomenou, K.; Biswas, S.; Sharma, G.D.; Coutsolelos, A.G. "**Two new bulky substituted Zn porphyrins bearing carboxylate anchoring groups as promising dyes for DSSCs**", Organic & Perovsite Solar Cells Conference and MC/WG Meetings of COST Action MP1307, 19-21 September **2016**, Heraklion, **Greece**. Poster presentation.

14. <u>Nikolaou, V.</u>; Charisiadis, A.; Charalambidis, G.; Fasoulakis, E.G.; Farré, Y.; Odobel, F.; Coutsolelos, A.G. "Synthesis and properties of porphyrin-fullerene dyads as sensitizers for NiO based dye-sensitized solar cells", Organic & Perovskite Solar Cells, COST ACTION MP1307, 19-21 September 2016, Heraklion, Greece. Poster presentation.

15. <u>Nikolaou, V.</u>; Charisiadis, A.; Charalambidis, G.; Fasoulakis, E.G.; Farré, Y.; Odobel, F.; Coutsolelos, A.G. **"Synthesis and properties of porphyrin-fullerene dyads as sensitizers for NiO based dye-sensitized solar cells**", 19th Postgraduates' Conference on Chemistry, Campus of the University of Crete, May 2-4, **2017**, Heraklion, **Greece**. Poster presentation.

16. Charisiadis, A.; <u>Nikolaou, V.</u>; Karikis, K.; Giatagana, C.; Chalepli, K.; Ladomenou, K.; Biswas, S.; Sharma, G.D.;

Coutsolelos, A.G. "**Two new bulky substituted Zn porphyrins bearing carboxylate anchoring groups as promising dyes for DSSCs**", 19th Postgraduates' Conference on Chemistry, Campus of the University of Crete, May 2-4, **2017**, Heraklion, **Greece**. Poster presentation.

17. <u>Nikolaou, V.</u>; Charisiadis, A.; Charalambidis, G.; Fasoulakis, E.G.; Farré, Y.; Odobel, F.; Coutsolelos, A.G. "Synthesis and properties of porphyrin-fullerene dyads as sensitizers for NiO based dye-sensitized solar cells", 20th European Symposium on Organic Chemistry (ESOC 2017), University of Cologne, July 2-6, 2017, Cologne, Germany. Poster presentation.

18. Charisiadis, A.; <u>Nikolaou, V.</u>; Karikis, K.; Giatagana, C.; Chalepli, K.; Ladomenou, K.; Biswas, S.; Sharma, G.D.; Coutsolelos, A.G. "Two new bulky substituted Zn porphyrins bearing carboxylate anchoring groups as promising dyes for DSSCs", 20th European Symposium on Organic Chemistry (ESOC 2017), University of Cologne, July 2-6, 2017, Cologne, Germany. Poster presentation.

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- 06/2012-09/2012 Πρακτική άσκηση στο Γενικό Χημείο του κράτους, Ρόδος.
- 11/2012-09/2016 Συμμετοχή στο Ερευνητικό πρόγραμμα «Perspect-H₂O-Supramolecular photocatalytic water splitting», στα πλαίσια διεθνών συνεργασιών.
 www.cost.eu/domains_actions/cmst/Actions/CM1202

01/07/2013-10/07/2013 Επισκέπτης ερευνητής στο Πανεπιστήμιο του Southampton, Αγγλία. Bio-organic and Materials Chemistry Lab, School of Chemistry. Καθηγητής Eugen Stulz. Σκοπός της επίσκεψης: "DNA modification with porphyrins for DNA templated supramolecular multiporphyrin assemblies".

01/12/2015-08/12/2015 Επισκέπτης ερευνητής στο Πανεπιστήμιο του Newcastle, Αγγλία. Artificial Photosynthesis Team, School of Chemistry. Καθηγήτρια Elizabeth Gibson. Σκοπός της επίσκεψης: "Photocatalytic hydrogen production experiments with metallated porphyrins and corroles as photosensitizers and catalysts".

 11/2012-10/2014
 Συμμετοχή στο Ερευνητικό πρόγραμμα του Πανεπιστημίου των

 Αθηνών με τίτλο: «Σύνθεση νέων υλικών προηγμένης τεχνολογίας
 με καταλύτες νέας γενιάς μέσω αντιδράσεων μεταθετικού

 πολυμερισμού με διάνοιξη δακτυλίου (ROMP)».
 Ε

12/2015-08/2017 Μεταπτυχιακή Υποτροφία από το Ίδρυμα Κρατικών Ερευνών (IKY). Τίτλος υποτροφίας: «Research Projects for Excellence IKY/Siemens».

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Χρηματοδότηση

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09/2012-12/2012	Βοηθός στο προπτυχιακό εργαστήριο Ανόργανης Χημείας, Τμήμα Χημείας, Πανεπιστήμιο Κρήτης. Υπεύθυνη καθηγήτρια Βαρδαλαχάκη Ε
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	Σχεδιασμός, σύνθεση, απομόνωση και χαρακτηρισμός χρωμοφόρων. Σύνθεση ενώσεων κάτω από αναερόβιες συνθήκες.
	Φασματοσκοπία NMR (¹ Η και ¹³ C), απορρόφησης (UV-Visible), υπερύθρου (FT-IR), αέρια χρωματογραφία (GC-MS), υγρή χρωματογραφία (HPLC) και φασματομετρία μάζας MALDI-TOF MS.
	Φασματοσκοπίας Εκπομπής (Fluorescence), μετρήσεων χρόνου ζωής διεγερμένης κατάστασης (Lifetime) και μέσω ηλεκτροχημικών μεθόδων (Electrochemistry).
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	Βασική γνώση προγραμμάτων θεωρητικών υπολογισμών: Gaussian, Εντολές Unix.
Δημοσιεύσεις	
	1. Zervaki, G.E.; Papastamatakis, E.; Angaridis, P.A.; <u>Nikolaou, V.</u> ; Singh, M.; Kurchania, R.; Kitsopoulos, Th.N.; Sharma, G.D.; Coutsolelos, A.G " <i>A propeller-shaped, triazine-linked porphyrin</i> <i>triad as efficient sensitizer for dye-sensitized solar cells</i> ", <i>Eur. J.</i> <i>Inorg. Chem.</i> 2014 , <i>6</i> , 1020-1033.

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19. <u>Nikolaou</u>, V.;[‡] Charisiadis, A.,[‡] Charalampidis, G.; Coutsolelos, A.G.; Odobel, F. **"Recent advances and insights in dye-sensitized NiO photo-cathodes for photovoltaic devices."**, *J. Mater. Chem. A*, **2017**, DOI: 10.1039/C7TA06500K.

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22. <u>Nikolaou</u>, V.;[‡] Woods, J.;[‡] Charalambidis, G.; Stulz, E.; Coutsolelos, A.G. "*Post-synthetic DNA modification with porphyrins for DNA templated supramolecular multiporphyrin assemblies*", In prog.

23. <u>Nikolaou, V.</u>; Charisiadis A.; Farre, Y.; Charalambidis, G.; Fasoulakis, E.; Odobel, F.; Coutsolelos, A.G.; "Synthesis of porphyrin derivatives as sensitizers for NiO based dye-sensitized solar cells", In prog.

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Σεμινάρια-Συνέδρια

1. "Scientific Conference Greek Medical Students and the 5th International Forum of Medical Students and young doctors of Greece", Μάιος 6-8, 2011, Ηράκλειο, Ελλάδα, Ξενοδοχείο Candia.

2. "Gas chromatography coupled with mass spectrometry", Συνέδριο. Ένωση Ελλήνων Χημικών, 6 Απριλίου, **2013**, Ηράκλειο, **Ελλάδα**.

3. "Bioinspired Material for Solar Energy Utilization", Summer School, Τμήμα Χημείας, Πανεπιστήμιο Κρήτης. 20 Ιουλίου-2 Αυγούστου, **2013**, Ηράκλειο, Ελλάδα.

4. "Safety Lab", Συνέδριο στο ερευνητικό κέντρο IMBB-ITE. 21 Ιανουαρίου, **2014**, Ηράκλειο, **Ελλάδα**.

5. <u>Nikolaou, V</u>. "Synthesis of new photosensitizers via click chemistry", Current Challenges in Supramolecular Artificial Photosynthesis, COST Action CM1202 PERSPECT-H2O, 9-13 Maptíou, 2014, Ιένα, Γερμανία. Προφορική παρουσίαση και παρουσίαση Poster.

6. <u>Nikolaou, V.</u>; Charalambidis, G.; Coutsolelos, A.G. "Novel Triazine-linked Porphyrin Dyads and Triads as Efficient Sensitization for Dye-Sensitized Solar Cells", Eighth International Conference on Porphyrins and Phthalocyanines (ICPP-8), 22-27 Ιουνίου, 2014, Κωνσταντινούπολη, Τουρκία. παρουσίαση Poster.

7. Charisiadis, A.; Stangel, C.; <u>Nikolaou, V.</u>; Sharma G.D; Coutsolelos A.G. "Synthesis, photophysical studies and theoretical calculations of four novel non-covalently linked porphyrin-molecular wire dyads for their application in supramolecular dye-sensitized solar cells", Synthesis of novel ligands for supramolecular photocatalytic active assemblies, COST Action CM1202 PERSPECT-H2O, 15-17 Απριλίου 2015, Αθήνα, Eλλάδα, Συμμετοχή με Poster.

8. <u>Nikolaou, V.</u>; Karikis, K.; Farre, Y.; Charalambidis, G.; Odobel, F.; Coutsolelos, A.G. "Click made porphyrin-corrole dyad: a system for photo-induced charge separation", International Discussion Meeting, Royal Society, "Solar Fuels: Moving from Materials to Devices", 7-8 Ιουλίου 2015, Λονδίνο, Αγγλία. Παρουσίαση Poster.

9. Charisiadis, A.; <u>Nikolaou, V.</u>; Costa, R.D; Coutsolelos A.G. "Synthesis and characterization of three new porphyrins, that bear four alkoxy chains each at their periphery with increasing length, for their application in LECs", Second European Symposium on Current Challenges in Supramolecular Artificial Photosynthesis of the COST Action CM1202 PERSPECT-H2O, 2-4 Σεπτεμβρίου **2015**, Γκντανσκ, Πολωνία. Συμμετοχή με Poster.

10. "Scientific Writing Workshop", ΕΑΡ Εισηγήτρια: Kallia Katsampoxaki-Hodgetts, Καθηγητής, Ομιλητής Tulpesh Patel, 21 Ιουλίου, 2015, Ηράκλειο, Ελλάδα.

11. <u>Nikolaou, V.</u> "**BDP-Porphyrin dyads for LEC devices**", 18th Conference of Postgraduate Chemistry students, 26-27 Μαρτίου **2016**, Ηράκλειο, **Ελλάδα**. Προφορική παρουσίαση.

12. Charisiadis, A.; <u>Nikolaou, V.</u>; Karikis, K.; Giatagana, C.; Chalepli, K.; Ladomenou, K.; Biswas, S.; Sharma, G.D.; Coutsolelos, A.G. **"Two new bulky substituted Zn porphyrins bearing carboxylate anchoring groups as promising dyes for DSSCs"**, COST Action CM1202 - PERSPECT-H2O - Supramolecular photocatalytic water splitting, 4-6 Σεπτεμβρίου **2016**, Μιλάτσο, Ιταλία. Συμμετοχή με Poster.

13. Charisiadis, A.; <u>Nikolaou, V.</u>; Karikis, K.; Giatagana, C.; Chalepli, K.; Ladomenou, K.; Biswas, S.; Sharma, G.D.; Coutsolelos, A.G. "**Two new bulky substituted Zn porphyrins bearing carboxylate anchoring groups as promising dyes for DSSCs**", Organic & Perovsite Solar Cells Conference and MC/WG Meetings of COST Action MP1307, 19-21 Σεπτεμβρίου **2016**, Ηράκλειο, **Ελλάδα**. Συμμετοχή με Poster.

14. <u>Nikolaou, V.</u>; Charisiadis, A.; Charalambidis, G.; Fasoulakis, E.G.; Farré, Y.; Odobel, F.; Coutsolelos, A.G. "Synthesis and properties of porphyrin-fullerene dyads as sensitizers for NiO

based dye-sensitized solar cells", Organic & Perovskite Solar Cells, COST ACTION MP1307, 19-21 Σεπτεμβρίου 2016, Ηράκλειο, Ελλάδα. Παρουσίαση Poster.

15. <u>Nikolaou, V.</u>; Charisiadis, A.; Charalambidis, G.; Fasoulakis, E.G.; Farré, Y.; Odobel, F.; Coutsolelos, A.G. **"Synthesis and properties of porphyrin-fullerene dyads as sensitizers for NiO based dye-sensitized solar cells**", 19th Postgraduates' Conference on Chemistry, Campus of the University of Crete, 2-4 Μαΐου, **2017**, Ηράκλειο, **Ελλάδα**. Παρουσίαση Poster.

16. Charisiadis, A.; <u>Nikolaou, V.</u>; Karikis, K.; Giatagana, C.; Chalepli, K.; Ladomenou, K.; Biswas, S.; Sharma, G.D.; Coutsolelos, A.G. "**Two new bulky substituted Zn porphyrins bearing carboxylate anchoring groups as promising dyes for DSSCs**", 19th Postgraduates' Conference on Chemistry, Campus of the University of Crete, 2-4 Μαΐου, **2017**, Ηράκλειο, **Ελλάδα**. Συμμετοχή με Poster.

17. <u>Nikolaou, V.</u>; Charisiadis, A.; Charalambidis, G.; Fasoulakis, E.G.; Farré, Y.; Odobel, F.; Coutsolelos, A.G. **"Synthesis and properties of porphyrin-fullerene dyads as sensitizers for NiO based dye-sensitized solar cells**", 20th European Symposium on Organic Chemistry (ESOC 2017), University of Cologne, 2-6 Ιουλίου, **2017**, Κολωνία, Γερμανία. Παρουσίαση Poster.

18. Charisiadis, A.; <u>Nikolaou, V.</u>; Karikis, K.; Giatagana, C.; Chalepli, K.; Ladomenou, K.; Biswas, S.; Sharma, G.D.; Coutsolelos, A.G. "**Two new bulky substituted Zn porphyrins bearing carboxylate anchoring groups as promising dyes for DSSCs**", 20th European Symposium on Organic Chemistry (ESOC 2017), University of Cologne, 2-6 Ιουλίου, **2017**, Κολωνία, **Γερμανία**. Συμμετοχή με Poster.

<u>Abstract</u>

This dissertation describes the preparation of novel porphyrin derivatives and their investigation as photosensitizers in various solar-based applications. The newly synthesized porphyrin entities were either modified with appropriate functional groups or linked with different chromophores, such as fullerene, corrole or BODIPY moieties. In the present thesis, the development of energy/electron transfer systems, light emitting electrochemical cells, supramolecular assemblies and dye-sensitized solar cells based on those porphyrin derivatives is examined. The main synthetic approach used for the successful formation of all the above mentioned porphyrinic dyes, was the azide-alkyne cycloaddition (or "click reaction"), which proved an efficient and facile method in stitching different moieties together.

Regarding the energy/electron transfer part, the synthesis, the photo-physical and the electrochemical characterization are described for a series of porphyrin-BODIPY dyads as well as for a click-made porphyrin-corrole compound. Overall, the studies presented in the particular section of the PhD suggest that upon photo-excitation, energy transfer and electron transfer processes occur for the porphyrin-BODIPY dyads and porphyrin-corrole moiety, respectively.

Furthermore, click chemistry was utilized for the synthesis of two porphyrin-BODIPY dyads and the first application of such compounds in light-emitting electrochemical cells is reported. The photo-physical and the electrochemical characterization of the novel dyads are presented along with their results in lighting schemes. The developed devices were comprised of unique features that led to remarkable stability and efficiency.

DNA modification by porphyrin derivatives is also discussed via three different synthetic approaches. More specifically, two different click reactions (copper-catalyzed and copper-free) and an amide coupling reaction were probed in order to efficiently attach various azide-porphyrins or amine-porphyrins onto a series of oligonucleotides. The developed DNA-multi-porphyrin arrays were assembled in supramolecular structures providing an efficient route for exciton coupling. Hence, an elegant method to create porphyrin wires linked to DNA strands that could be utilized in applications such as bio-nanotechnology.

Lastly, a series of porphyrin-fullerene dyads as well as two modified porphyrin derivatives have been prepared and studied as sensitizers in p- and n-type dye-sensitized solar cells, respectively. Concerning the click-made porphyrin-fullerene dyads, the optimal position of a spacer was examined, with respect to the device performance. While for the modified porphyrin derivatives that were prepared for n-type solar cells, the presence of a new electron withdrawing unit between the porphyrin macrocycle and the anchoring group was studied.

Keywords: Porphyrin, click chemistry, energy/electron transfer, solar cells, light emitting electrochemical cells, supramolecular assemblies, BODIPY, fullerene, corrole.

<u>Περίληψη</u>

Η παρούσα διδακτορική διατριβή περιγράφει την σύνθεση νέων πορφυρινικών παραγώγων και την χρήση τους ως φωτο-ευαισθητοποιητές σε ποικίλες εφαρμογές αξιοποίησης της ηλιακής ενέργειας. Τα νεοσυντιθέμενα πορφυρινικά σύμπλοκα έχουν τροποποιηθεί με κατάλληλες λειτουργικές ομάδες είτε έχουν συνδεθεί με διάφορα χρωμοφόρα, όπως φουλερένιο, κορρόλη ή BODIPY. Στην παρούσα εργασία εξετάζεται η ανάπτυξη συστημάτων μεταφοράς ενέργειας ή/και ηλεκτρονίων, ηλεκτροχημικών κελιών εκπομπής φωτός, υπερμοριακών συγκροτημάτων αλλά και ηλιακών κυψελίδων ευαισθητοποιούμενης χρωστικής βασισμένα σε πορφυρινικά παράγωγα. Η κύρια συνθετική προσέγγιση που χρησιμοποιήθηκε για τον επιτυχή σχηματισμό όλων των προαναφερθέντων χρωστικών ήταν η κυκλοπροσθήκη αζιδίουαλκινίου (ή "αντίδραση κλικ"), η οποία αποδείχθηκε μία αποτελεσματική και εύχρηστη μέθοδος για την ένωση διαφορετικών οντοτήτων.

Πιο συγκεκριμένα, στο τμήμα που αναφέρεται στα συστήματα μεταφοράς ενέργειας ή/και ηλεκτρονίων, περιγράφεται η σύνθεση, ο φωτο-φυσικός και ηλεκτροχημικός χαρακτηρισμός δυάδων πορφυρίνης-BODIPY καθώς επίσης και ενός συμπλόκου πορφυρίνης-κορρόλης. Συνολικά, οι μελέτες που παρουσιάζονται στο συγκεκριμένο τμήμα της διδακτορικής διατριβής υποδηλώνουν ότι έπειτα από φωτοδιέγερση λαμβάνουν χώρα διεργασίες μεταφοράς ενέργειας καθώς και μεταφοράς ηλεκτρονίων για δυάδες πορφυρίνης-BODIPY και για το σύμπλοκο πορφυρίνης-κορρόλης, αντίστοιχα.

Επιπρόσθετα, μέσω "αντίδρασης κλικ" συντέθηκαν δύο δυάδες πορφυρίνης-BODIPY και πραγματοποιήθηκε για πρώτη φορά η εφαρμογή τέτοιων ενώσεων σε ηλεκτροχημικά κελιά εκπομπής φωτός. Παρουσιάζεται ο φωτο-φυσικός και ο ηλεκτροχημικός χαρακτηρισμός των νέων αυτών δυάδων μαζί με τα αποτελέσματα της ενσωμάτωσής σε τέτοιου είδους συστήματα φωτισμού. Τα εξαιρετικά χαρακτηριστικά των ενώσεων και κατ' επέκταση των συσκευών που παρασκευάστηκαν οδήγησαν σε αξιοσημείωτες τιμές σταθερότητας και σε μεγάλη αποτελεσματικότητα εκπομπής φωτός.

Παρουσιάζεται επίσης η τροποποίηση αλυσίδων DNA με τη χρήση πορφυρινικών παραγώγων μέσω τριών διαφορετικών συνθετικών προσεγγίσεων. Πιο συγκεκριμένα, διερευνήθηκαν δύο διαφορετικές "αντιδράσεις κλικ" (με τη χρήση χαλκού ή απουσία

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αυτού) και μία αντίδραση σύζευξης μέσω αμιδικού δεσμού, με στόχο την αποτελεσματική σύνδεση διαφόρων άζιδο-πορφυρινών ή άμινο-πορφυρινών στο DNA. Τα σύμπλοκα DNA-πορφυρίνη που δημιουργήθηκαν συγκροτήθηκαν σε υπερμοριακές δομές αποδεικνύοντας πως μπορούν να χρησιμοποιηθούν ως μία αποτελεσματική μέθοδος η οποία προάγει τη σύζευξη εξιτονίων. Συμπερασματικά, περιγράφεται μία μέθοδος για τη δημιουργία συρμάτων πορφυρινών οι οποίες είναι συνδεδεμένες σε έλικες του DNA με σκοπό την χρήση τους σε εφαρμογές αναγνώρισης όπως η βιο-νανοτεχνολογία με βάση το DNA.

Τέλος, συντέθηκαν και μελετήθηκαν δυάδες πορφυρίνης-φουλερενίου καθώς και δύο τροποποιημένα πορφυρινικά παράγωγα ως ενώσεις-χρωμοφόρα σε ηλιακές κυψελίδες ευαισθητοποιούμενης χρωστικής τύπου-p και τύπου-n, αντίστοιχα. Σχετικά με τις δυάδες πορφυρίνης-φουλερενίου, εξετάστηκε η βέλτιστη θέση μίας γέφυρας, σε σχέση με την απόδοση της φωτοβολταϊκής συσκευής. Ενώ, όσον αφορά τα τροποποιημένα παράγωγα πορφυρίνης που παρασκευάστηκαν για τα ηλιακά κύτταρα τύπου-n, εξετάστηκε η παρουσία μιας νέας ομάδας η οποία έλκει ηλεκτρόνια και βρίσκεται μεταξύ του πορφυρινκού δακτυλίου και της ομάδας πρόσδεσης.

Λέξεις κλειδιά: Πορφυρίνη, μεταφορά ενέργειας/ηλεκτρονίων, φωτοβολταϊκά κελιά, ηλεκτροχημικές συσκευές εκπομπής φωτός, υπερμοριακά συγκροτήματα, BODIPY, φουλερένιο, κορρόλη.

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Abbreviations

Å	Angstrom
Ac ₂ O	Acetic anhydride
AFM	Atomic Force Microscopy
BCN	Bicyclo[6.1.0]nonyne
BODIPY	Boron dippyromethene or 4,4-difluoro-4-bora-3a,4a-diaza-s-indace
CB	Conduction band
CE	Counter electrode
CFL	Compact fluorescent lamp
CuAAC	Copper catalyzed azide-alkyne 1,3-dipolar cycloaddition
CV	Cyclic voltammetry
DBU	1,8-Diazabicyclo(5.4.0)undec-7-ene
DDQ	2,3-Dichloro-5,6-dicyano-p-benzoquinone
DFT	Density Functional Theory
DIPEA	N,N-Diisopropylethylamine
DMF	Dimethyl formamide
DMSO	Dimethyl sulfoxide
DNA	2'-deoxyribose nucleic acid
DSCs	Dye-sensitized solar cells
ECD	Electro-chemical doping
ED	Electro-dynamical doping
EDLs	Electric double layers
EL	Electroluminescence
ff	Fill factor
FMOs	Frontier Molecular Orbitals
Gt	Gigatons
H-L (e)	HOMO-LUMO electrochemical gap
H-L (t)	HOMO-LUMO theoretical gap
НОМО	Highest occupied molecular orbital
HPLC	High-performance liquid chromatography
IC	Interval conversion
ISC	Intersystem crossing

ITO	Indium-tin-oxide
IUPAC	International Union of Pure and Applied Chemistry
J _{sc}	Short circuit photocurrent density
KW/h	Kilowatt per hour
LECs	Light emitting electrochemical cells
LED	Light-emitting diode
Lm/W	Lumens per watt
LUMO	Lowest unoccupied molecular orbital
NBS	N-Bromosuccinimide
NMR	Nuclear Magnetic Resonance
°C	Degrees Celsius
ODN	Oligonucleotide
OLEDs	Organic light emitting diodes
OSCs	Organic solar cells
p-chloranil	Tetrachloro-1,4-benzoquinone
PDT	Photodynamic therapy
PEDOT:PSS	poly-(3,4-ethylenedioxythiophene) polystyrene sulfonate
PEnT	Photo-induced energy transfer
PL	Photoluminescence
PSII	Photosystem II
RT	Room temperature
Rt	Retention time
SCE	Saturated Calomel Electrode
SQ	Square wave
SSL	Solid-state lighting
TCO	Transparent conductive oxide
TFA	Trifluoroacetic acid
THF	Tetrahydrofuran
TPP	5,10,15,20-tetraphenyl-porphyrin
TW	Terawatt
UV	Ultra-Violent
VB	Valence band
Vis	Visible
V_{oc}	Open circuit voltage

Chapter 1: General Introduction

1.1 The global energy demand

In the next decades the world's population is expected to increase significantly and as a consequence the global energy consumption as well.¹ Recent studies postulated that the global population will continue to increase with a rate of 2.3% per year until 2050.² The current value of the global energy consumption is approximately 17 terawatt (TW) and it is estimated to rise over 27 TW until 2050 and over 43 TW by the end of 2100.²

To this end, there is a growing concern regarding the carbon dioxide (CO₂) emissions from the usage of fossil fuels and their effect on the environment.³ The world's energy need is covered mainly by fossil fuels (almost 80%) producing adverse CO₂ levels, with devastating costs such as the escalation of the "greenhouse effect", the global warming and the worldwide climate change.^{1,4} In order to supply enough energy to cover the universal energy needs the use of fossil fuels will undoubtedly continue to grow. Consequently, the levels of CO₂ emissions are expected to increase annually reaching over 48 gigatons (Gt) in 2100.⁵ Based on the current energy consumption, fossil fuel reserves are expected to be depleted in less than 200 years.^{6,7} The overwhelming environmental issues arising from the combustion of fossil fuels, along with their certain future depletion makes it imperative for using alternate energy sources.⁸ As a consequence, the development of environmentally sustainable energy systems based on renewable energy sources is urgent.⁹

There are many carbon neutral renewable energy sources that could contribute in the global energy demands, namely wind, biomass, geothermal, hydroelectric, nuclear and solar. The use of the above mentioned renewable energies offer a lot of benefits, nonetheless containing potential drawbacks. In addition, it is imperative to find an ideal

¹ Hussain, A.; Arif, S.M.; Aslam, M., Renew. Sust. Energ. Rev., 2017, 71, 12-28.

² Lewis, N.S.; Nocera, D.G., Proc. Natl. Acad. Sci. U.S.A. 2006, 103, 15729-15735.

³ International Energy Agency (IEA), Energy Climate and Change World Energy Outlook Special Report, **2015**.

⁴ Esswein, A.J.; Veige, A.S.; Nocera, D.G., J. Am. Chem. Soc. 2005, 127, 16641-16651.

⁵ Annual Energy Outlook; U.S. Department of Energy, Washington, DC, 2013.

⁶ Murray, J.; King, D., Nature, 2012, 481, 433-435.

⁷ Shafiee, S.; Topal, E., *Energy Policy*, **2009**, *37*, 181-189.

⁸ Armaroli, N.; Balzani, V., Energy for a Sustainable World-From the Oil Age to a Sun Powered Future, Wiley-VCH, Weinheim, Germany, **2011**.

⁹ Dresselhaus, M.S.; Thomas, I. L., Nature, 2001, 414, 332-337.

combination of these renewable energies in order to decrease the combustion of fossil fuels as soon as possible.¹⁰ Generating energy from wind power is one of the best established processes and is already being used in medium to large scale production facilities. Wind is very likely to form a major part of the global energy assortment in near future because of its simple technological model. Noteworthy, the potential power generation from wind could reach over 2 TW.¹¹ The fastest growing sector of all renewable energy sources are biofuels. However, the required amount of land to produce "energy crops" is vast and exceeds available land. Therefore, the large scale production is not a feasible option due to the rising global population and scarcity of food supplies. What is more, similar to biofuels, the use of geothermal power is constrained to certain locations owing to the lack of appropriate geological characteristics. Another class of renewable energy sources is hydroelectric power. Despite being a major form of power generation in some areas,¹² the current hydrological sources are responsible for a small amount of produced power (0.6 TW).⁵ Nuclear power is being used in many developed countries and the global power productivity from this source is almost 1 TW.⁵ The technological cost of constructing nuclear power plants is the limiting factor for global use of nuclear energy. In addition, the lack of sufficient uranium supplies (almost 100 years of ore remain with consumption at current rate) is an additional reason which limits this type of technology offering a broad solution.

Among the available renewable sources, solar energy is presumably the most enduring carbon-neutral solution, being the most exploitable.¹³ In only one hour, the amount of solar energy that reaches the earth's surface is nearly 120.000 TWh. As presented in **Figure 1.1**,⁵ fossil fuels still provide 83% of the global primary supply while renewables sources reach an overall of 17%.^{3, 14}

¹⁰ Bensaid, S.; Centi, G.; Garrone, E.; Perathoner, S.; Saracco, G., *ChemSusChem*, **2012**, *5*, 500-521.

¹¹ Lewis, N.S., Science, 2007, 315, 798-801.

¹² Punys, P.; Dumbrauskas, A.; Kvaraciejus, A.; Vyciene, G., *Energies*, **2011**, *4*, 1258-1277.

¹³ Esswein, A.J.; Nocera, D.G., Chem. Rev. 2007, 107, 4022-4047.

¹⁴ British Petroleum Statistical Review of World Energy, BP-Global, **2016**.



Figure 1.1: The annual worldwide amount of energy used in 2013 (left part), in comparison with the solar energy that reaches Earth in one hour (right).⁵

It is worth mentioning that a solar conversion device big enough to cover the 2% of earth's surface with an energy conversion efficiency only of 12%, would be capable to fulfill the global energy consumption for 14 days in only 8 hours of collecting such radiation.⁵ Another report suggested that the universal power requirements could be realized by covering less than 1% of Earth's surface with solar devices of 8% efficiency.¹⁵

Photovoltaic technology may offer a possible solution to satisfy the energy demands concerning the global electricity generation; however, solar energy does have its disadvantages.¹⁶ There are significant obstacles in using solar power as a primary energy source, such as the night hours and low light conditions.¹⁷ Furthermore, vast areas of photovoltaic cells will be needed for the required solar energy collection. Another limiting factor regarding large scale production of photovoltaic devices is the economic disparity. Namely, the production of electricity through coal or gas costs less than 0.005 \notin per kilowatt hour (KW/h), whereas through photovoltaic technology (crystalline silicon solar cells) the present cost is around 0.035 \notin per KW/h.¹⁸ From the economic point of view, in order for the solar cells industry to reach the fossil fuels one, novel scientific achievement are required enabling the replacement of the currently used silicon solar cells. Noteworthy, photovoltaic devices based on multi-junction solar cells

¹⁷ Nocera, D.G., Acc. Chem. Res., 2012, 45, 767-776.

¹⁵ Bishop, J.K.B.; Rossow, W.B., Journal of Geophysical Research, 1991, 96, 16839-16858.

¹⁶ Young, K.J.; Martini, L.A.; Milot, R.L.; Snoeberger, R.C.; Batista, V.S.; Schmuttenmaer, C.A.; Crabtree, R.H.; Brudvig, G.W., *Coord. Chem. Rev.*, **2012**, *256*, 2503-2520.

¹⁸ AEO, Annual Energy Outlook, EIA, levelized cost, NEMS, **2013**.

are produced on commercial level with reported efficiencies in the scale of 44%.^{19, 20} The viability of solar energy as a primary energy source relies on the high solar-toenergy conversion efficiencies along with the use of inexpensive and abundant materials. Consequently, the development of photovoltaic cells capable of efficiently converting, capturing and storing solar energy will potentially provide the solution for the global energy demand.

Nature for millions of years uses solar energy and through the process of natural photosynthesis successfully transforms abundant substances of low energy, which consist of carbon dioxide and water, to high-energy substances such as dioxygen and carbohydrates.^{21, 22} The natural photosynthetic apparatus has evolved over billions of years and it is remarkably complex. As presented in the equation below (**equation 1.1**), the natural photosynthetic apparatus uses sunlight to convert CO_2 and H_2O to carbohydrates and O_2 .

$$6CO_2 + 6H_2O \xrightarrow{hv} C_6H_{12}O_6 + 6O_2$$

Equation 1.1: The conversion CO₂ and H₂O to carbohydrates and O₂.

Understanding the basic principles of natural photosynthetic schemes could lead to the construction of devices that perform either the conversion of solar energy to fuel or/and the preparation of efficient artificial photosynthetic schemes.²³ The latter approach, would be applicable if only the design of a cost-effective artificial photosynthetic device and its potentially industrial construction was feasible. In this field, intensive research has been devoted regarding the preparation of a device known as artificial leaf.¹⁷ More specifically, in such device molecular oxygen (O₂) and hydrogen (H₂) can be produced via solar driven water splitting by a photoelectrochemical cell.²⁴

The transition from fossil fuels to renewable energy sources is already ongoing. However, since currently there is a vast present energy system with complex power

¹⁹ Saga, T. NPG Asia Materials, **2010**, *2*, 96-102.

²⁰ Li, N.; Baran, D.; Forberich, K.; Machui, F.; Ameri, T.; Turbiez, M.; Carrasco-Orozco, M.; Drees,

M.; Facchetti, A.; Krebs, F.C.; Brabec, C., Energy Environ. Sci., 2013, 6, 3407-3413.

²¹ Renger, G., *Photosynth. Res.*, **2007**, 92, 407-425.

 ²² Ferreira, K. N.; Iverson, T. M.; Maghlaoui, K.; Barber, J.; Iwata, S., *Science*, 2004, 303, 1831-1838.
 ²³ Blankenship, R.E.; Tiede, D.M.; Barber, J.; Brudvig, G.W.; Fleming, G.; Ghirardi, M.; Gunner,

M.R.; Junge, W.; Kramer, D.M.; Melis, A.; Moore T.A.; Moser C.C.; Nocera D.G.; Nozik A.J.; Ort

D.R.; Parson W.W.; Prince R.C.; Sayre R.T., *Science*, **2011**, *332*, 805-809.

²⁴ Li, H.; Han, J.; Guo, N.; Yu, H., Chem. Commun., 2016, 52, 4080-4083.

facilities spread all over the planet, it will be a long-lasting, complicated and challenging process.²⁵ Certainly, this is a venture with big challenges that will hopefully offer promising results leading to radical changes in the way of living.²⁶

1.2 Porphyrins and their Properties

Porphyrins are plentiful organic molecules found in natural systems which are biochemically important as well as medically valuable.²⁷ Porphyrins and other closely related tetrapyrrole pigments, often play a vital role in several biological processes.²⁸ The etymology of "*porphyrin*" originates from the Greek word " $\pi o \rho \phi i \rho a$ " (*porphyra*), which corresponds to the deep purple or violet color. Due to their great importance in natural systems, porphyrins are referred to as "pigments of life".^{29, 30} Natural photosynthetic organisms use porphyrin macrocycles as light-harvesters owing to their ability to capture sunlight and transfer it rapidly to the reaction centers through efficient processes.³¹ Metallated porphyrin rings (metalloporphyrins) are found in numerous biological systems as active components with essential functions such as: a) oxygen transfer and storage (*heme b* in hemoglobin),³² b) electron transfer (*heme c* in cytochrome c)³³ and c) energy conversion (chlorophyll)³⁴ (**Figure 1.2**).

²⁵ Smil, V., Energy Transitions: History, Requirements, Prospects, Praeger, ABC-CLIO, Santa Barbara, CA, USA, **2010**.

²⁶ Armaroli, N.; Balzani, V., Angew. Chem. Int. Ed., 2007, 46, 52-66.

²⁷ Guilard, R.; Kadish, K.M.; Smith, K., The Porphyrin Handbook, Academic Press, **2012**.

²⁸ Kadish, K. M.; Smith, K. M.; Guilard, R., Eds. Handbook of Porphyrin Science, Word Scientific, Singapore, **2003**.

²⁹ Milgrom, L.R., The colours of life: An introduction to the chemistry of porphyrins, Oxford University Press, **1997**.

³⁰ Battersby, A.R.; Nat. Prod. Rep., **2000**, 17, 507-526.

³¹ Lee S.H.; Blake I.M.; Larsen A.G.; McDonald J.A.; Ohkubo K.; Fukuzumi S.; Reimers J.R.; Crossley M.J., *Chem. Sci.*, **2016**, *7*, 6534-6550.

³² Caughey, W.S.; Smythe, G.A.; O'Keeffe, D.H.; Maskasky, J.E.; Smith, M.I., *J. Biol. Chem.* **1975**, 250, 7602-7622.

³³ Sheldon, R.A., Metalloporphyrins in Catalytic Oxidations; CRC Press, 1994.

³⁴ Trebst, P.D.A.; Avron, P.D.M.; Eds.; Encyclopedia of Plant Physiology; Springer Berlin Heidelberg, **1977**.


Figure 1.2: Metalloporphyrins found in biological systems: a) *heme b* in hemoglobin, b) *heme c* in cytochrome c and c) *chlorophyll b*.

Aromaticity is the foremost reason that porphyrins and their derivatives have been utilized in many natural processes. Aromatic compounds are characterized by great stabilitity, planarity, and reactivity, possessing sole spectroscopic and magnetic properties. Porphyrin macrocycle is an aromatic heterocyclic system (20 carbons and 4 nitrogens) containing 22 π -electrons. Porphyrins are consisted of four pyrrole rings that are linked by methine bridges at their a-positions. However, only 18 π -electrons are delocalized according to the Hückel's rule of aromaticity (4n+2 delocalized π -electrons, where n = 4). The planar structure of porphyrins is strongly related to the linkage of the pyrrolic units with each other and the conjugated 18 π -electron system is being responsible for the aromatic behavior of porphyrins (**Figure 1.3**). This rigid and large system along with the efficient delocalization of electrons prevents the oxidation or the reduction of porphyrins is easily observed by Nuclear Magnetic Resonance (NMR) spectroscopy. When an external magnetic field is applied perpendicular to the porphyrin plane, the magnetic field causes diamagnetic ring current.³⁵ This circulation

³⁵ Mallion, R.B., Chem. Rev., **2001**, 101, 1349-1384.

of aromatic electrons in a different direction regarding the applied field induces a higher field at the outer protons of the porphyrin macrocyle and a lower field in the inner protons (NH protons).³⁶ Therefore the outer protons are moved downfield (higher δ values, deshielding), while the inner protons are moved upfield (lower δ values, shielding).



Figure 1.3: Chemical structure of porphyrin macrocycles along with the number of π -electrons implied in aromaticity.

The structure of porphyrins was first suggested by Küster W. in 1913^{37} with subsequent investigations proving that the NH-tautomer was the most stable form. The bridging methine carbons at 5, 10, 15 and 20 positions are defined as *meso*-positions, while the pyrrolic carbons at 2, 3, 7, 8, 12, 13, 17 and 18 positions are designated as β -positions (**Figure 1.4**). The basic structure in every porphyrin derivative is similar, though they may have various substituents on β - and *meso*-positions. Porphyrins are tetradentate ligands and the size of the macrocycle is perfectly suited to bind almost all metal ions. The square planar environment along with the rigid cavity of 0.6-0.7 Å radius is ideal for metal incorporation. A great number of metal ions can be inserted in the center of the macrocycle (Fe, Zn, Cu, Ni, Hg, Co, etc.). The porphyrinic complexes that are obtained in the presence of a metal ion are called metalloporphyrins and a large variety of geometries is presented depending on the nature of the metal ion.³⁸

³⁶ Katz, J.J.; Scheer, H., Porphyrins and Metalloporphyrins, Nuclear magnetic resonance spectroscopy of porphyrins and metalloporphyrins, Elsevier Publishing Company, New York, **1975**.

³⁷ Küster, W.Z.Z., *Physiol. Chem.* **1913**, 82, 463-483.

³⁸ Harvey, P.D.; Stern, C.; Gros, C.P.; Guilard, R., *Coord. Chem. Rev.*, **2007**, *251*, 401-428.



Figure 1.4: Numbering of porphyrin positions according to the IUPAC (International Union of Pure and Applied Chemistry).

The chemical modification of porphyrins as well as their derivatives can be achieved easily at their *meso-* and β -positions, hence developing new specific properties for targeted applications.^{39, 40} Consequently, porphyrins are extremely versatile materials in a synthetic manner⁴¹ and have been extensively used in many fields of chemistry, namely opto-electronics,^{42, 43} catalysis,^{44, 45} electrochemistry^{46, 47} etc. In addition, the ability to tailor the chemical and physical properties of synthetic porphyrins has stimulated the broad use of such derivatives in applications such as solar energy conversion,⁴⁸ medical applications,⁴⁹ artificial photosynthesis^{50, 51} and so forth. A great number of covalently linked donor-acceptor supramolecular porphyrin based compounds have become of major interest also for application in solar cells^{52, 53} and data storage.⁵⁴ The great impact of porphyrin chemistry on the research community can

³⁹ Bhyrappa, P., *Tetrahedron*, **2016**, *57*, 5150-5167.

⁴⁰ Pratviel, G., Coord. Chem. Rev., **2016**, 308, 460-477.

⁴¹ Hiroto, S.; Miyake, T.; Shinokubo, H., Chem. Rev., 2017, 117, 2910-3043.

⁴² Li, Y.; Wang, W.; Leow, W.R.; Zhu, B.; Meng, F.; Zheng, L.; Zhu, J.; Chen, X., *Small*, 2014, 10, 2776-2781.

⁴³ Chen, Y.; Royal, G.; Flahaut, E.; Cobo, S.; Bouchiat, V.; Marty, L.; Bendiab, N., *Adv. Mater.*, **2017**, *29*, 1605745.

⁴⁴ Zhang, W.; Lai, W.; Cao, R., Chem. Rev., 2017, 117, 3717-3797.

⁴⁵ Ladomenou, K.; Natali, M.; Iengo, E.; Charalambidis, G.; Scandola, F.; Coutsolelos, A.G., *Coord. Chem. Rev.*, **2015**, *304-305*, 38-54.

⁴⁶ Pascal, S.; Bucher, L.; Desbois, N.; Bucher, C.; Andraud, C.; Gros, C.P., *Chem. Eur. J.*, **2016**, *22*, 4971-4979.

⁴⁷ Hebié, S.; Dimé, A.K.D.; Devillers, C.H.; Lucas, D., Chem. Eur. J., **2015**, 21, 8281-8289.

⁴⁸ Chen, Y.; Li, A.; Huang, Z.-H.; Wang, L.-N.; Kang, F., *Nanomaterials*, **2016**, *6*, 51.

⁴⁹ Mango, L.M.; Bezerra, F.; Freire, L.E.S.; Guerra, R.A.; Bakuzis, A.F.; Goncalves, P.J., *J. Phys. Chem. A*, **2017**, *121*, pp 1924-1931.

⁵⁰ Guldi, D.M., Chem. Soc. Rev., 2002, 31, 22-36.

⁵¹ Fukuzumu, S., Phys. Chem. Chem. Phys., **2008**, 10, 2283-2297.

⁵² Higashino, T.: Imahori, H., Dalton Trans., 2015, 44, 448-463.

⁵³ Li, L.-L.; Diau, E.W.-D., Chem. Soc. Rev., 2013, 42, 291-304.

⁵⁴ Erickson, N.R.; Holstrom, C.D.; Rhoda, H.M.; Rohde, G.T.; Zatsikha, Y.V.; Galloni, P.; Nemykin, V.N., *Inorg. Chem.*, **2017**, *56*, 4716-4727.

be clearly documented based on the vast number of publications that has been dramatically increased over the last 15 years (**Figure 1.5**). Moreover, in 1997 a scientific journal entitled "Journal of Porphyrins and Phthalocyanines" was founded, as well as the Society of Porphyrins and Phthalocynines in 2000. Nowadays, new synthetic methodologies allow the preparation of new porphyrin derivatives with unexplored properties and characteristics to be thoroughly examined in plenty disciplines of chemistry.



Figure 1.5: Publications related to porphyrins (per year) according to Scopus Database.

1.2.1 General Synthetic Methodology

Synthetic methodologies regarding porphyrin derivatives have been developed dramatically over the last 80 years, since the first reported porphyrin synthesis by Rothemund in 1936.⁵⁵ There are many chemical strategies one can follow to construct the porphyrin core and several synthetic procedures have been reported over the years.^{41,56} More specifically, porphyrin macrocycles can be synthesized via numerous building blocks such as pyrroles, aldehydes, dipyrromethanes, tripyranes and linear tetrapyrroles. Being present in plenty natural systems, porphyrins can be provided by nature. Namely, chorophyll and heme can be extracted from plants and from blood cells, respectively. Thus, those derivatives can both be used as starting materials for the synthesis of modified porphyrin entities. Particularly, chlorophyll can be extracted by

⁵⁵ Rothemund, P., J. Am. Chem. Soc., **1936**, 58, 625-627.

⁵⁶ Tanaka, T.; Osuka, A., *Chem. Rev.*, **2017**, *117*, 2584-2640.

boiling leaves in methanol (or acetone) which is then followed by purification through silica gel column chromatography. In case of heme, first the separation from fresh blood takes place (via straining, defibrination etc.) and then heme is poured into hot acetic acid that contains sodium chloride. By cooling the solution heme crystallizes, and consequently is filtered and obtained in pure form.

Using natural heme and chlorophyll, only β -substituted porphyrins can be synthesized though. Therefore, to obtain different substituted porphyrin derivatives, is essential to synthesize porphyrin macrocycles from scratch. The main building block for porphyrin synthesis is pyrrole and there are various synthetic protocols to synthesize different *meso-* and β -substituted porphyrins. The most important methodologies for the preparation of such porphyrin derivatives are described below.

Rothemund's method

The initial synthesis of *meso*-substituted porphyrin was first developed by Rothemund with the preparation of 5, 10, 15, 20-tetraphenyl-porphyrin (TPP).⁵⁷ More specifically, the above mentioned porphyrin was synthesized using pyrrole and benzaldehyde in presence of pyridine (in a sealed tube at 220°C), to afford TPP in almost 10% yield (**Scheme 1.1**).



Scheme 1.1: Synthesis of 5,10,15,20-tetraphenylporphyrin (TPP) by Rothemund.⁵⁷

The Alder-Longo method

⁵⁷ Rothemund, P.; Menotti, A.R., J. Am. Chem. Soc., **1941**, 63, 267-270.

Adler, Longo and coworkers reported a simple way to obtain symmetrical tetraarylporphyrins in 1964.⁵⁸ This method is the acid-catalyzed condensation reaction of pyrrole with a specific aldehyde. The acid activates the benzaldehyde by protonating the carbonyl group. The role of 2,3-Dichloro-5,6-dicyano-p-benzoquinone (DDQ) is to oxidize the produced porphyrinogen (A) resulting in the formation of tetraphenylporphyrin (**Scheme 1.2**). Different organic acids were tested as solvents, such as propionic acid, acetic acid, trifluoroacetic acid and benzene containing chloroacetic acid. Using this experimental protocol, which is relatively simple and suited for large scale production, tetraarylporphyrins can be prepared in almost 40% yields. In addition, by changing the aldehyde, various symmetrical porphyrins can be synthesized with this method.



Scheme 1.2: Synthesis of 5,10,15,20-tetraphenylporphyrin (TPP) by Adler, Longo and coworkers.⁵⁸

The Alder-Longo method can be applied for the synthesis of unsymmetrical porphyrin compounds as well. As presented in **Scheme 1.3** this is achieved via mixed condensations of aldehydes in the presence of pyrrole. Using two different aldehydes, a statistical mixture of products is obtained. In this case though, in order to separate the desired porphyrin from the other produced porphyrin analogues purification via column chromatography is needed.

⁵⁸ Adler, A.D.; Longo, F.R.; Shergalis, W., J. Am. Chem. Soc. **1964**, 86, 3145-3149.



Scheme 1.3: Synthesis of unsymmetrical porphyrins via mixed condensation reaction of two different aldehydes and pyrrole.

The possible mechanism for the formation of TPP (**Scheme 1.4**) is initiated by the condensation of the protonated benzaldehyde on the α -pyrrolic position forming the carbonium ion A.^{58, 59} Whereupon, the formed carbonium ion A attacks the α -pyrrolic position of another pyrrole in the presence of another benzaldehyde to give the *meso*-substituted dipyrrylmethane carbinol B. The chain building continues until the formation of tetrapyrrylcarbinols C. Afterwards, ring closure takes place and porphyrinogens D are formed. The last step is the oxidation of porphyrinogens for the successful formation of TPP.

⁵⁹ Cavaleiro, J.A.S.; Condesso, M.P.N.; Olmstead, M.M.; Oram, D.E.; Snow, K.M.; Smith, K.M.; *J. Org. Chem.*, **1988**, *53*, 5847-5849.



Scheme 1.4: The possible mechanism for the formation of TPP.58,59

Lindsey's method

Lindsey and his collaborators developed a synthetic protocol for the preparation of tetraphenyl-porphyrin using milder reaction conditions (**Scheme 1.5**).⁶⁰ More specifically, in this preparation method TPP was produced using benzaldehyde, pyrrole, a Lewis acid as the catalyst (Trifuoroacetic acid, TFA or Boron trifluoride diethyl etherate, BF₃.OEt₂) and an organic solvent (chloroform, CHCl₃ or dichloromethane, CH₂Cl₂). This was indeed a more practical preparation method compared to Alder-Longo, despite the slightly lower yields. The Lindsey method can be applied for the synthesis of porphyrin derivatives that originate from acid-unstable aldehydes that cannot be produced through Adler-Longo conditions. In addition, some porphyrin entities cannot be crystallized and precipitated in presence of an acid (propionic acid

⁶⁰ Lindsey, J.S.; Schreiman, I.C.; Hsu, H.C.; Kearney, P.C.; Marguerettaz, A.M., *J. Org. Chem.* **1987**, *52*, 827-836.

e.g.) making the separation of the synthesized porphyrins troublesome. Furthermore, in case of mixed-aldehyde condensation, it is almost impossible to separate the desired porphyrin from the byproducts (expanded and N-confused porphyrins) that are formed due to the harsh reaction conditions that are used in this particular method.



Scheme 1.5: Lindsey's method for the preparation of tetraarylporphyrins.⁶⁰

Dippyromethanes

Another approach for the preparation of porphyrin macrocycles is via condensation reaction with dipyrromethane instead of pyrrole. Di(1*H*-pyrrol-2-yl)methane or dipyrromethane is an important precursor in porphyrin synthesis consisted of two pyrrole units linked via a methylene bridge (**Scheme 1.6**). Dipyrromethanes can be synthesized via condensation reaction of two equivalents of unsubstituted pyrroles with any aryl benzaldehyde. Lindsey and coworkers reported the synthesis of dipyrromethanes by using a mild Lewis acid (i.e. InCl₃) that catalyzes the reaction.^{61, 62}



Scheme 1.6: Lindsey's method for the preparation of dipyrromethanes.

Dipyrromethanes have been widely used in porphyrin chemistry over the years, especially in the case of *trans*-substituted *meso*-porphyrins. In 1960 MacDonald et al.

⁶¹ Littler, B.J.; Ciringh, Y.; Lindsey, J.S., J. Org. Chem., 1999, 64, 2864-2872.

⁶² Rao, P.D.; Dhanalekshmi, S.; Littler, B.J.; Lindsey, J.S., J. Org. Chem., 2000, 65, 7323-7344.

performed the first reaction of this kind using dipyrromethane and various aryl aldehydes in presence of TFA and CH_2Cl_2 (Scheme 1.7).⁶³



Scheme 1.7: Trans-substituted meso-porphyrin synthesized by MacDonald et al.⁶¹

A variety of substituted dipyrromethanes have been extensively utilized in porphyrin synthetic protocols and many important improvements were achieved over the years.^{56, 64, 65} Moreover, this class of precursors have been the key factor for the proficient development of the tetra *meso*-substituted porphyrin synthesis, aiding to the synthesis of five different classes of *meso*-functionalized porphyrins as presented in **Figure 1.6**.



Figure 1.6: The five different classes of *meso*-functionalized porphyrins.

⁶³ Arsenault, G.P.; Bullock, E.; MacDonald, S.F., J. Am. Chem. Soc., 1960, 82, 4384-4389.

⁶⁴ Smith, K.M., New J. Chem., 2016, 40, 5644-5649.

⁶⁵ de la Torre, G.; Bottari, G.; Sekita, M.; Hausmann, A.; Guldi, D.M.; Torres, T., *Chem. Soc. Rev.*, **2013**, *42*, 8049-8105.

1.2.2 <u>Electronic Properties</u>

Martin Gouterman was the first to interpret the electronic absorption spectrum of porphyrin derivatives in 1961.^{66, 67} As a result of their extended aromatic system, porphyrins possess an atypical UV-Vis absorption spectrum. Their absorption features derive from single electron transitions between the two highest occupied (HOMO, HOMO-1) π -orbitals and the two lowest unoccupied (LUMO and LUMO+1) π^* orbitals. In Figure 1.7 the UV-Vis absorption spectra of a free base and a zinc metallated porphyrin are presented. In both cases the most intense band is at around 420 nm and it is called B or "Soret" band. Generally, the range of absorption regarding Soret is between 400-450 nm depending on whether the porphyrin is β - or mesosubstituted. This absorption feature is very strong due to an allowed transition to the second singlet excited state ($S_0 \rightarrow S_2$). In the red spectral region, namely between 500-700 nm we can observe less intense bands that are called Q bands and are relative to "semi-allowed" $S_0 \rightarrow S_1$ transitions. Concerning the free base porphyrin, four Q bands are detected. Noteworthy, Q bands are classified according to increasing λ values as IV, III, II and I and one can identify the symmetry and the metalation status of the porphyrin. In case of zinc porphyrin though, the symmetry of the macrocycle changes from D_{2h} to D_{4h} and degeneration of the four bands into two is observed, due to a more symmetrical electronic configuration.



Figure 1.7: The UV-Vis absorption spectra of a free base porphyrin (black line) and a zinc metallated porphyrin (red line).

⁶⁶ Gouterman, M., J. Mol. Spectrosc, **1961**, *6*, 138-163.

⁶⁷ Gouterman, M.; Wagnière, G.H., J. Mol. Spectrosc, 1963, 11, 108-127.

Variation of the peripheral substituents causes minor changes to the intensity as well as the wavelength of the absorption features. However, structural modification (protonation or coordination of a metal) of the porphyrin macrocycle affects the relative energies of the above mentioned transitions followed by changes in the absorption spectra. A schematic representation of the two Highest Occupied Molecular Orbitals (HOMOs) along with the two Lowest Unoccupied Molecular Orbitals (LUMOs) is illustrated in **Figure 1.8**. As presented in this figure the two HOMOs (a_{1u} and a_{2u}) lie close in energy, while the LUMO ($e_{gx,y}$) are doubly degenerated. Despite the fact that eg orbitals have almost the same energy leading to almost coincident absorption bands, this is not the fact. More specific, $a_{1u} \rightarrow eg$ and $a_{2u} \rightarrow eg$ transitions result in two bands with different wavelengths and intensities. Namely, constructive interference leads to the intense B band at short wavelengths, while destructive combination leads to the weak long-wavelength Q band.



Figure 1.8: Representation of the Gouterman four-orbital model.⁶⁷

For describing the possible pathways of a photon excited porphyrin moiety an energy level diagram (Jablonski diagram, e.g.) is provided in **Figure 1.9**. This diagram illustrates the processes that take place after the absorption of a photon from the singlet ground state (S₀). Initially, excitation of the ground state (S₀) to any singlet excited state (S_x) leads to the population of the first singlet excited state S₁ through very fast radiationless decay (interval conversion, IC). The S₁ excited state can decay through three different processes: a) radiative decay (S₁ \rightarrow S₀, fluorescence), b) non-radiative decay back to S₀ and c) intersystem crossing (ISC) to the lowest energy triplet state T₁. The newly formed triplet excited state (T_1) can radiative decay to S_0 (phosphorescence) or non-radiative decay ground state S_0 .



Figure 1.9: Jablonski diagram illustrating the singlet and triplet states formed of a photon excited porphyrin moiety. Solid lines represent the radiation processes while dashed lines radiationless processes.

The fluorescence spectra of two typical porphyrins (free base and zinc metallated) are illustrated in **Figure 1.10**. The porphyrin emission occurs from the π - π * state of the macrocycle. In the fluorescence spectrum of the free-base porphyrin we observe two bands at 660 and 720 nm. On the other hand the fluorescence bands corresponding to the zinc metallated derivative are located at 600 and 650 nm. In general, the metal contributes small electronic perturbations with small spectral changes, leading to different fluorescent, phosphorescent quantum yields and triplet lifetimes though.

Concerning the insertion of a heavy metal (platinum e.g.), the fluorescence quantum yield is expected to be decreased due to the heavy atom effect. The insertion of a heavy metal increases the rate of ISC, therefore the dominant pathway is the radiative decay through phosphorescence. Such porphyrin derivatives usually don't possess either observable fluorescence bands or fluorescence quantum yields. In addition, their high rate of ISC leads to long lifetimes of the triplet state and high phosphorescent quantum yields.



Figure 1.10: Typical fluorescence spectra of a free base porphyrin (black line) and a zinc metallated porphyrin (red line).

1.3 Fullerene Chemistry

Fullerenes are spherical molecules which can be described by the empirical formula $C_{20}+2_n$ (n = the number of hexagons). In these allotropes, the carbon atoms are arranged in hexagonal and pentagonal rings. Kroto et al. reported the first fullerene derivative in 1985,⁶⁸ which was called "*buckminsterfullerene*" (C₆₀, **Figure 1.11**). This name was given as a reference to Buckminster Fuller R., an American architect and inventor who worked on geodesic sphere constructions.



Figure 1.11: Chemical structure of a fullerene C₆₀.

The rigid structure of fullerene allows the stabilization of charged moieties through the delocalization of electrons or holes. Thus, there has been a significant contribution in the field of artificial photosynthesis by such entities, as a result of their exciting electronic and photophysical properties. Fullerenes and their derivatives exhibit

⁶⁸ Kroto, H.W.; Heath, J.R.; O'Brien, S.C.; Curl, R.F.; Smalley, R.E., Nature, 1985, 318, 162-163.

reversible redox states and possess rich electrochemical properties. Namely, we can detect six equally spaced reversible reductions in their cyclic voltammograms (CV). Regarding their photophysical properties, they display weak and strong absorption bands in the Visible (Vis) and Ultra-Violent (UV) region, respectively.

One of the major factor in systems mimicking artificial photosynthesis is the photoinduced electron transfer process that takes place. To achieve an efficient electron transfer in such schemes, the applied electron acceptor ought to facilitate fast charge separation and slow charge recombination, aiming to increase the lifetime of the ionpair. Fullerene is an electron acceptor that possess such qualities and can decrease the charge recombination process, due to its small reorganization energy. The high degree of delocalization along with the structural similarity of C_{60} in the ground and the excited state are the essential factors for this behavior.

1.3.1 Structural and chemical properties.

Fullerene C₆₀ retain an icosahedral symmetry (*Ih*) consisted of twelve pentagons and twenty hexagons. All stable fullerene materials satisfy the "isolated pentagon rule", which demands that every pentagon in the structure is surrounded by hexagons, avoiding the possible formation of pentalene analogues.⁶⁹ In the formed icosahedron each carbon atom is identical and the ¹³C NMR in benzene reveals only one peak at 143 ppm. In addition, investigating the formed double bonds exposes that the junctions between two hexagons are 1.39 Å, significantly shorter than the 1.47 Å of the bonds between pentagons and hexagons (**Figure 1.12**).⁷⁰ As a consequence of this deviance, C₆₀ is not considered as an aromatic compound.



Figure 1.12: Structure of C₆₀ showing the bond lengths of the different ring junctions.

⁶⁹ Kroto, H.W.; Allaf, W.; Balm, S.P., Chem. Rev. 1991, 91, 1213-1235.

⁷⁰ Bürgi, H.-B.; Blanc, E.; Schwarzenbach, D.; Liu, S.; Lu, Y.-J.; Kappes, M. M.; Ibers, J.A., *Angew. Chem., Int. Ed.*, **1992**, *31*, 640-643.

The molecular frontier orbitals prove the above mentioned conclusion and are presented in **Figure 1.13**. As illustrated in this figure, the HOMO is h_u five-fold degenerated, while the LUMO is t_{1u} and t_{1g} degenerated. In addition, LUMO is fairly low energetically revealing the enhanced ability of C_{60} to gain up to six electrons in reversible one-electron reductions.⁷¹ The capability of fullerene derivatives to obtain electrons made them frequently used as acceptor moieties in photo-induced electron transfer processes. It is worth mentioning though that C_{60} could also be by a one-electron oxidized.⁷² C_{60} has a relatively small HOMO-LUMO gap which makes it active in nucleophilic reactions and inert in electrophilic substitutions.



Figure 1.13: Frontier molecular orbitals of C₆₀.

When a fullerene absorbs energy (photon), immediately its single excited state is formed. As illustrated in the Jablonski diagram below (**Figure 1.14**), the singlet excited state (${}^{1}C_{60}$) either decays through fluorescence process or exhibits rapid intersystem crossing forming the triplet excited state (${}^{3}C_{60}$). It is worth mentioning that the decay through intersystem crossing is generally achieved with lifetimes longer than 40 µs. A suitable photosensitizer (porphyrin, e.g.) can quench this state by forming the triplet state of the sensitizer (${}^{3}P$). Through an electron transfer process, the radical cation or

⁷¹ Ohsawa, Y.; Saji, T., J. Chem. Soc., Chem. Commun., **1992**, 781-782.

⁷² Reed, C.A.; Bolskar, R.D., Chem. Rev., 2000, 100, 1075-1120

anion (most likely) will be formed. Notably, porphyrin quenches the triplet state of C_{60} relatively slower compared to other photosensitizers forming the radical anion of C_{60} which is observed at 1080 nm.



Figure 1.14: Jablonski diagram of C_{60} . Solid lines represent the radiation processes while dashed lines radiationless processes.

1.3.2 <u>Reactivity and synthetic protocols.</u>

The reactivity of fullerenes has been widely studied, despite the fact of being very stable molecules. More specifically, in many research studies the attachment of fullerenes onto surfaces as well as complexes of fullerenes with metals have been explored.⁷³ Through functionalization of the fullerene entity, particularly on the junction between the two hexagon rings, either a molecule or an anchoring group could be attached. To achieve that, an electrophilic addition at a ring junction of C₆₀ has to be performed. This reaction increases the stability of fullerene, since the functionalized ring is not planar.⁷⁴ Furthermore, attractive interactions with surfaces and self-aggregation have been investigated. As a result of the partial delocalization of the π -electron density and the curved distribution on their surface, fullerenes show non-covalent van der Waal's interactions. Taking into consideration the structural and electronic parameters of fullerene C₆₀ we can conclude that it is an electronegative system that behaves like an electron-poor conjugated moiety. A great number of

⁷³ Hirsch, A.; Brettreich, M., Fullerenes-Chemistry and Reactions, Wiley-VCH, Weinheim, **2005**.

⁷⁴ Hirsch, A., Angew. Chem., **1993**, 105, 1189-1192.

nucleophilic addition reactions have been performed in C_{60} with different nucleophiles as presented in **Scheme 1.8**.^{73, 75}



Scheme 1.8: Representative examples of C₆₀ addition reactions.

Even if the formation of the 1,2-isomer is the most preferable, when sterically hindered nucleophiles or electrophiles are used, the 1,4- or the 1,6- isomer are produced (reaction a and b).⁷⁶ In addition another typical reaction of C_{60} is with Grignard compounds containing alkyl or aryl groups (reaction c). As presented in reaction d of the above scheme, a BINGEL reaction could be performed using a bromo-malonate molecule in the presence of an auxiliary base (1,8-Diazabicyclo(5.4.0)undec-7-ene, DBU e.g.). Cycloadditions represent another versatile approach for the functionalization of fullerene derivatives. Namely, C_{60} can react as a dienophile and cycloaddition takes place between two hexagons, producing mainly one product. One of the most widely used cycloadditions is Diels-Alder [4+2] reaction (d) in which the reactivity of the diene is the limiting factor for its successful completion. The periphery

⁷⁵ Giacalone, F.; Martin, N., Chem. Rev., 2006, 106, 5136-5190.

⁷⁶ Hirsch, A., Top. Curr. Chem. 1999, 199, 1-65.

of C_{60} can also be functionalized through [3+2] or [2+2] cycloaddition using amino acids in the presence of an aldehyde (e) or azides (f) as reactants.

1.4 Boron dipyrromethane

Boron dipyrromethene (or 4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene) is a highly fluorescent dye that is commonly abbreviated as BODIPY. The first BODIPY was synthesized by Triebs et al. in 1968⁷⁷ and subsequently a great number of such dyes have been used as laser dyes,^{78, 79} as fluorescent labels^{80, 81} in imaging and as indicators in sensor applications.^{82, 83} In this first reported synthesis (**Scheme 1.9**), the initial step is the acylation of 2,4-dimethylpyrrole by BF₃.OEt₂ and acetic anhydride (Ac₂O) that resulted in the formation of the fluorescent dyes BDP₁ and BDP₂.



Scheme 1.9: Synthesis of the first BOPIDY dyes by Triebs et al.

Lately, BODIPYs have been used in several research areas such as artificial photosynthesis,⁸⁴ solar energy conversion,⁸⁵ polymer chemistry,⁸⁶ photodynamic

⁷⁷ Treibs, A.; Kreuzer, F.-H., *Liebigs Ann. Chem.*, **1968**, 718, 208-223.

⁷⁸ Guggenheimer, S.C.; Boyer, J.H.; Thangaraj, K.; Shah, M.; Soong, M.-L.; Paviopoulos, T.G., *Appl. Opt.*, **1993**, *32*, 3942-3943.

⁷⁹ Abrahamse, H.; Hamblin, M.R., *Biochem. J.*, **2016**, *473*, 347-364.

⁸⁰ Rao, J.; Dragulescu-Andrasi, A.; Yao, H., Curr. Opin. Biotechnol., 2007, 18, 17-25.

⁸¹ Boison, D.; Lu, W.-L.; Xu, Q.-M.; Yanga, H.; Huangb, T.; Chena, Q.-Y.; Gaob, J.; Zhao Y., *Colloids and Surfaces B*, **2016**, *147*, 387-396.

⁸² Antina, E.V.; Bumagina, N.A.; V'yugin, A.I.; Solomonov, A.V., Dyes Pigm., 2017, 136, 368-381.

⁸³ Suzukia, S.; Kozakia, M.; Nozakib, K.; Okada, K., J. Photochem. Photobiol. C., 2011, 12, 269-292.

⁸⁴ El-Khouly, M.; Fukuzumi, S.; D'Souza, F., ChemPhysChem, 2014, 15, 30-47.

⁸⁵ Singh, S.P.; Gayathri, T., Eur. J. Org. Chem., 2014, 2014, 4689-4707.

⁸⁶ Kim, H.N.; Ren, W.X.; Kim, J.S.; Yoon, J., Chem. Soc. Rev., 2012, 41, 3210-3244.

therapy^{87, 88} and organic light emitting diodes (OLEDs).⁸⁹ Their application versatility in so many diverse research fields is due to their attractive properties. Specifically, their straightforward synthesis, the ease in their structural modification and their fascinating photophysical features. The latter, includes high molecular absorption co-efficient numbers, small Stokes Shift and high fluorescence quantum yields. In addition, all their above mentioned spectroscopic properties are mostly not influenced by the different pH values or types of solvent. The negligible formation of triplet state and the moderate redox potentials that BODIPYs possess, are responsible for the great thermal as well as chemical stability, decomposing only in harsh acidic or basic conditions. Their optical and physical properties can be modified through functionalization or/and modification of their structure, leading to entities with the ability to receive or donate electrons. This fact is the main reason why BODIPYs are extensively used by synthetic chemists in solar energy harvesting schemes as a building block.

1.4.1 Structural properties and synthesis of BOPIDY dyes

BODIPYs are composed of a dipyrromethane compound along with a boron difluoride group that acts as an electron deficient atom. Despite the structural similarities with dipyrromethanes, BODIPYs have a whole different nomenclature. More specifically, the IUPAC name of BOPIDY is based on the *s*-indacene molecule and not on the ligand. Following the terminology that originates from porphyrin chemistry the central position on the BODIPY core is defined as *meso-* or 8-position (**Figure 1.15**). Furthermore, the 1, 2, 6 and 7 carbons are called β -positions, while 3 and 5 carbons as are defined α -positions. Due to the charge delocalization over the entire BODIPY structure, this boron dipyrrin core is not considered as a zwitter ion, despite the fact that the boron atom is negatively charged while nitrogen is positively charged (**Figure 1.15**).

⁸⁷ Kamkaew, A.; Lim, S.H.; Lee, H.B.; Kiew, L.V.; Chungc, L.Y.; Burgess, K., *Chem. Soc. Rev.*, **2013**, *42*, 77-88.

⁸⁸ Zhao, J.; Xu, K.; Yang, W.; Wanga, Z.; Zhong, F., Chem. Soc. Rev., 2015, 44, 8904-8939.

⁸⁹ Chapran, M.; Angioni, E.; Findlay, N.J.; Breig, B.; Cherpak, V.; Stakhira, P.; Tuttle, T.; Volyniuk, D.; Grazulevicius, J.V.; Nastishin, Y.A.; Lavrentovich, O.D.; Skabara, P.J., *ACS Appl. Mater. Interfaces*, **2017**, *9*, 4750-4757.



Figure 1.15: IUPAC numbering and structure of BODIPY and s-indacene.

Regarding the synthetic protocols followed for the preparation of BODIPYs, there are two distinct synthetic approaches that were adapted from porphyrin chemistry.⁹⁰ In the first approach, pyrrole is used along with an aldehyde while in the second one two pyrroles are selected, specifically one acyl-pyrrole and one pyrrole. In **Scheme 1.10** those two different approaches are presented, both being acidic condensations of pyrrole.

In the first synthetic method, the reaction is initiated by the acid catalyzed condensation of pyrrole with an aldehyde, forming a dipyrromethane.^{91, 92} Afterwards, the oxidation of the dipyrromethane takes place using DDQ or tetrachloro-1,4benzoquinone (*p*-chloranil). The formed dipyrrin is then subjected to an excess of $BF_3.OEt_2$ so that the desired BODIPY is produced.

The second approach is also an acidic condensation between a 2-acyl-pyrrole and an unsubstituted pyrrole unit in the 2-position.^{93, 94} The first step is the formation of the dipyrrinium entity and then the deprotonation of it by BF₃.OEt₂. The great difference between the two illustrated procedures is that there is no limitation in using only aryl-substituents, which eventually end up at the *meso*-position of the BODIPY. Thus, a great number of BODIPYs can be synthesized following such an approach. To that end, the preparation of unsymmetrical BOPIDYs is possible using this protocol via using different pyrrole molecules.

⁹⁰ Wood, T.; Thompson, A., Chem. Rev., 2007, 107, 1831-1861.

⁹¹ Lee, C.-H.; Lindsey, J.S., *Tetrahedron*, **1994**, *50*, 11427-11440.

⁹² Littler, B.; Miller, M.; Hung, C.-H.; Wagner, R.; O'Shea, D; Boyle, P.; Lindsey, J.S., *J. Org. Chem.* **1999**, *64*, 1391-1396.

⁹³ Haugland, R.P.; Kang, H.C., U.S. Patent US4774339, 1988.

⁹⁴ Wories, H.J.; Koek, J.H.; Lodder, G.; Lugtenburg, J.; Fokkens, R., *Recl. Trav. Chim. Pays-Bas*, **1985**, *104*, 288-291.



Scheme 1.10: Two different acidic condensations of pyrrole for the synthesis of BOPIDY molecules.

1.5 Click Chemistry

"Click chemistry" is a term that was first introduced by Sharpless in 2001⁹⁵ denoting a set of reactions able to link moieties together in a very efficient, facile and reliable way. In general, click reactions are high yielding, stereospecific and chemo selective, offering simple purification methods and can be conducted under mild conditions producing minimal byproducts.^{96, 97} There are many types of reactions that fulfil the above criteria, such as cycloadditions of unsaturated species (1,3-dipolar and [4+2] Diels Alder),^{98, 99} nucleophilic substitution/ring-openings,¹⁰⁰ carbonyl of non-aldol type¹⁰¹ thiol-ene additions¹⁰² and carbon-carbon additions.¹⁰³ In **Scheme 1.11** some of the most representative examples are illustrated.

⁹⁵ Kolb, H.C.; Finn, M.G.; Sharpless, K.B., Angew. Chem. Int. Ed., 2001, 40, 2004-2021.

⁹⁶ Wanga, C. Ikhlefb, D.; Kahlalb, S.; Saillardb, J.-Y, Astruc, D., Coord. Chem. Rev., **2016**, 316, 1-20.

⁹⁷ Tiwari, V.K.; Mishra, B.B.; Mishra, K.B.; Mishra, N.; Singh, A.S.; Chen, X., *Chem. Rev.*, **2016**, *116*, 3086-3240.

⁹⁸ Rostovtsev, V.V.; Green, L.G.; Fokin, V.V.; Sharpless, K.B., *Angew. Chem. Int. Ed.*, **2002**, *41*, 2596-2599.

⁹⁹ Tasdelen, M.A., *Polym. Chem.*, **2011**, *2*, 2133-2145.

¹⁰⁰ Siu, T.; Yudin, A.K, J. Am. Chem. Soc., 2002, 124, 530-531.

¹⁰¹ Kolb, H.C.; Sharpless, K.B., *Drug. Discov. Today*, **2003**, *8*, 1128-1137.

¹⁰² Hoyle, C.E.; Bowman, C.N., *Angew. Chem. Int. Ed.*, **2010**, *49*, 1540-1573.

¹⁰³ Moses, J.E.; Moorhouse, A., *Chem. Soc. Rev.*, **2007**, *36*, 1249-1262.



Scheme 1.11: Representative examples regarding the different types of click reactions.

Copper catalyzed azide-alkyne 1,3-dipolar cycloaddition (CuAAC) is the best known and widely used reaction and is often referred to as "click chemistry". This reaction was reported by Huisgen in 1963 and it originates from the 1,3-dipolar cycloaddition of azides with dipolarophiles.¹⁰⁴ The research groups of Sharpless⁹⁸ and Meldal¹⁰⁵ have proven (in independent studies) that the 1,3-dipolar cycloaddition of azides with terminal alkynes could further be enhanced when catalyzed by copper(I) complexes. More specifically, in the presence of a copper complex, the cycloaddition between a terminal alkyne and an azide group takes place forming a 1,2,3-triazole ring. The produced triazole is formed with great potential ($\Delta G^o > -60$ kcal mol⁻¹) and the use of copper ligand species ensures also the high regioselectivity for the 1,4-regioisomer.

One of the fundamental aspects of CuAAC reaction is its robust and straight-forward synthetic methodology that enables the usage of "click chemistry" in wide variety of fields.^{96, 97} CuAAC is considered by many researchers as one of the most promising synthetic approaches and therefore various biological and chemical applications are based on click reactions. Specifically, in biological research click reaction is currently used in medical applications (e.g. protein tagging), for drug discovery, and various

¹⁰⁴ Huisgen, R., Angew. Chem. Int. Ed., 1963, 2, 565-598.

¹⁰⁵ Tornøe, C.W.; Christensen, C.; Meldal, M., J. Org. Chem., 2002, 67, 3057-3064.

biochemical studies.^{106, 107} The impact of "click chemistry" is enormous in materials science, specifically in building versatile structures of dendrimers as well as polymers. One additional research area that Cu(I)-catalyzed reaction has also been applied is the field of bioconjugation.¹⁰⁸ It is feasible to stitch biological entities together and efficiently modify them, even in compatible experimental conditions to biological environments. Supramolecular nanomaterials are fragile compounds that cannot easily be isolated and purified. However, CuAAC reaction is a versatile tool that can be applied in the functionalization processes of such materials. Consequently, in the field of nanoscience, bulk materials, inorganic nanoparticles, but mostly flat surfaces have been prepared and studied using copper(I) catalyzed reactions.^{109, 110}

1.5.1 Mechanism of Copper-catalyzed Alkyne-Azide Cycloaddition

The mechanism of CuAAC reaction was proposed by Fokin and his co-workers using Density Functional Theory (DFT) calculations and kinetic studies (**Scheme 1.12**).¹¹¹



Scheme 1.12: The proposed mechanism of CuAAC reaction.¹¹¹

¹⁰⁶ Lapinsky, D.J.; Johnson, D.S., Future Med. Chem., 2015, 7, 2143-2171.

¹⁰⁷ Pagel, M.; Beck-Sickinger, A.G., Biol. Chem., 2017, 398, 3-22.

¹⁰⁸ Sletten, E.M.; Bertozzi, C.R., Angew. Chem. Int. Ed., 2009, 48, 6974-6998.

¹⁰⁹ Sanchez-Sanchez, A.; Baena-Pérez, I.; Pomposo, J.A., *Molecules*, **2013**, *18*, 3339-3355.

¹¹⁰ Escorihuela, J.; Marcelis, A.T.M.; Zuilhof, H., Adv. Mater. Interfaces, 2015, 2, 1500135.

¹¹¹ Hein, J.E.; Fokin, V.V., Chem. Soc. Rev., 2010, 39, 1302-1315.

The first step of the reaction mechanism (1) is the π -coordination of an alkyne molecule with copper in order to form a copper (I) acetylide complex. Afterwards, with the addition of another Cu(I) species a σ -coordinated complex is formed (2). Note that in non-aqueous solvents the presence of an amine base is mandatory for the completion of the reaction. The following step (3) is the coordination of an azide molecule at the already formed π -coordinated copper. This coordination occurs either through substituted nitrogen or through the terminal nitrogen of the azide. On the contrary to the terminal nitrogen which is π -accepting, the substituted nitrogen is π -donating. As illustrated in Scheme 1.12 the coordination from the substituted nitrogen (4) increases the electron density on the metal center, resulting in oxidative coupling. The prime fact for the 1,4-regioisomer selectivity derives from the formation of the coordinated copper complex to the α -carbon of the acetylide, which drives the nucleophilic attack of the β carbon. The nucleophilic attack in the terminal electrophilic nitrogen is responsible for the formation of the six-member ring due to oxidative coupling. The final two steps in this mechanism (5 and 6) are the exclusion of the of the Cu(I) through reductive elimination that leads to the formation of the triazolide and the composition of the triazole ring, allowing the Cu(I) to resume the catalytic cycle.

One of the most important features in a click reaction is the selection of the correct solvent. There are specific solvents which advance the ligand exchange and at the same time prevent the polynuclear copper acetylide to form, which would have adverse results for the reaction. In addition, there are plenty monometallic and bimetallic Cu(I) complexes that enhance the reactivity and the efficiency in CuAAC reactions. Also, the culmination of the catalytic cycle and the use of ligands that promote CuAAC mechanism are strongly dependent on the nature of the Cu(I) complex. Finally, the application of bridging ligands is another benefit that arises the rate of the click reaction by protecting the copper complex from oxidation and also prevents the formation of polymeric complexes.

1.5.2 Click reaction on tetrapyrrolic derivatives.

Despite all the unique properties of the click reaction, synthetic chemists have extensively applied this set of reactions in tetrapyrolic chemistry only recently. Since the first report of Trabolsi et al.,¹¹² in which the stability of a supramolecular complex was established through a click reaction, many groups have followed this approach for the preparation of various porphyrin derivatives. More specifically, over the last years (2005-2016) there is an almost exponential increase regarding the published works on porphyrins and click chemistry (**Figure 1.16**). From the initial two publications in 2005^{112, 113} we have currently reached more than twenty over the last two years (2014-2016). Especially in 2015 the publications on porphyrins and click chemistry reached the maximum value of twenty eight.



Figure 1.16: Publications related to porphyrins and click chemistry (per year) according to Scopus Database.

Many tetrapyrolic entities have been synthesized and/or modified via click reactions such as porphyrins, phthalocyanines and corroles.^{114, 115} Click-made porphyrin derivatives have been used in a wide range of applications. Namely self-assembly,^{116,}

¹¹² Trabolsi, A.; Elhabiri, M.; Urbani, M.; de la Cruz, J.L.D.; Ajamaa, F.; Solladie', N.; Albrecht-Gary, A.-M.; Nierengarten, J.-F., *Chem. Commun.*, **2005**, 5736-5738.

¹¹³ Hasegawa, T.; Numata, M.; Sakurai, K.; Shinkai, S., *Polymer Preprints, Japan*, **2005**, *54*, 4895-4896.

¹¹⁴ Dumoulin, F.; Ahsen, V., J. Porphyr. Phthalocyanines, 2011, 15, 481-504.

¹¹⁵ Buckley, H.L.; Rubin, L.K.; Chrominski, M.; McNicholas, B.J.; Tsen, K.H.Y; Gryko, D.T.; Arnold, J., *Inorg. Chem.*, **2014**, *53*, 7941-7950.

¹¹⁶ Roberts, D.A.; Schmidt, T.W.; Crossley, M.J.; Perrier, S., Chem. Eur. J., 2013, 19, 12759-12770.

¹¹⁷ photodynamic therapy (PDT),^{118, 119} polymers,¹²⁰ dye-sensitized solar cells,¹²¹ light emitting devices and energy/electron transfer schemes.¹¹⁴ Moreover, the use of clicked porphyrin entities have also been applied in different scientific fields, such as biochemistry and materials chemistry.¹¹⁴ Most of the porphyrins that have been used in the above mentioned clicked projects were metallated. When a free base porphyrin is used in a click reaction, there is a great possibility that copper will be inserted in the macrocycle ring and its catalytic ability would be reduced. What is more, copper-based porphyrin derivatives lack fluorescence, therefore are not frequently used in applications as solar energy conversion schemes. This is the reason why mainly zinc porphyrins have been used in click reactions targeting numerous applications.

Various experimental conditions have been applied for the synthesis of click-made porphyrin derivatives. The successful selection of optimal conditions for the click reaction depends on the nature of the alkyne and azide group on the porphyrin macrocycle. More specifically, the position of these functional groups (azide, alkyne) is strongly related to the successful completion of such cycloaddition reaction. Many alkynyl- and azido-porphyrins have been synthesized for the preparation of different click-made derivatives with varied positions of azide or alkyne groups on the porphyrin ring. Namely, porphyrins with alkyne and azide group on three different positions have been examined: i) on the *meso*-phenyl ring, ii) on the *meso*- or β -position and iii) on an aliphatic chain (**Figure 1.17**). In each case, click reactions that were performed with porphyrins functionalized on the *meso*-phenyl ring proved to be more efficient. Especially when an aliphatic chain was incorporated between the porphyrin and the functional group the reactions were performed in room temperature for a few hours and aqueous solvents were applied.

¹¹⁷ Toganoh, M.; Harada, H.; Ikawa, Y.; Furuta, H., Chem. Lett., **2010**, *39*, 252-253.

¹¹⁸ Garcia, G.; Naud-Martin, D.; Carrez, D.; Croisy, A.; Maillard, P., *Tetrahedron*, **2011**, *67*, 4924-4932.

¹¹⁹ Thandu, M.; Rapozzi, V.; Xodo, V.; Albericio, F.; Comuzzi, C.; Cavalli, S., *ChemPlusChem*, **2014**, 79, 90-98.

¹²⁰ Fiset, E.; Morin, J.F.; *Polymer*, 2009, *50*, 1369-1377.

¹²¹ Nikolaou, V.; Angaridis, P.A.; Charalambidis, G.; Sharma, G.D.; Coutsolelos, A.G., *Dalton Trans.*, **2015**, *44*, 1734-1747.



Figure 1.17: The different positions of alkyne and azide groups on the porphyrin macrocycle. Note that in *meso*-phenyl position aliphatic alkynes and azides have also been used.

Chapter 2: Scope and Outline

The main motivation for this PhD thesis is the widespread occurrence of porphyrin moieties and their diverse role in natural systems. As discussed in the previous chapter of this dissertation, porphyrins possess unique characteristics such as: strong absorption features, tunable photo-physical and electro-chemical properties as well as great photoand thermal-stability.¹²² Therefore, the intention of this work is the development of novel porphyrin derivatives and their investigation as photosensitizers in various solar energy harnessing applications. To this end, porphyrin entities presented herein have been functionalized with different chromophores, namely corroles, fullerenes and BODIPY molecules. The ability of the newly synthesized porphyrin hybrids as lightharvesters has been comprehensively studied in different solar-based applications. More specifically, the formed porphyrin derivatives have been applied in energy/electron transfer schemes,^{123, 124} in solar cell devices,^{125, 126} in light emitting electrochemical cells¹²⁷ and in DNA-porphyrin supramolecular assemblies. Notably, each of the above mentioned applications comprises one individual chapter in this PhD thesis manuscript. In order to achieve the formation of the different porphyrinchromophore entities, mainly the click chemistry synthetic approach was applied. This strategy proved to be a very valuable methodology towards the synthesis of such complex derivatives providing an alternative way to avoid tedious synthetic procedures that produce both unstable and difficult to purify intermediates.¹²⁸

This thesis is comprised of eight chapters in total. Chapter 1 discusses the background and the inspiration for the presented research project, including a literature survey about the chromophores as well as the main synthetic procedure used for the preparation of the porphyrin derivatives. There are four main chapters in this

¹²² Ladomenou, K.; Nikolaou, V.; Charalambidis, G.; Coutsolelos, A.G., *Dalton Trans.*, **2016**, *45*, 1111-1126.

¹²³ Nikolaou, V.; Karikis, K.; Farré, Y.; Charalambidis, G.; Odobel, F.; Coutsolelos, A.G., *Dalton Trans.*, **2015**, 44, 13473-13479.

¹²⁴ Panda, M.K.; Lazarides, T.; Charalambidis, G.; Nikolaou, V.; Coutsolelos, A.G., *Eur. J. Inorg. Chem.*, **2015**, *3*, 468-477.

¹²⁵ Nikolaou, V.; Charisiadis, A., Charalambidis, G.; Coutsolelos, A.G.; Odobel, F., *J. Mater. Chem. A*, **2017**, DOI: 10.1039/C7TA06500K.

¹²⁶ Nikolaou, V.; Charisiadis, A., Chalkiadaki, S.; Alexandropoulos I.; Soman, S.; Panda, M.K.; Coutsolelos, A.G., *Polyhedron*, **2017**, accepted.

¹²⁷ Weber, M.D.; Nikolaou, V.; Wittmann, J.E.; Nikolaou, A.; Angaridis, P.A.; Charalambidis, G.;
Stangel, C.; Kahnt, A.; Coutsolelos, A.G.; Costa, R.D., *Chem. Commun.*, **2016**, *52*, 1602-1605.
¹²⁸ Ladomenou, K.; Nikolaou, V.; Charalambidis, G.; Coutsolelos, A.G., *Coord. Chem. Rev.*, **2016**, 306, 1-42.

dissertation (Chapters 3 to 6). In each of these chapters the research background (introduction part), the synthetic approaches (experimental part) and the results of the studies (results and discussion part) are thoroughly discussed. The above distribution in those four chapters was made with respect to the application of the synthesized porphyrin derivatives. More specifically, the outline of these chapters is the following:

Chapter 3: Energy/Electron transfer Schemes

In this section two individual projects are presented that involve the synthesis and characterization of porphyrin entities developed as compounds in artificial photosynthetic schemes.^{123, 124, 129} As illustrated in **Figure 2.1**, a porphyrin-corrole dyad as well as two porphyrin-BODIPY complexes were prepared and studied in photo-induced electron or energy transfer processes, respectively. In the porphyrin-corrole system when the porphyrin is excited, an intramolecular electron transfer takes place from the porphyrin entity towards the corrole chromophore. ¹²³ On the other hand, in the project regarding the two porphyrin-BODIPY compounds, photo-induced energy transfer is observed. In detail, when the BODIPY chromophore is excited, energy transfer from the BOBIPY molecule to the porphyrin moiety is detected.¹²⁴

¹²⁹ Ladomenou, K.; Nikolaou, V.; Charalambidis, G.; Charisiadis, A.; Coutsolelos, A.G., C. R. Chim., **2017**, 20, 314-322.



Figure 2.1: The structures of the porphyrin-corrole dyad (upper part)¹²³ and the two porphyrin-BODIPY hybrids (lower part).^{124, 129}

Chapter 4: Light Emitting Electrochemical Cells (LECs)

The preparation of two porphyrin-BODIPY derivatives and their application in light emitting electrochemical cells (LECs) are reported in this section of the PhD thesis. We have synthesized those compounds and we have performed the investigation of their photo-physical and electrochemical properties in lighting schemes.¹²⁷ In **Figure 2.2** the chemical structures of the dyads are presented, in which the only difference lies in the bridging unit between the porphyrin macrocycle and the BODIPY chromophore. The obtained results for the constructed lighting devices were almost similar in terms of device stability and luminous efficiency.



Figure 2.2: The chemical structure of porphyrin-BODIPY dyad used in LEC devices along with a representative figure regarding the LEC device.¹²⁷

Chapter 5: DNA and Porphyrin Assemblies

This chapter focuses on the use of click chemistry, both Cu-free and Cu-catalyzed, to attach different porphyrins onto DNA sequences. Azido- and amino-porphyrins were efficiently attached to modified oligonucleotides either through click chemistry or amide coupling. For that reason the DNA sequences were modified with alkyne, cyclooctyne or dioxopyrrolidin groups. The efficiency of all click reactions was compared to the amide coupling reaction. We concluded that in contrast to unsuccessful internal modification, terminal attachment using the different methodologies provides porphyrin-DNA hybrids in high yields. Such modification enables the transformation of the porphyrin-DNA complexes into multi-porphyrin arrays using DNA templated assembly (**Figure 2.3**).



Figure 2.3: Structures of the porphyrins used for modification, the sequences of the modified oligonucleotides as well as the DNA templated supramolecular assembly of multiporphyrin arrays.

Chapter 6: Solar Cells

This chapter describes the development of porphyrin derivatives for their use in dyesensitized solar cells (DSCs). As it will be described comprehensively in this section, DSCs can be divided in two separate architectures depending on the operation principle (p- or n-type DSCs). In this part the syntheses as well as the measurements of porphyrin derivatives both in p- and n-type DSCs are presented. The general chemical structures of the porphyrin compounds that were synthesized and studied for p- and n-DSCs are illustrated in **Figure 2.4**. Regarding p-type DSCs, a series of porphyrin-fullerene dyads were synthesized. Whereas, porphyrin derivatives modified with a penta-fluoro triazole accepting bridge were composed and studied for n-type DSCs.¹²⁶



Figure 2.4: The general chemical structures of porphyrin-fullerene dyads for n-type DSCs (left part)¹²⁶ and the porphyrin derivatives for p-type DSCs (right part).

Finally the summary along with the concluding remarks of this PhD thesis are provided in chapter 7. This chapter presents the implementation of our findings and discusses recommendations towards the design of novel porphyrin compounds that are considered for future work. The last chapter of this dissertation (Chapter 8) is the appendix in which all the supporting information regarding each separate project are provided. Specifically, photo-physical measurements, NMR spectra (¹H and ¹³C), photovoltaic measurements, electrochemical characterization, transient absorption measurements and so forth are illustrated in this section.

Chapter 3: Energy/Electron transfer Schemes

3.1 Introduction

The principal process in natural photosynthesis is the conversion of sunlight into chemical energy and its storage in the form of carbohydrates and lipids. This conversion is achieved through photo-induced energy and electron transfer processes after light absorption in the reaction center of the photosynthesis. The photosynthetic reaction center of photosystem II (PSII) is a protein scaffold that consists of porphyrinoids in a self-assembled structure.¹³⁰ As illustrated in **Figure 3.1** each light-harvesting complex is consisted of 45 chlorophylls which are bound to the PSII protein. This collection of chromophores is called a light-harvesting antenna system which absorbs sunlight and efficiently transfers it to the reaction center. In the reaction center electron-transfer process takes place resulting in the formation of long-lived charge-separated states for the production of chemical energy.

Light-harvesting complexes



Reaction centre of Photosystem II

Figure 3.1: Nature's photosynthetic solar cell. Light-harvesting complexes surrounding a pair of photosystem II (PSII) reaction center.¹³⁰

The research community has been inspired by nature in developing artificial photosynthetic systems that convert solar energy in the forms of electricity and/or fuels.

¹³⁰ Bredas, J.-L, Sargent, E.H., Scholes, G.D., Nat. Mater., 2017, 16, 35-44.

In general, an ideal artificial photosynthetic scheme consists of a light harvesting dye that absorbs sunlight and rapidly transfers energy to a photosensitizer. Consequently, the photosensitizer produces charge separated state via electron transfer into an electron acceptor. Overall, the fundamental processes are light harvesting, followed by energy and electron transfer. **Figure 3.2** presents the photo-induced electron and energy transfer processes.¹³¹ The orbitals are represented in horizontal lines and the electrons in arrows. Both processes are initiated by the excitation of the chromophore via solar irradiation in which an electron from its HOMO is transferred to the LUMO. Subsequently, an electron is transferred from the LUMO orbital of the chromophore to the LUMO of the acceptor generating a charge-separated state while reducing and oxidizing the quencher and the chromophore, respectively (electron transfer process). In energy transfer though, the excited state of the quencher is formed while the chromophore returns to its ground state.



Figure 3.2: Schematic representation of the excitation of the chromophore, electron and energy transfer processes in the presence of a quencher.¹³¹

To understand all the important processes that govern photosynthesis so as to develop efficient artificial photosynthetic schemes, simple systems have to be prepared. Therefore, many compounds have been developed throughout the last decades that feature all the essential properties to perform electron and or energy transfer between two or more components. Most of these systems are based on porphyrins or tetrapyrrole

¹³¹ Chandra B. KC.; D'Souza, F., Coord. Chem. Rev., 2016, 322, 104-141
derivatives due to their unique properties that have been already discussed in the previous chapters. Porphyrin derivatives that have been coupled with an energy donor and/or an electron acceptor are the most studied systems concerning such schemes. Specifically, chromophores such as BODIPYs or ferrocenes have been used as energy donors, while fullerenes, carbon nanotubes and naphthalene diimide compounds as electron acceptors.^{132, 133} There are mainly three approaches to link donor and acceptor compounds together. Namely, covalently, non-covalently and mechanically interlocked conjugates have been reported.¹³⁴ Some representative examples of such donoracceptor hybrids are presented in Figure 3.3. The first example (a) is a covalently linked ferrocene-porphyrin-fullerene hybrid which is the most efficient donor-acceptor system in terms of intramolecular charge transfer.¹³⁵ In this work the longest value of the charge separated state lifetime was reported (0.38 seconds), a value comparable to that observed for the bacterial photosynthetic reaction center. Regarding the noncovalently linked porphyrin-fullerene dyad (b), a pyridyl functionalized fullerene was incorporated with a zinc porphyrin to form a supramolecular donor-acceptor system.¹³⁶ The excitation of zinc porphyrin leads to a very efficient electron transfer from the porphyrin to the fullerene entity with charge-separation values in the order of 10^{10} s⁻¹. The last presented example (c) is a mechanically interlocked supramolecular structure in which a rotaxane bears electron donors (zinc porphyrins) and an electron acceptor (fullerene).¹³⁷ The photo-physical investigation in this project revealed that upon excitation of the zinc porphyrins to their singlet excited state, energy is transferred to the copper phenanthroline complex and consequently electron transfer takes place to the fullerene moiety. The formed charge separated state between the oxidized porphyrin and the reduced fullerene decays back to the ground state on the microsecond time scale.138

¹³² Bottari, G.; Trukhina, O.; Ince, M.; Torres, T., Coord. Chem. Rev., 2012, 256, 2453-2477.

¹³³ Frischmann, P.D.; Mahata, K.; Wurthner, F., Chem. Soc. Rev., **2013**, 42, 1847-1870.

¹³⁴ Rudolf, M.; Kirner, S.V.; Guldi, D.M., Chem. Soc. Rev., **2016**, 45, 612-630.

¹³⁵ Imahori, H.; Guldi, D.M.; Tamaki, K.; Yoshida, Y.; Luo, C.; Sakata, Y.; Fukuzumi, S., *J. Am. Chem. Soc.*, **2001**, *123*, 6617-6628.

¹³⁶ Tsuchiya, T.; Rudolf, M.; Wolfrum, S.; Radhakrishnan, S.G.; Aoyama, R.; Yokosawa, Y.; Oshima, A.; Akasaka, T.; Nagase S.; Guldi, D.M., *Chem. Eur. J.*, **2013**, *19*, 558-565.

¹³⁷ Megiatto, J.D.; Spencer, R.; Schuster, D.I., Org. Let., 2009, 11, 4152-4155.

¹³⁸ Megiatto, J.D.; Schuster, D.I.; Abwandner, S.; de Miguel, G.; Guldi, D.M., *J. Am. Chem. Soc.*, **2010**, *132*, 3847-3861.



Figure 3.3: Chemical structures of representative examples regarding covalent, non-covalent and mechanically interlocked conjugates.

3.2 Photo-induced charge separation in a porphyrin-corrole dyad

3.2.1 Introduction

In this project the synthesis along with the photo-physical and electrochemical characterization of a porphyrin-corrole dyad is reported.¹²³ This is the first example in the literature where the preparation of a porphyrin-corrole dyad was achieved through click reaction. All the presented measurements suggested that upon photo-excitation an efficient excited state interaction between the two chromophores occurs. The performed theoretical calculations confirmed the above hypothesis denoting that zinc porphyrin acts as donor while copper corrole as acceptor. Overall, the click-made porphyrin-corrole dyad could possibly act as a molecular system in energy conversion schemes.

Porphyrins and corroles are ideal candidates for mimicking natural processes such as photosynthesis, due to their structural similarity with natural systems.⁴⁴ In addition, both of these types of chromophores can act either as donor or/and acceptor moieties providing insights about electron and energy transfer mechanisms. Thus, the development of such dyads consisting of different dyes is crucial for understanding complex processes. Porphyrin and corrole derivatives have been reported in several

research fields, for instance solar cells,^{52, 139} materials chemistry,¹⁴⁰ biochemistry¹⁴¹ and medical applications.¹⁴² Consequently, newly synthesized porphyrin-corrole dimers are promising agents in all those aforementioned applications. The first example was presented by Paolesse et al. in 1996, in which the synthesis of the first porphyrin-corrole heterodimer was reported.¹⁴³ However, only few publications followed, due to the challenging corrole synthesis and the instability of the produced porphyrin-corrole dyads.¹⁴⁴ Mainly three different synthetic approaches have been applied for the preparation of such dimers, namely functionalization of the *meso* position,^{145, 146} via amide¹⁴⁷ or phenolic bond.¹⁴⁸ Since corroles are unstable in harsh reaction conditions, the selection of the synthetic protocol is essential for the formation of the desired dimer. Click chemistry provides mild reaction conditions along with simple purification that enables the desired linkage between properly functionalized corrole and porphyrin derivatives. As a result, we have used click reaction to perform the synthesis between a zinc porphyrin and a copper corrole (**Figure 3.4**).



Figure 3.4: The chemical structure the porphyrin-corrole dyad.¹²³

¹³⁹ Odobel, F.; Pellegrin, Y.; Gibson, E.A.; Hagfeldt, A.; Smeigh A.L.; Hammarstrom, F., *Coord. Chem. Rev.*, **2012**, 256, 2414-2423.

¹⁴⁰ Noori, M.; Sadeghi, H.; Lambert, C.J., Nanoscale, 2017, 9, 5299-5304.

¹⁴¹ Clave, G.; Chatelain, G.; Filoramo, A.; Gasparutto, D.; Saint-Pierre, C.; Le Cam, E.; Pietrement,

O.; Guerineau, V.; Campidelli, S.; Org. Biomol. Chem., 2014, 12, 2778-2783.

¹⁴² Aviv, I.; Gross, Z., Chem. Commun., 2007, 1987-1999

¹⁴³ Paolesse, R.; Pandey, R.K.; Forsyth, T.P.; Jaquinod, L.; Gerzevske, K.R.; Nurco, D.J.; Senge, M.O.; Licoccia, S.; Boschi T.; Smith, K.M., *J. Am. Chem. Soc.*, **1996**, *118*, 3869-3882.

¹⁴⁴ Orłowski, R.; Gryko, D.; Gryko, D.T.; Chem. Rev., **2017**, 117, 3102-3137.

¹⁴⁵ Guilard, R.; Burdet, F.; Barbe, J.M.; Gros, C.P.; Espinosa, E.; Shao, J.G.; Ou, Z.P.; Zhan R.Q.; Kadish, K.M.; *Inorg. Chem.*, **2005**, *44*, 3972-3983.

¹⁴⁶ Poulin, J.; Stern, C.; Guilard, R.; Harvey, P.D., *Photochem. Photobiol.*, **2006**, 82, 171-176.

¹⁴⁷ Flamigni, L.; Ventura, B.; Tasior, M.; Gryko, D.T.; *Inorg. Chim. Acta*, **2007**, 360, 803-813.

¹⁴⁸ Ngo, T.H.; Nastasi, F.; Puntoriero, F.; Campagna, S.; Dehaen. W.; Maes, W., *Eur. J. Org. Chem.*, **2012**, 5605-5617.

3.2.2 Experimental

As presented in **Scheme 3.1** the preparation of the porphyrin-corrole dyad (4) was achived through a click reaction between the zinc porphyrin functionalized with an azide group (2) and a copper corrole bearing an alkyne group on its periphery (3). The dyad (4) consists of those two chromophores which are covalently linked through a 1,2,3,-triazole ring. In addition, the porphyrin is functionalized with a benzoic acid which can function as anchoring group for efficient attachment on the surface of a semiconductor. The azide-carboxy-porphyrin (2) was derived from the azide-methoxycarbonyl-porphyrin (1)¹²¹ through the hydrolysis of the ester group using tetrahydrofuran (THF), methanol (MeOH) and potassium hydroxide (KOH). Furthermore, corrole (3) was prepared according to a previously published procedure.¹⁴⁹ To efficiently attach the two entities together click reaction conditions have been applied, namely copper iodide (CuI), dry THF and N,N-Diisopropylethylamine (DIPEA). The click reaction was completed in 12 hours at room temperature under constant stirring.



Scheme 3.1: The experimental procedure followed for the synthesis of porphyrin-corrole dyad (4).

¹⁴⁹ Buckley, H.L.; Rubin, L.K.; Chrominski, M.; McNicholas, B.J.; Tsen, K.H.Y.; Gryko, D.T.; Arnold, J., *Inorg. Chem.*, **2014**, *53*, 7941-7950.

Synthesis of 2. To a solution of [5-(4-methoxycarbonylphenyl)-15-(4-azidophenyl)-10,20- bis(2,4,6 trimethylphenyl) porphyrinato zinc]¹²¹ (50 mg, 0.058 mmol) in 20 mL of a THF/MeOH mixture (2:1), an aqueous solution (7 mL) of KOH (300 mg, 5.35 mmol) was added and the mixture was stirred at room temperature overnight. Then the solvents were evaporated under reduced pressure and distilled water (15 mL) was added to the resulting residue. After acidification of the mixture by addition of HCl (aq) 1 M, the product was precipitated, filtered, washed with distilled H₂O and dried resulting in 46 mg of porphyrin (yield: 94%).

¹**H NMR** (500 MHz, DMSO-*d*₆): δ 13.2 (s, 1H), 8.74 (d, *J* = 4.6 Hz, 2H), 8.71 (d, *J* = 4.6 Hz, 2H), 8.59 (d, *J* = 4.5 Hz, 4H), 8.33 (m, 4H), 8.22 (d, *J* = 8.45 Hz, 2H), 7.52 (d, *J* = 8.45 Hz, 2H), 7.31 (s, 4H), 2.58 (s, 6H), 1.78 (s, 12H) ppm.

HRMS (MALDI-TOF): m/z calc for C₅₈H₄₁N₅O₂Zn [M-2N+2H]⁺: 819.26; found: 819.28.

<u>Synthesis of 4.</u> Equimolar amounts of 3 (48 mg, 0.059 mmol) and 2 (50 mg, 0.059 mmol) were dissolved in THF (3 mL) under nitrogen atmosphere. Afterwards, CuI (9 mg, 0.047 mmol) and DIPEA (10 μ L, 0.059 mmol) were added and the reaction mixture was stirred at room temperature for 12 hours. Upon reaction completion, the volatiles were removed under reduced pressure and the crude solid, after diluting in dichloromethane (CH₂Cl₂), was purified by column chromatography of silica gel using a mixture of CH₂Cl₂/MeOH, 98:2 as eluent, yielding 41 mg of **4** (yield: 42%).

¹**H NMR** (500 MHz, DMSO-*d*₆): δ 13.22 (s, 1H), 9.33 (s, 1H), 8.80 (d, *J* = 4.4, 3H), 8.72 (m, 3H), 8.61 (m, 6H), 8.38 (m, 10H), 7.52 (m, 3H), 7.39 (s, 3H), 7.31 (s, 4H), 5.49 (s, 2H), 2.57 (s, 6H), 1.78 (s, 12H) ppm.

¹³**C NMR** (125 MHz, DMSO-*d*₆): δ 167.6, 159.1, 149.6, 149.2, 149.0, 148.8, 147.3, 144.9, 144.6, 144.0, 143.2, 139.1, 138.4, 137.0, 136.0, 135.5, 135.3, 134.4, 131.9, 130.5, 129.8, 127.6, 125.0, 123.4, 118.6, 118.4, 118.3, 114.6, 61.4, 21.5, 21.0.

¹⁹**F NMR** (470 MHz, DMSO-*d*₆): δ -137.0 (d, *J* = 16.5 Hz, 4F), -152.4 (t, *J* = 20.7 Hz, 2F), -160.9 (m, 4F).

HRMS (MALDI-TOF): m/z calc. for $C_{91}H_{54}CuF_{10}N_{11}O_3Zn$ [M]⁺: 1668.41; found 1668.66.

3.2.3 Results and Discussion

The composition of the final porphyrin-corrole dyad (**4**) was verified by NMR (¹H, ¹³C and ¹⁹F) and infrared (IR) spectroscopies as well as mass spectrometry (MALDI-TOF). The ¹H NMR spectrum of **2** and **4** are provided in the appendix chapter of this thesis. In **Figures 8.1** the ¹H NMR spectrum of porphyrin **2** is illustrated, in which the signal corresponding to the carboxylic acid unit appears at 13.21 ppm. The most noticeable feature in the ¹H NMR spectrum of **4** (**Figure 8.2**) is the characteristic triazole signal at 9.33 ppm. Regarding the ¹³C NMR spectrum of **4**, we observe the characteristic peak of the triazole ring and the carboxylate group at 135.5 ppm and 167.6 ppm, respectively (**Figure 8.3** and **8.4**). Concerning the ¹⁹F NMR spectrum of **4**, typical signals for a bis-pentafluoro-corrole are observed¹⁴⁹ as presented in **Figure 8.5**. Moreover, the mass spectrum of **4** using MALDI-TOF mass spectrometry shows a peak at 1668.66 m/z (**Figure 8.6**), corresponding to the molecular ion of **4**, with the appropriate isotopic distribution.

The IR spectra of **2**, **3** and **4** are presented in **Figure 3.5**. The characteristic peaks of **2** and **3**, namely the C-H stretching of the triple bond (at 3298 cm⁻¹) and the N=N=N stretching of the azide group (at 2117 and 2080 cm⁻¹) are absent in the final dyad (**4**). In addition, we can detect peaks that can be assigned to the newly formed triazole ring. Those characteristic peaks are the C-N stretching vibration band at 1336 cm⁻¹, N=N stretching at 1491 cm⁻¹ and C=C stretching at 1603 cm⁻¹.



Figure 3.4: IR spectra of 2 (red), 3 (black) and 4 (blue).

To shed light into the molecular and the electronic properties of 4, density functional theory calculations (DFT)¹⁵⁰ were performed using the B3LYP/6-31G(d)^{151, 152} level of theory. In Figure 8.7 the gas-phase geometry optimized structure of 4 is illustrated while the corresponding coordinates are provided in table 8.1. In the gas-phase geometry optimized structure of **4** we observe that the porphyrin and the corrole units are almost perpendicular to the triazole group and the bridging phenyl groups. In addition, all those groups adopt a perpendicular orientation with respect to the terminal phenyl ring of the porphyrin unit, which is bearing the carboxylic acid group. The electron density distributions along with the corresponding energies of the Frontier Molecular Orbitals (FMOs) of the dyad are depicted in Figure 3.5. In the HOMO the electron density is mainly spread over the central zinc-porphyrin unit, with some additional distribution on the carboxylic acid group and bridging phenyl group. On the other hand, the corresponding electron densities of the two lowest energy unoccupied molecular orbitals (LUMO and LUMO+1) are predominantly located on the coppercorrole, and partially on the bridging phenyl ring. Consequently, dyad (4) can be described as a donor-acceptor system (D-A), with the zinc-porphyrin bearing the carboxylic acid group as donor and the corrole unit as acceptor. Thus, intramolecular electron transfer from the porphyrin moiety to the corrole is favored considering the electron density distributions on HOMO, LUMO and LUMO+1.

¹⁵⁰ Kohn, W.; Sham, L.J., J. Phys. Rev., **1965**, 140, A1133.

¹⁵¹ Becke, A.D., *Phys. Rev. A*, **1988**, *38*, 3098-3100

¹⁵² Lee, C.T.; Yang, W.T.; Parr, R.G., Phys. Rev. B: Condens. Matter, 1988, 37, 785-789.



Figure 3.5: Frontier molecular orbitals of the dyad (4) with the corresponding energy levels.

The photo-physical properties of the click-made porphyrin-corrole dyad (4) as well as the zinc-porphyrin (2) and copper-corrole (3) derivatives were examined through absorption and steady state fluorescence spectroscopy. The UV-Vis absorption spectra of 2, 3, and 4 are depicted in **Figure 3.6**. In the case of 2 and 3 typical absorption features of a zinc-porphyrin and a copper-corrole are observed. More specifically, regarding porphyrin 2 the spectral features observed are: a) the Soret band at 424 nm and b) two Q-bands at 556 and 597 nm, which are attributed to π - π * electronic transitions within the porphyrin macrocycle. As for corrole 3, two broad bands in the range of 400 to 435 nm and two bands at 553 and 613 nm are detected. As expected, the absorption spectrum of 4 can be described as the superimposition of the UV-Vis spectra of 2 and 3.



Figure 3.6: Absorption spectra of 2 (red), 3 (black) and 4 (blue) in THF.

A collection of the absorption and emission data along with the corresponding quantum yields of **4** and the starting compounds (**2** and **3**) are listed in **Table 3.1**. To determine the quantum yield of the zinc porphyrin and the porphyrin-corrole dyad, Zn(TPP) was used as a reference compound. The quantum yield of porphyrin **2** was almost two times greater comparing to that of the dyad, suggesting that the excited state of the porphyrin in the dyad is strongly quenched due to the presence of corrole. In addition, the normalized absorption spectra of **2** and **3** indicate that the lowest absorption peak of **2** appears at 597 nm whereas **3** features an absorption peak at 615 nm (**Figure 8.8**). These facts suggest that porphyrin **2** can act as energy donor and corrole **3** as energy acceptor in dyad (**4**), similar to the corrole-porphyrin dyad that was studied by Harvey, Guilard and coworkers.¹⁵³

<u>**Table 3.1:**</u> Absorption and fluorescence data of 2, 3 and 4 in THF solution at room temperature (RT) and in toluene glass at 77 K^a.

	Absorption	Fluorescence			
Compound	λ _{max} /nm	Emission Emission		Φ	
		λ _{max} /nm	λ _{max} /nm	$(\lambda_{ex} = 550$	
		at RT	at 77 K	nm)	
2	424; 556; 597	607; 657	607; 657; 793	0.044	
3	405; 433; 553; 615	-	-	-	
4	424; 556; 596	608; 656	604; 654	0.0021	

a Zn(TPP) was used as reference for the determination of quantum yields.

¹⁵³ Poulin, J.; Stern, C.; Guilard, R.; Harvey, P.D., Photochem. Photobiol., 2006, 82, 171-176.

We have also performed emission measurements at room temperature (RT) and at 77 K, in order to gain insight regarding the fluorescence properties of 2, 3 and 4. Upon photoexcitation of porphyrin 2, two strong emission signals appear at 607 nm and 658 nm, while in the case of corrole 3 no emission is detected either at room temperature or at 77 K. The emission spectra of 2 and 4 in isoabsorbing solutions (0.1 A at 550 nm), are depicted in Figure 3.7, taking into account the residual absorbance of 3 in order to determine the quenching percentage. Therefore, we calculated that the porphyrin unit exhibits 95% quenching in the dyad by comparing the fluorescence spectra of 2 and 4. The fluorescence quantum yields concerning the porphyrin chromophore are given in **Table 3.1** and the exact values are: $\Phi = 0.044$ in for **2** and $\Phi = 0.0021$ for **4**. All the above mentioned studies indicate that there is an efficient interaction between the porphyrin and the corrole unit in the excited state. Nevertheless, additional studies were performed at 77 K revealing that porphyrin 2 showed a peak at 792 nm, which is attributed to the phosphorescence of the porphyrin (Figure 8.9). However, in the dyad this characteristic signal is absent suggesting that the singlet excited state of the porphyrin has been efficiently quenched by copper-corrole.



Figure 3.7: Room temperature emission spectra of isoabsorbing solutions (A = 0.1, at 550 nm) of **2** (red) and **4** (blue) in THF, when exciting the porphyrin chromophore at 550 nm.

Cyclic and square wave voltammetry measurements were performed for the determination of the electrochemical properties of the final dyad (4) as well as the

starting compounds (2 and 3). All the electrochemical redox data of 2, 3 and 4 are summarized in **Table 3.2**. Porphyrin 2 exhibits typical redox data for *meso* tetra-aryl-substituted zinc-porphyrins,¹⁵⁴ in particular two reversible oxidations at 1.03 and 1.38 V and two reversible reductions at -1.16 and -1.52 V (**Figure 8.11**). Copper-corrole exhibits two reversible reductions, the first at 0.16 V [due to copper reduction Cu(III)/Cu(II)]¹⁵⁵ and the second at -1.6 V. In addition, one reversible oxidation process is clearly noticeable at 1.04 V (**Figure 8.12**). Identifying the redox potentials of 2 and 3 led to the successful assignment of the signals in the voltammogram of 4 (**Figure 3.8**).



Figure 3.7: Cyclic (black) and square wave (blue) voltammograms of **4** in THF. All potentials are reported vs. Saturated Calomel Electrode (SCE) and Ferrocene (FcH/FcH⁺) was used as the internal standard ($E_{1/2}Ox$ is 0.55V).

The dyad undergoes two reversible oxidations $E_{1/2}Ox^1 = 1.03$ V and $E_{1/2}Ox^2 = 1.34$ V and three reversible reductions $E_{1/2}Red^1 = 0.14$ V, $E_{1/2}Red^2 = -1.39$ V and $E_{1/2}Red^3 = -1.61$ V. The first and the third reduction are attributed to the redox properties of **3**, on the contrary to the second oxidation and the second reduction that are assigned to **2**. The only overlapping oxidation signal is the one at 1.03 V which corresponds to simultaneous oxidation of both the zinc porphyrin and copper corrole units. It is worth

¹⁵⁴ Balke, V.L.; Walker, F.A.; West, J.T., J. Am. Chem. Soc., 1985, 107, 1226-1233.

¹⁵⁵ Pomarico, G.; Nardis, S.; Stefanelli, M.; Cicero, D.O.; Vicente, M.G.H.; Fang, Y.Y.; Chen, P.; Kadish, K.M.; Paolesse, R., *Inorg. Chem.*, **2013**, *52*, 8834-8844.

mentioning that the difference between the values of the first oxidation and first reduction, which is defined as the HOMO-LUMO gap, was calculated 0.89 V.

<u>**Table 3.2:**</u> Summary of the electrochemical redox data and the HOMO-LUMO electrochemical gap (H-L gap) of **2**, **3** and **4** in THF. All potentials are reported vs. SCE and FcH/FcH⁺ was used as the internal standard ($E_{1/2}$ Ox is 0.55V).

Compound	E1/2	E1/2	E1/2	E1/2	E1/2	H-L gap
	$\operatorname{Red}^{1}(V)$	$\operatorname{Red}^{2}(V)$	$\operatorname{Red}^{3}(V)$	$Ox^1(V)$	$Ox^2(V)$	(V)
2	-1.16	-1.52	-	1.03	1.38	2.19
3	0.16	-1.6	-	1.04	-	0.88
4	0.14	-1.39	-1.61	1.03	1.34	0.89

In summary, upon photo-excitation intramolecular electron transfer from the zincporphyrin to the copper-corrole possibly occurs. The calculations of the charge separation driving force ($\Delta G_{cs} = -1.21 \text{ eV}$) also support the above conclusion. Those calculations were performed according to the simplified Rehm-Weller equation (1) presented below:

$$\Delta G_{cs} = E_{Ox}(ZnP^{+}/ZnP) - E_{00}(ZnP^{*}) - E_{Red}(Co/Co^{-})$$
 (1)

The value of $E_{00}(ZnP^*)$ is 2.1 eV for a typical zinc porphyrin and stands for the energy of its singlet excited state. Another possible deactivation process for the fluorescence of zinc-porphyrin is energy transfer. The zero-zero energy of the singlet excited state of similar corroles and porphyrins is 1.9 eV in both cases, indicating that those state will lie very close in dyad 4 too. Therefore energy transfer is less likely than electron transfer for mainly two reasons. Firstly, because the driving force is certainly weaker and secondly because the overlapping of the porphyrin's emission and the corrole's absorption spectra is also weak.

3.3 Photo-induced energy transfer in porphyrin-BOPIDY dyads

3.3.1 Introduction

A series of porphyrin-BODIPY dyads was prepared and their photo-physical properties were examined by UV-Vis and fluorescence studies both at room temperature and at 77 K as well.¹²⁴ The synthesized dyads were composed of an indium-porphyrin axially substituted with either a carboxylate or a phenolate BODIPY. The formation of the porphyrin-BODIPY dyads was confirmed through NMR spectroscopy and electrochemical measurements. Moreover, theoretical calculations were carried out in order to gain insight about the structural and electronic properties of the dyads.

Derivatives that consist of different chromophores are capable of broader light absorption in the visible and near infra-red region. Such multi-chromophore molecules have been extensively used in solar cells,^{156, 157} optoelectronic applications¹⁵⁸ and artificial photosynthesis.^{133, 159} Metallated porphyrin derivatives are ideal candidates for designing such multi-chromophore entities. Except from their accessible periphery sites for substitution, metallated porphyrins possess axial sites capable of coordinating a different chromophore. In this respect, metallated porphyrins with aluminum (III)^{160, 161} and tin (IV)¹⁶² have been prepared to form covalent bonds with carboxylate or phenolate functionalized chromophores.

The multi-chromophores formed through axial coordination are more stable in polar solvents and in robust experimental conditions in comparison to the non-covalent derivatives. Moreover, the axial coordination on the porphyrin macrocycle prevents the π - π stacking between the chromophores, a common problem that leads in the formation of aggregates reducing the efficiency of porphyrin-based solar cells.^{163, 164} BODIPYs

¹⁵⁶ Ooyama, Y.; Kanda, M.; Enoki, T.; Adachi, Y.; Ohshita, J., *RSC Adv.*, **2017**, *7*, 13072-13081.

¹⁵⁷ Watson, B.L.; Moore, T.A.; Moore, A.L.; Gust, D., *Dyes Pigm.*, **2017**, *136*, 893-897.

¹⁵⁸ Wong, W.-Y.; Ho, C.L., Coord. Chem. Rev., 2009, 253, 1709-1758.

¹⁵⁹ Bernardi, M..; Grossman, J., J. Phys. Chem. C, 2013, 117, 26896-26904.

¹⁶⁰ Poddutoori, P. K.; Poddutoori, P.; Maiya, B. G.; Prasad, T. K.; Kandrashkin, Y. E.; Vasilev, S.; Bruce, D.; van der Est, A., *Inorg. Chem.*, **2008**, *47*, 7512-7522.

¹⁶¹ Kanematsu, M.; Naumov, P.; Kojima, T.; Fukuzumi, S., Chem. Eur. J., 2011, 17, 12372-12384.

¹⁶² Lazarides, T.; Kuhri, S.; Charalambidis, G.; Panda, M. K.; Guldi, D. M.; Coutsolelos, A.G., Inorg. Chem., **2012**, *51*, 4193-4204.

 ¹⁶³ Wamser, C.C.; Walter, M.G.; Rudine, A.B., *J. Porphyrin. Phthalocyanines*, **2010**, *14*, 759-792.
 ¹⁶⁴ Luo, L.; Lin, C.-J.; Tsai, S.-y.; Wu, H.-P.; Li, L.-L.; Lo, C.-F; Lin, C.-Y.; Diau, E.W.-G., *Phys. Chem. Chem. Phys.*, **2010**, *12*, 1064-1071.

have been studied as antenna chromophores, especially in developing multichromophoric systems with porphyrin and are able to play that part due to their desirable properties.^{84, 165} Such desired properties are the high fluorescence quantum yields, the large extinction coefficients and the long excited state lifetimes.¹⁶⁶ Especially when used with porphyrin the spectral overlap is ideal for efficient intramolecular energy transfer between the donor BODIPY and the acceptor porphyrin. To this end, we have synthesized the porphyrin-BODIPY dyads (**TPP**)**In-O-BDP** and (**TPP**)**In-OOC-BDP** presented in **Figure 3.8** observing that exited state energy transfer from the BODIPY unit to the indium-porphyrin occurs.



Figure 3.8: The chemical structure of (TPP)In-O-BDP and (TPP)In-OOC-BDP.¹²⁴

3.3.2 Experimental

The experimental procedure that we followed to successfully synthesize the desired porphyrin-BODIPY dyads (**TPP**)**In-O-BDP** and (**TPP**)**In-OOC-BDP**, as well as the reference compounds (**TPP**)**In-O-Ph** and (**TPP**)**In-OOC-Ph** is illustrated in **Scheme 3.2**. To synthesize all those derivatives, indium-tetraphenyl porphyrin ((**TPP**)**In-Cl**) was used as a starting material.¹⁶⁷ In addition, the two BOPIDYs: **BDP-OH** and **BDP-COOH** were prepared following the synthetic approach reported by Akkaya and coworkers.^{168,169} All the desired compounds were formed by the reaction of (**TPP**)**In-**

¹⁶⁵ Bandi, V.; D'Souza, F.P.; Gobeze, H.B.; D'Souza, F., Chem. Eur. J., 2015, 21, 2669-2679.

¹⁶⁶ Loudet, A.; Burgess, K., Chem. Rev., 2007, 107, 4891-4932.

¹⁶⁷ Bhatti, M.; Bhatti, W.; Mast, E., Inorg. Nucl. Chem. Lett., 1972, 8, 133-137.

¹⁶⁸ Coskun, A.; Deniz, E.; Akkaya, E.U., Org. Lett., 2005, 7, 5187-5189.

¹⁶⁹ Kolemen, S.; Bozdemir, O.A.; Cakmak, Y.; Barin, G.; Erten-Ela, S.; Marszalek, M.; Yum, J.-H.; Zakeeruddin, S.M.; Nazeeruddin, M.K.; Gratzel, M., Akkaya, E.U., *Chem. Sci.*, **2011**, *2*, 949-954.

CI with the corresponding BOPIDY or phenyl compound in the presence of NaH base, in refluxed toluene, for 12 hours, under nitrogen atmosphere (N_2) .



<u>Scheme 3.2:</u> Synthetic route for the dyads ((TPP)In-O-BDP, (TPP)In-OOC-BDP) and the reference compounds ((TPP)In-OOC-Ph, (TPP)In-O-Ph).

General experimental approach for the synthesis of (**TPP**)**In-O-BDP**, (**TPP**)**In-OOC**-**BDP**, (**TPP**)**In-O-Ph** and (**TPP**)**In-OOC-Ph**:

Equimolar amounts of (**TPP**)**In-Cl** and the corresponding BODIPY or phenyl compound were dissolved in dry toluene (10 mL) and refluxed in the presence of NaH (2 equivalents) for 12 h under nitrogen atmosphere. The reaction mixture was filtered through celite and the solvent was removed under reduced pressure obtaining the product as a purple solid.

(**TPP**)**In-O-BDP**: (yield = 66%).

¹**H NMR (300 MHz, CDCl₃):** δ = 9.12 (s, 8H, porphyrin β -H), 8.42 (m, 4H, Ar-H), 8.17 (br. s, 4H, Ar-H), 7.82 (m, 12H, Ar-H), 5.87 (d, J = 8.3 Hz, 2H, BODIPY Ph-H), 5.78 (s, 2H, BODIPY pyrrolic-H), 3.19 (d, J = 8 Hz, 2H, BODIPY Ph-H), 2.47 (s, 6H, CH₃), 0.80 (s, 6H, CH₃) ppm.

¹³C NMR (75 MHz, C₆D₆): δ = 162.5, 154.6, 150.1, 144.2, 142.9, 142.3, 135.5, 134.9, 134.4, 133.0, 132.4, 129.3, 128.4, 128.1, 127.7, 127.3, 127.0, 122.4, 121.1, 117.1, 14.7, 14.5 ppm.
HRMS (MALDI-TOF): calc. for C₆₃H₄₆BF₂InN₆O [M]⁺: 1066.2833; found 1066.2835.

(**TPP**)**In-OOC-BDP**: (yield = 67%).

¹**H NMR (300 MHz, CDCl₃):** δ = 9.10 (s, 8H, porphyrin β -H), 8.14 (d, J = 6.3 Hz, 4H, Ar-H), 8.05 (d, *J* = 7.4 Hz, 4H, Ar-H), 7.47 (m, 12H, Ar-H), 6.27 (d, *J* = 8.3 Hz, 2H, BODIPY Ph-H), 5.63 (d, *J* = 8.3 Hz, 2H, BODIPY Ph-H), 5.25 (s, 2H, BODIPY pyrrolic-H), 2.39 (s, 6H, BODIPY CH₃), 0.30 (s, 6H, BODIPY CH₃) ppm.

¹³**C NMR (75 MHz, C₆D₆):** δ = 169.9, 155.4, 150.3, 142.7, 142.5, 141.2, 137.6, 135.5, 134.6, 132.8, 130.4, 130.1, 129.3, 126.9, 126.8, 126.5, 122.3, 121.0, 14.5, 14.3 ppm.

HRMS (MALDI-TOF): calc. for C₆₄H₄₆BF₂InN₆O₂ [M]⁺: 1094.2782; found 1094.2772.

(**TPP**)**In-O-Ph**: (yield = 74%).

¹**H NMR (500 MHz, C₆D₆):** $\delta = 9.05$ (s, 8H, porphyrin β -H), 8.11 (d, J = 7.0 Hz, 4H, Ar-H), 8.07 (d, J = 7.2 Hz, 4H, Ar-H), 7.49 (m, 12H, Ar-H), 6.15 (br. s, 3H, phenol-H), 3.40 (br. s, 2H, phenol-H) ppm.

HRMS (MALDI-TOF): calc. For C₅₀H₃₃InN₄O [M]⁺: 820.1693; found 820.1697.

(**TPP**)**In-OOC-Ph**: (yield = 76%).

¹**H** NMR (500 MHz, C₆D₆): $\delta = 9.05$ (s, 8H, porphyrin β -H), 8.40 (m, 4H, Ar-H), 8.13 (m, 4 H, Ar-H), 7.78 (m, 12H, Ar-H), 6.80 (t, J = 7.4 Hz, 1H, benzoic-H), 6.54 (t, J = 7.9 Hz, 2H, benzoic-H), 6.11 (dd, $J_1 = 8.4$, $J_2 = 1.3$ Hz, 2H, benzoic-H) ppm.

HRMS (**MALDI-TOF**): calc. for C₅₁H₃₃InN₄O [M]⁺: 848.1642; found 848.1647.

3.3.3 Results and Discussion

The characterization of the final dyads ((TPP)In-O-BDP, (TPP)In-OOC-BDP) and the reference compounds ((TPP)In-OOC-Ph, (TPP)In-O-Ph) was performed by NMR (¹H, ¹³C) spectroscopy and MALDI-TOF spectrometry. The ¹H NMR spectra of the final dyads exhibit characteristic doublets of the BODIPY phenyl groups at $\delta = 5.87$ and 3.19 ppm for (**TPP**)**In-O-BDP** and at $\delta = 6.27$ and 5.63 ppm for (**TPP**)**In-OOC-BDP** (Figure 8.10 and 8.11, respectively). Specifically, in case of (TPP)In-O-BDP we observe that the phenyl protons of the BODIPY were shifted upfield due to the shielding effect of the porphyrin ring current. On the other hand, less up field shifts are detected for the respective proton signals of (TPP)In-OOC-BDP, owing to the longer distance between the porphyrin macrocycle and BODIPY phenyl ring. In addition, the characteristic pyrrolic protons of the BODIPY units are observed at $\delta = 5.78$ and 5.25 ppm for (TPP)In-O-BDP and (TPP)In-OOC-BDP, respectively. Concerning the methyl protons (CH₃) on each pyrrole of the BODIPY moiety, for (TPP)In-O-BDP are detected at $\delta = 2.47$ and 0.80 ppm, whereas for (**TPP**)**In-OOC-BDP** at $\delta = 2.39$ and 0.30 ppm. The ¹H NMR spectra of the reference compounds ((**TPP)In-O-Ph** and (TPP)In-OOC-Ph) are provided in Figures 8.12 and 8.13, respectively. Furthermore, the final dyads were also characterized through ¹³C NMR spectroscopy (Figures 8.14 and 8.15). The characteristic peak regarding the carboxylic acid group of (TPP)In-**OOC-BDP** was detected at 169.9 ppm. Additionally, the carbons of the CH₃ groups were observed at $\delta = 14.7$ and 14.5 ppm for (**TPP**)**In-O-BDP** and at $\delta = 14.5$ and 14.3 ppm for (TPP)In-OOC-BDP.

The photo-physical investigation regarding the final and the reference compounds was achieved via UV-Vis absorption measurements, emission and excitation fluorescence experiments both at room temperature and at 77 K. The absorption spectra of all synthesized compounds were measured in toluene and are presented in **Figure 3.9**.



Figure 3.9: Absorption spectra of (**TPP**)**In-OOC-Ph** (orange), (**TPP**)**In-OOC-BDP** (blue) and **BDP-COOH** (magenta) in toluene (left part). Absorption spectra of (**TPP**)**In-O-BDP** (black), (**TPP**)**In-O-Ph** (green) and **BDP-OH** (red) in toluene (right part).

The reference compounds feature equivalent absorption bands at 428, 560 and 601 nm which correspond to the Soret and the two Q bands, respectively. The two BODIPY reference compounds (**BDP-OH** and **BDP-COOH**) exhibit absorption signals at 501 and 504 nm, respectively. Those signals correspond to the first singlet π - π * excited states. Concerning the two final porphyrin-BODIPY dyads ((**TPP)In-O-BDP** and (**TPP)In-OOC-BDP**), exhibited combined absorption features of both the indium-porphyrin and the BODIPY chromophore. As expected, (**TPP)In-O-BDP** exhibits a porphyrin Soret band at 426 nm, a bodipy-based peak at 501 nm and two porphyrin Q bands at 561 and 601 nm. In addition, (**TPP)In-OOC-BDP** features the equivalent absorption signals at 428, 504, 562 and 601 nm, respectively. All the absorption data along with the respective extinction coefficients numbers are provided in **Table 3.3**.

<u>Table 3.3:</u> Absorption and emission data of compounds (**TPP**)**In-O-BDP**, (**TPP**)**In-OOC-BDP** and reference compounds (**TPP**)**In-O-Ph** and (**TPP**)**In-OOC-Ph** in toluene solution at room temperature (RT) and in toluene glass at 77 K.

	Abcomption	Emiss	sion Data	Φ	
Compound	Data	λmax(emssn)[1	nm] ($\lambda_{ext}[nm]$)	(quantum	τ [ns]
	$\lambda_{max}[nm]$	RT	77 K	yield) ^a	
(TPP)In- O-BDP	426, 501, 561, 601	518 (487) 609, 662 (563)	518 (487) 609, 662 (563) 787 (563)	0.006	2.9 ^b <1 ^c 8.4×10 ^{6d}
(TPP)In- OOC-BDP	428, 504, 562, 601	521 (487) 610, 660 (563)	519 (487) 609, 662, (563) 786 (563)	0.008	2.5 ^b <1 ^c 11.2×10 ^{6d}
(TPP)In- O-Ph	428, 562, 601	610, 662 (563)	-	0.006	<1°
(TPP)In- OOC-Ph	427, 560, 601	608, 660 (563)	-	0.006	<1°

^aZn(TPP) was used as the reference for the determination of quantum yields at room temperature. ^bUsing a 40 nm filter centred at 500 nm for bodipy fluorescence. ^cUsing a 40 nm filter at 670 nm for indium-porphyrin fluorescence. ^dMeasured with a JASCO FP- 6500 phosphorimeter.

The observed weak electronic coupling in the absorption measurements suggests that the two constituent chromophores do not interact in the ground state. This weak coupling was also supported by DFT calculations that we have performed. More specifically, the frontier orbital analysis of (**TPP**)**In-O-BDP** and (**TPP**)**In-OOC-BDP** exhibit poor delocalization of electron density between the two moieties (**Figure 3.10**). We have also performed time-dependent density functional theory calculations (TDFFT) in order to obtain a better insight into the vertical transitions that occur in (**TPP**)**In-O-BDP** and (**TPP**)**In-OOC-BDP**. It is worth mentioning that both gas and solvent phase calculations provided the same result in the distribution of the frontier molecular orbitals. The calculated electronic transitions along with the corresponding molecular orbitals are listed in **Table 8.2**. The gas-phase geometry optimized structures of (**TPP**)**In-O-BDP** and (**TPP**)**In-OOC-BDP** are presented in **Figure 8.16**, while their corresponding coordinates are provided in **Table 8.3** and **8.4**, respectively. The TDDFT calculation regarding (**TPP**)**In-O-BDP** reveals two closely spaced intense peaks at 397.9 nm and 396.7 nm which involve major contributions from HOMO-3 to LUMO+1, HOMO-2 to LUMO, HOMO-3 to LUMO and HOMO-2 to LUMO+1. All those contributions correspond to the Soret band of the porphyrin. Concerning (**TPP**)**In-OOC-BDP**, similar calculation results were obtained with contributions from HOMO to LUMO+1, HOMO-2 to LUMO, HOMO to LUMO+1, HOMO-2 to LUMO, to C-BDP, and (**TPP**)**In-OOC-BDP** and (**TPP**)**In-OOC-BDP**, respectively (**Table 8.2**).



Figure 3.10: Frontier molecular orbitals of **(TPP)In-O-BDP** (upper part) and **(TPP)In-OOC-BDP** (lower part).

The emission spectra of the dyads in comparison with the BODIPY molecules and the reference compounds are illustrated in **Figures 3.11** and **8.17**, respectively. In the fluorescence spectra of **BDP-OH** and **BDP-COOH** we can detect emission signals at 518 and 521 nm that are strongly quenched by the indium-porphyrin in the spectra of the dyads (**TPP**)**In-O-BDP** and (**TPP**)**In-OOC-BDP**, respectively. This suggests that the formation of the BODIPY-based first singlet π - π * excited states decays giving rise

to the formation of the porphyrin's excited state. Therefore, a comparison between the fluorescence spectra of isoabsorbing solutions of each BODIPY with the corresponding dyad has been performed, upon selective excitation of the BODIPY unit at 487 nm (**Figure 3.11**). The observed quenching of the BODIPY emission is associated with the appearance of the porphyrin fluorescence peaks at 610 and 660 nm (**Figures 3.11** and **8.17**).



Figure 3.11: Room temperature emission spectra of isoabsorbing (A = 0.1) solution of (**TPP**)**In-O-BDP** (black) and **BDP-OH** (red) (left part), (**TPP**)**In-OOC-BDP** (blue) and **DBP-COOH** (magenta) (right part), when excited at BODIPY chromophore (487 nm).

Furthermore, the excitation spectra of the dyads both at RT and at 77 K when monitored at the low-energy porphyrin emission peak (660 nm), reveal absorption features that correspond to the porphyrin unit along with the clear absorption features of BODIPY at 501 nm (**Figure 3.12**). These results suggest that excitation of the BODIPY unit (first singlet excited state) is followed by energy transfer to the porphyrin (first singlet excited state). In case of (**TPP)In-O-BDP** dyad, 59% quenching of the BODIPY emission was calculated, while for the (**TPP)In-O-BDP** 89%. It is clear that the energy transfer process in the phenolate derivative was significantly lower comparing to the benzoate one. In **Table 3.3** the fluorescence data, the quantum yields and the emission lifetimes of the final dyads as well as the reference compounds are presented.



Figure 3.12: Excitation spectra of **(TPP)In-O-BDP** (left part) and **(TPP)In-OOC-BDP** (right part) at 77 K in toluene glass when monitoring the emission at 662 nm (dashed line) and 787 nm (solid line).

We have also performed emission experiments regarding the dyads at 77 K in frozen toluene glass. As presented in **Figure 3.13** the characteristic porphyrin emission bands at 609 and 662 nm are better observed and accompanied by the quenched bodipy emission (519 nm) upon exciting the BODIPY chromophore at 487 nm (left part). Consequently in both formed dyads the energy transfer from the excited BODIPY chromophore to the indium-porphyrin occurs. Furthermore, when exciting the porphyrin chromophore, the emission spectra of both dyads at 77 K reveal a weak band at 787 nm (**Figure 3.13**, right part). This band is attributed to the phosphorescence of indium-porphyrin which was confirmed by the long emission life-times of 8.4 ms and 11.2 ms measured for (**TPP)In-O-BDP** and (**TPP)In-OOC-BDP**, respectively. In addition, when monitoring the phosphorescence at 788 nm the absorption features of both BODIPY and porphyrin are detected (**Figure 3.12**). This is a clear indication that the first singlet excited state of the porphyrin decays in part by intersystem crossing (ISC) to the corresponding porphyrin triplet excited state.



Figure 3.13: Emission spectra of **(TPP)In-O-BDP** (black) and **(TPP)In-OOC-BDP** (blue), at 77K in toluene glass when selectively excited the BODIPY chromophore (487 nm, left part) or the porphyrin chromophore (563 nm, right part).

As illustrated in the below simplified energy diagram (**Figure 3.14**), excitation of (**TPP**)**In-O-BDP** and (**TPP**)**In-O-BDP** leads to the formation of the first singlet excited state of the BODIPY chromophore (S₁). Then the deactivation process follows, partly by fluorescence directly back to the S₀ ground state and partly by energy transfer to the lower lying indium-porphyrin (InTPP) first singlet excited state. Finally, apart from the decay of the formed S₁ state of InTPP through fluorescence, also phosphorescence decay takes place after intersystem crossing of the sinlet InTPP excited state to the triplet one (T₁).



Figure 3.14: Simplified energy level diagram showing the possible events which follow after excitation of the dyads to the BODIPY first singlet excited state. The energies are estimated from the emission spectra in rigid matrix at 77 K. PEnT denotes photo-induced energy transfer and ISC denotes intersystem crossing.

The electrochemical properties of the final dyads as well as the reference complexes were studied by cyclic and square wave voltammetry in degassed CH₂Cl₂, with tetrabutylammonium tetrafluorophosphate as the supporting electrolyte. All the redox potentials are listed in **Table 3.4** and the voltammograms of the final dyads and the reference compounds are displayed in **Figure 3.15** and **Figure 8.18**, respectively. After comparison of the redox signals of the reference compounds we were able to successfully assign the signals in voltammograms of the two porphyrin-BODIPY dyads.

<u>**Table 3.4:</u>** Electrochemical redox data of (**TPP**)**In-O-BDP**, (**TPP**)**In-OOC-BDP** and reference compounds (**TPP**)**In-O-Ph**, (**TPP**)**In-OOC-Ph** and **BDP-OH** are presented. All potentials are reported vs. SCE. FcH/FcH⁺ was used as the internal standard ($E_{1/2}Ox$ is 0.44 V). Red¹ stands for $E_{1/2}Red^1$ and so on. H-L (e) stands for the HOMO-LUMO electrochemical gap, while H-L (t) stands for HOMO-LUMO theoretical gap.</u>

Compound	Red ¹	Red ²	Ox ¹	Ox ²	Ox ³	H-L (e)	H-L (t)
(TPP)In-O-Ph	-1.11	-1.49	0.93	1.17	1.47	-	-
(TPP)In-OOC-Ph	-1.15	-1.51	-	1.16	1.44	-	-
BDP-OH		-1.29	-	1.15	-	-	-
(TPP)In-O-BDP	-1.13	-1.51	0.93	1.09	1.4	2.22	2.69
(TPP)In-OOC-BDP	-1.11	-1.49	-	1.09	1.25	2.20	2.75

Both dyads exhibit three reversible reduction processes at -1.13, -1.20 and -1.51 V for (**TPP**)**In-O-BDP** and at -1.11, -1.21 and -1.49 V for (**TPP**)**In-OOC-BDP**. The reductions observed at -1.20 V and -1.21 V are assigned as BODIPY reductions that partly overlap with the first porphyrin reductions. On the other hand, the reduction peaks of (**TPP**)**In-O-BDP** at -1.13 and -1.51 V as well as the reduction peaks of (**TPP**)**In-OOC-BDP** at -1.11 and -1.49 V can be attributed as typical indium-porphyrin reductions. In the case of (**TPP**)**In-OOC-BDP** we can detect one irreversible oxidation at 1.09 V, which corresponds to the overlapping between BODIPY and porphyrin oxidations along with one second porphyrin oxidation at 1.25 V. The first irreversible oxidation of (**TPP**)**In-O-BDP** though is observed at 0.93 V, which is assigned to the

oxidation of the coordinated phenolic groups of the indium-porphyrin to the corresponding phenoxyl radicals. The remaining two oxidations of (**TPP**)**In-O-BDP** dyad at 1.09 and 1.4 V are similarly assigned as in the case of (**TPP**)**In-OOC-BDP**. The electrochemical HOMO-LUMO gaps were found 2.22 V for compound (**TPP**)**In-O-BDP** and 2.20 V for (**TPP**)**In-OOC-BDP** and are in agreement with calculated HOMO-LUMO gaps (2.69 eV and 2.75 eV for (**TPP**)**In-O-BDP** and (**TPP**)**In-OOC-BDP**, respectively).



Figure 3.15: Cyclic voltammogram (black) and square wave (blue) of (TPP)In-O-BDP (left part) and (**TPP)In-OOC-BDP** (right part) in dry degassed CH₂Cl₂. Potentials are measured vs. SCE and referenced FcH/FcH⁺.

To sum up, a comprehensive investigation regarding the photo-physical and the electrochemical properties of the two final porphyrin-BODIPY dyads in which the BODIPY chromophore is axially coordinated either via a phenolate ((**TPP)In-O-BDP**), or via a benzoate bridge ((**TPP)In-OOC-BDP**) is reported. In both cases the intermolecular ground state interactions were minimal. In the excited state though, energy transfer occurs from the singlet excited state of the BODIPY to the singlet excited state of the indium-porphyrin. Photo-induced energy transfer was considerably more efficient in the benzoate-bridged system. Consequently, in such systems the sensitization of the highly redox active indium-porphyrin excited state is evidently observed, thereby providing a potentially useful supramolecular antenna system.

Chapter 4: Light Emitting Electrochemical Cells (LECs)

4.1 Introduction

The electric power used for lighting is over 20% of the total annual consumption, producing almost 10% of the global CO₂ emissions.¹⁷⁰ In addition, during the last decade the energy consumption regarding illumination is continuously increasing with the rate of 7%.¹⁷¹ Nevertheless, it is estimated that almost 2 billion people around the world still lack access to electricity and are forced to use fossil fuels to obtain illumination.¹⁷² Consequently, it is imperative to develop sustainable and affordable lighting systems that can be applied worldwide.

One of the most historical achievements in the field of artificial lighting was the patent of the incandescent lamp by Thomas Edison in 1879. Despite the fact that this filament lamp converted only the 0.2% of electricity into light, it was twenty times more efficient than a candle.¹⁷³ It is worth mentioning that the most important contribution to this discovery was the electric arc by Humphry D. in 1803.¹⁷⁴ Over the next years, various systems were invented that are still used nowadays. In **Figure 4.1** the historical trend of common lighting systems in comparison to their luminous efficacy are presented. Firstly, the fluorescent tube was invented in 1938 which is currently utilized for street illumination as well as in large internal environments.¹⁷⁵ In addition, the halogen lamp and the high pressure sodium-vapor lamp were first used in 1959 and 1965, respectively. In the mid-90s, two new technologies were presented showing an exponential rise regarding their luminous efficacy. Those two new technologies are based on the same operation principle of light-emitting diodes and are applied mostly in televisions and mobile phone displays.

¹⁷⁰ International Energy Agency, Light's Labour's Lost-Policies for Energy-Efficient Lighting, <u>http://www.iea.org/</u>, **2006**.

¹⁷¹ Electricity and heat statistics, Eurostat, <u>http://ec.europa.eu/eurostat/statistics-</u> <u>explained/index.php/Electricity_and_heat_statistics</u>, July **2016**

¹⁷² Mills, E., Science, **2005**, *308*, 1263-1264.

¹⁷³ Smil, V., Creating the Twentieth Century: Technical Innovations of 1867-1914 and Their Lasting Impact, Oxford University Press, Oxford, **2005**.

¹⁷⁴ Friedel, R., Edison's electric light: the art of invention, Johns Hopkins University Press, Baltimore, **2010**.

¹⁷⁵ Brox, J., Brilliant : The Evolution of Artificial Light, Houghton Mifflin Harcourt, New York, **2010**.



Figure 4.1: The most common light sources in comparison to their luminous efficacy over the years.¹⁷⁶

It is obvious that there is a vast progress in this area over the last 20 years, improving the availability of artificial lighting. The two main technologies responsible for this progress are incandescent- and discharge-based lamps.¹⁷⁰ The operation principle of incandescent lamps is very simple, particularly a wire filament emits light upon heating in a vacuum. However, their efficiency is intrinsically low since they lose up to 95% of the electrical power via non-emissive heat radiation. On the other hand discharge lamp, generate light via an internal electrical discharge; thus producing UV radiation. Discharge lamps are more efficient than the incandescent counterpart, nonetheless their expense of color quality lacks variation.

It is imperative to replace current conversional light sources with other alternatives such as compact fluorescent lamps (CFLs) and light-emitting diodes (LEDs).¹⁷⁷ This replacement with more efficient technologies will decrease the huge power consumption resulting in environmental and economic savings as well. Some major advantages of the above mentioned technologies are the longer lifetimes and higher efficiencies. These technologies are based on solid-state lighting (SSL) phenomena in which the conversion of electrical energy into light (electroluminescence, EL) occurs by using organic or inorganic materials.¹⁷⁸ As illustrated in **Figure 4.2**, when an

¹⁷⁶ Costa, R.D.; Orti, E.; Bolink, H.J.; Monti, F.; Accorsi, G.; Armaroli, N., *Angew. Chem. Int. Ed.*, **2012**, *51*, 8178-8211.

¹⁷⁷ Lim, S.R.; Kang, D.; Ogunseitan, O.A.; Schoenung, J.M., *Environ. Sci. Technol.*, **2013**, *47*, 1040-1047.

¹⁷⁸ Xua, H.; Sunb, Q.; Anb, Z.; Weia, Y; Liu, X., Coord. Chem. Rev., 2015, 293-294, 228-249.

external circuit is applied to a light-emitting device, electrons and holes migrate through the film of the device. More specifically, at the cathode electrons are injected into the LUMO whereas at the anode electrons are extracted (hole injection) by the HOMO. Eventually, this migration leads to a meeting point in which upon the return of the electron to the ground state a photon is released.



Figure 4.2: The principle of electroluminescence (EL). The cathode is illustrated at the left, whereas the anode at the right hand side.

The two main devices that are based on SSL are light-emitting diodes (LEDs)^{179, 180} and organic light-emitting diodes (OLEDs).^{181, 182} Regarding LED devices, basically inorganic semi-conductors are applied providing efficient light sources of various colors. LEDs are used for traffic signaling, decoration, automotive applications and black lighting.¹⁸³ On the other hand, in OLED devices the illumination is generated by electroluminescence through the film of the system.¹⁸⁴ OLEDs are used as displays in mobile screens and in televisions. The most essential layer for the device performance is the one that contains the luminescent material, which is either a phosphorescent transition metal compound or a fluorescent molecule. In most of the produced OLED devices there are more than 15 individual layers that form a multilayer stack.¹⁸⁵ The construction of such devices can be achieved by vacuum sublimation, thus using only

¹⁷⁹ Crawford, M.H., IEEE J. Sel. Top. Quantum Electron. 2009, 15, 1028-1040.

¹⁸⁰ Li, J.; Yan, J.; Wen, D.; Khan, W.U.; Shi, J.; Wu, M.; Sua, Q.; Tanner, P.A., *J. Mater. Chem. C*, **2016**, *4*, 8611-8623.

¹⁸¹ Xu, R.-P.; Li, Y.-Q.; Tang, J.-X., J. Mater. Chem. C, 2016, 4, 9116-9142.

¹⁸² Kordt, P.; van der Holst, J.J.M.; Al Helwi, M.; Badinski, A.; Lennartz, C.; Andrienko, D., *Adv. Funct. Mater.*, **2015**, *25*, 1955-1971.

¹⁸³ Humphreys, C.J., *MRS Bull.*, **2008**, *33*, 459-470.

¹⁸⁴ Li, Z.; Meng, H., Organic Light-Emitting Materials and Devices, CRC, Boca Raton, FL, 2007.

¹⁸⁵ Highly Efficient Oleds with Phosphorescent Materials (Ed.: Yersin, H.), Wiley-VCH, Weinheim, **2008**.

thermally stable non-ionic materials is feasible. As a result, the selection of suitable compounds is a difficult task since the majority of luminescent transition-metal complexes are ionic species.¹⁸⁶ The main limitations of OLEDs are the high manufacturing cost due to the mandatory multi-layer evaporation processes and the need for rigorous encapsulation of the devices.

The above described obstacles of OLEDs have stimulated the need for the development of technologies in the field of electroluminescent lighting devices.¹⁸⁷ Light-emitting electrochemical cells (LECs) are the most popular between those technologies and possess a simpler device architecture which is consisted of fewer layers and constructed through less packaging procedures.¹⁸⁸ Moreover, LECs do not rely on air-sensitive materials and the formed layers can be processed from solution samples. LECs consist of an ionic luminescent material, usually a conjugated light-emitting polymer or an ionic transition-metal complex that is sandwiched between two electrodes (**Figure 4.3**). Overall, as presented in **Figure 4.3** for the construction of a typical OLED multiple layers are deposited stepwise by thermal vacuum evaporation. In OLEDs the electron injection is achieved through two unstable in air methods, either by using an injection layer or by the use of a function metal. However, a LEC device is consisted of only one active layer in which air stable metals are applied and whose function is the efficient electron and hole injection via external electric current.



Figure 4.3: Schematic representation of a typical OLED (left) and LEC (right).¹⁸⁹

¹⁸⁶ Photochemistry and Photophysics of Coordination Compounds I and II: Balzani, V.; Campagna, S., Topics in Current Chemistry, *280-281*, Springer, Berlin, **2007**.

¹⁸⁷ Sessolo, M.; Bolink, H.J., Adv. Mater., **2011**, 23, 1829-1845.

¹⁸⁸ Su, H.-C.; Wong, K.-T.; Wu, C.-C., in WOLEDs and Organic Photovoltaics-Recent Advances and Applications (Hrsg.: Yam, V.W.W.), Springer, Berlin, **2010**.

¹⁸⁹ Hu, T.; He, L.; Duan, L.; Qiu, Y., J. Mater. Chem., **2012**, 22, 4206-4215.

Plenty types of LECs have been studied in the last 20 years comprised of different materials and device concepts.¹⁹⁰ In a LEC device the basic function of the anode, which is typically indium-tin-oxide (ITO), is to inject holes or positive charges into the HOMO of the emissive layer. The cathode on the other hand, injects electrons or negatively charged particles into the LUMO of the active layer and is commonly comprised of aluminum. By applying an electric current the holes migrate towards the cathode, whereas the electrons towards the anode. The operation principle of LEC devices can be described by two mechanistic models, the electro-chemical doping (ECD)¹⁹¹ and the electro-dynamical doping (ED).¹⁹² Both of these models are illustrated in Figure 4.4 presenting the electronic and the ionic charge distribution in a LEC device. The negatively charged carriers (electrons and anions) are presented in blue while the positively charged (holes and cations) in red. Furthermore, the blue line represents the potential profile, the orange area corresponds to the high-field region and the yellow zone stands for the low-field region. In both models the application of bias leads to the injection of electrons and holes and consequently the separation of ions in the light-emitting layer. In the ED model, electric double layers (EDLs) are formed due to the accumulation of ions at the electrodes, dropping the electric potential near the electrodes and promoting charge injection from them. The field-free region that is formed through the interaction of cations with anions causes the emission of light from the device. Concerning the ECD model though, two regions are formed from the accumulation of cations and anions, namely the positive doping p-doped region which is originated by removal of an electron and the negative n-doped region by the addition of an electron. Those regions are enlarged over device operation and the p-i-n junction (i stands for intrinsic region) between them is formed which favors charge recombination and light emission.^{193, 194}

¹⁹⁰ Maness, K.M.; Terrill, R.H.; Meyer, T.J.; Murray, R.W.; Wightman, R.M., *J. Am. Chem. Soc.*, **1996**, *118*, 10609-10616.

¹⁹¹ Pei, Q.; Yu, G.; Zhang, C.; Yang, Y.; Heeger, A.J., *Science*, **1995**, *269*, 1086-1088.

¹⁹² deMello, J.C.; Tessler, N.; Graham, S.C.; Friend, R.H., *Phys. Rev. B*, **1998**, *57*, 12951.

¹⁹³ deMello, J.C., *Phys. Rev. B*, **2002**, *66*, 235210.

¹⁹⁴ van Reenen, S.; Janssen, R.A.J.; Kemerink, M., Org. Electron., **2011**, *12*, 1746-1753.



Figure 4.4: Illustration of the two possible operation principles in a LEC device. The ED model (upper part) and the ECD model (lower part).¹⁹⁵

4.2 Porphyrin-BODIPY dyads for light emitting devices

4.2.1 Introduction

This project demonstrates the synthesis of two porphyrin-BODIPY dyads through click chemistry and the first application of such compounds in LEC devices.¹²⁷ Photophysical and electrochemical characterization of the novel dyads is presented along with their results in lighting schemes. The developed lighting devices are comprised of unique features, specifically excellent film morphology leading to good electronic alignment and efficient energy transfer in solution and in solid state between the two chromophores. The above characteristics led to remarkable stabilities of 1000 h and efficiencies of 0.13 lumens per watt (Lm/W) at the deep-red lighting devices that we developed.

Various porphyrin derivatives have been successfully incorporated in OLED devices as emitters via a host-guest approach.¹⁹⁶ Functionalized porphyrins with other chromophores sustain efficient energy/electron transfer processes and thus possess enhanced light-harvesting and photoluminescence (PL) properties. However in LEC devices porphyrin derivatives had never been used since our attempt.¹²⁷ As a matter of

¹⁹⁵ van Reenen, S.; Matyba, P.; Dzwilewski, A.; Janssen, R.A.J.; Edman, L.; Kemerink, M., *J. Am. Chem. Soc.*, **2010**, *132*, 13776-13781.

¹⁹⁶ Ostrowski, J.C.; Susumuru, K.; Robinson, M.R.; Therien, M.J.; Bazan, G.C., *Adv. Mater.*, **2003**, *15*, 1296-1300.

fact, the concept of small-molecule LECs has been reported only recently by Tang et al.¹⁹⁷ In this work the application of non-ionic small molecules was reported as active materials in LECs. The authors suggested that the LEC library regarding the active compounds could be expanded, using small molecules that are easily synthesized and purified. The LEC community has already started to follow this novel approach; yet with moderate results. In such devices red electroluminescence is achieved by using benzothiadiazole or cyanines derivatives.^{198, 199} As reported in many publications, to enhance device lifetime and efficiency the decoupling of charge transport and emission processes is obligatory.^{200, 201}

To tackle this aspect, our work represents the unique example of using the wellknown properties of the porphyrin-BODIPY dyads in terms of energy transfer to provide a novel strategy to decouple charge transport and emission processes in LECs. The above mentioned characteristics of our dyads are essential for lighting schemes, since the emission as well as the decoupled charge transport processes are achieved by using only one active compound. This is the most critical factor determining the device operation since the active layer assists the charge injection process. In addition, the emission process initiated by the charge transport and the electron-hole recombination occurs via the emitter.

In this context, our work represents a distinctive example of porphyrin-BODIPY dyads as active materials in LEC. In addition, the performance in terms of both efficiency and stability (1000 h) clearly stands out as the state-of-the-art in LECs.^{202, 203} Furthermore, by exploiting the well-known properties of the porphyrin dyads in terms of energy transfer we provided a novel strategy to decouple charge transport and emission processes in LECs, leading to a remarkable device performance. The chemical structures of the two click-made porphyrin-BODIPY dyads are illustrated in **Figure 4.5** below.

¹⁹⁷ Tang, S.; Tan, W.-Y.; Zhu, X.-H.; Edman, L., Chem. Commun., **2013**, 49, 4926-4928.

¹⁹⁸ Huang, J.; Liu, Q.; Zou, J.-H.; Zhu, X.-H.; Li, A.-Y.; Li, J.-W.; Wu, S.; Peng, J.; Cao, Y.; Xia, R.; Bradley, D.D.C.; Roncali, J., *Adv. Funct. Mater*, **2009**, *19*, 2978-2986.

¹⁹⁹ Li, Y.; Li, A.-Y.; Li, B.-X.; Huang, J.; Zhao, L.; Wang, B.-Z.; Li, J.-W.; Zhu, X.-H.; Peng, J.; Cao, Y.; Ma, D.-G.; Roncali, J., *Org. Lett.*, **2009**, *11*, 5318-5321.

²⁰⁰ Qian, G.; Lin, Y.; Wantz, G.; Davis, A.R.; Carter, K.R.; Watkins, J.J., *Adv. Funct. Mater.*, **2014**, *24*, 4484-4490.

²⁰¹ Liao, C.-T.; Chen, H.-F.; Su, H.-C.; Wong, K.-T., Phys. Chem. Chem. Phys., 2012, 14, 1262-1269.

 ²⁰² Weber, M.D.; Adam, M.; Tykwinski, R.R.; Costa, R.D., *Adv. Funct. Mater.*, **2015**, *25*, 5066-5074.
 ²⁰³ Subeesh, M.S.; Shanmugasundaram, K.; Sunesh, C.D.; Won, Y.S.; Choe, Y., *J. Mater. Chem. C*, **2015**, *3*, 4683-4687.



Figure 4.5: Chemical structure of the two porphyrin-BODIPY dyads that were applied in LEC devices.¹²⁷

4.2.2 Experimental

The synthesis of porphyrin-BODIPY dyads **1** and **2** is illustrated in **Scheme 4.1**. The formation of **1** and **2** was achieved via click reaction between an azize-porphyrin and the corresponding BODIPY molecule that was functionalized with a triple bond. The azide-porphyrin, (**Zn**)**DMP-N₃-COOH** was prepared following the same experimental approach of a previous publication.¹²³ While the functionalized alkyne BODIPY's (**BDP-Triple** and **BDP-O-Triple**) were synthesized according to published procedures as well.^{204, 205} Both formed dyads (**1** and **2**) consist of two chromophores (porphyrin and BODIPY) which are covalently linked through a 1,2,3,-triazole ring. As illustrated in the figure above the only difference between those two dyads is the presence of one ether bridge in case of dyad **1**. On the contrary, this bridge is absent in dyad **2** where the phenyl group of the BODIPY entity is directly attached to the 1,2,3-triazole unit on the porphyrin macrocycle. In order to link the two chromophores together click reaction was performed. In detail, the chromophores were dissolved in a 1:1 solution of dry THF/CH₃CN and in the presence of CuI as catalyst. The reaction was completed in 12 hours at room temperature and under constant stirring.

²⁰⁴ Li, Zi.; Bittman, R., J. Org. Chem., **2007**, 72, 8376-8382.

²⁰⁵ Atilgan, S.; Ozdemir, T.; Akkaya, E.U., Org. Lett., **2010**, 12, 4792-4795.



<u>Scheme 4.1:</u> The experimental procedure that we followed to synthesize porphyrin-BODIPY dyads 1 and 2.

<u>Synthesis of 1.</u> Equimolar amounts of porphyrin (**Zn**)**DMP-N₃-COOH** (26 mg, 0.031 mmol) and **BDP-O-Triple** (11.7 mg, 0.031 mmol) were dissolved in a 1:1 mixture of THF/CH₃CN (5 mL) under nitrogen atmosphere. Afterwards CuI (6 mg, 0.032 mmol) and DIPEA (5 μ lt, 0.031 mmol) were added and the reaction mixture was stirred at room temperature for 12 hours. Upon reaction completion, the volatiles were removed under reduced pressure and the crude solid, was purified by column chromatography (silica gel, CH₂Cl₂) yielding the 20 mg of **1** (0.016 mmol, yield: 53%).

¹H NMR (300 MHz, DMSO-*d*₆): δ = 13.17 (s, 1H), 9,29 (s, 1H), 8.79 (d, *J* = 4.6 Hz, 2H), 8.72 (d, *J* = 4.6 Hz, 2H), 8.61 (m, 4H), 8.42 (d, *J* = 8.4 Hz, 2H), 8.33 (m, 6H), 7.34 (s, 4H), 7.32 (s, 4H), 6.19 (s, 2H), 5.42 (s, 2H), 2.58 (s, 6H), 2.46 (s, 6H), 1.79 (s, 12H), 1.44 (s, 6H) ppm. ¹³C NMR (75 MHz, DMSO-*d*₆): δ = 167.7, 158.7, 154.7, 149.2, 149.0, 148.8, 147.3, 143.8, 143.1, 142.8, 142.1, 139.1, 138.4, 137.0, 136.0, 135.3, 134.4, 131.9, 131.2, 130. 5, 130.0, 129.3, 127.6, 127.5, 126.6, 123.5, 121.4, 118.6, 118.4, 118.3, 115.8, 61.4, 21.5, 21.1, 14.3 ppm. HRMS (MALDI-TOF): calc. for C₇₃H₆₁BFN₉O₃ Zn [M + H]⁺: 1224.4250; found 1224.4263.

<u>Synthesis of 2.</u> Equimolar amounts of porphyrin (**Zn**)**DMP-N₃-COOH** (26 mg, 0.031 mmol) and **BDP-Triple** (10.8 mg, 0.031 mmol) were dissolved in a 1:1 mixture of THF/CH₃CN (5 mL) under nitrogen atmosphere. In the next step, CuI (6 mg, 0.032

mmol) and DIPEA (5 µlt, 0.031 mmol) were added and the reaction mixture was stirred at room temperature for 12 hours. Upon reaction completion, the volatiles were removed under reduced pressure and the crude solid was purified by column chromatography using silica gel and CH_2Cl_2 as eluent, affording the 22 mg of **2** (0.018 mmol, yield: 59%).

¹**H NMR (300 MHz, DMSO-***d*₆**):** δ = 13.09 (s, 1H), 9,76 (s, 1H), 8.83 (d, *J* = 4.4 Hz, 2H), 8.73 (d, *J* = 4.1 Hz, 2H), 8.63 (d, *J* = 4.1 Hz, 2H), 8.61 (m, 2H), 8.47 (d, *J* = 7.8 Hz, 2H), 8.35 (m, 6H), 8.28 (d, *J* = 7.4 Hz, 2H), 7.60 (d, *J* = 7.5 Hz, 2H), 7.32 (s, 4H), 6.22 (s, 2H), 2.58 (s, 6H), 2.50 (s, 6H) 1.79 (s, 12H), 1.50 (s, 6H) ppm.

¹³C NMR (75 MHz, DMSO- d_6): $\delta = 167.7, 155.1, 149.4, 149.2, 149.1, 148.8, 147.3, 146.8, 143.2, 142.8, 141.6, 139.1, 138.4, 137.0, 136.0, 135.4, 134.4, 134.0, 132.0, 131.2, 130.8, 130.5, 129.8, 128.8, 127.6, 126.2, 121.5, 120.7, 118.6, 118.4, 118.3, 21.5, 21.1, 14.3 ppm.$

HRMS (MALDI-TOF): calc. for $C_{72}H_{59}BN_9O_2Zn [M + H]^+$: 1194.4144; found 1194.4161.

4.2.3 Results and Discussion

The successful formation of both dyads was verified through ¹H and ¹³C NMR spectroscopy and via MALDI-TOF mass spectrometry. In **Figure 8.18** and **8.19** the ¹H NMR spectrum of **1** is presented, while the corresponding ¹H NMR spectrum of **2** is provided in **Figures 8.20** and **8.21**. The characteristic proton signal of the formed triazole ring is appeared at 9.29 ppm for dyad **1** and at 9.76 ppm regarding dyad **2**. In addition, we can detect the proton signal concerning the carboxylic acid unit at 13.17 and 13.09 ppm for **1** and **2**, respectively. The relevant carbon peaks in the ¹³C NMR spectra were found at 123.5 and 120.7 ppm for the carbon of the triazole ring for dyad **1** and **2**, respectively (**Figures 8.22-8.25**). Noteworthy, both the carbon signals of the dyads regarding the carboxylate unit were observed at 167.7 ppm. The MALDI-TOF spectrum of **1** is provided in **Figure 8.26** along with the isotope pattern of the mass peak comparing the theoretical with the experimental (**Figure 8.27**). Accordingly the obtained MALDI-TOF spectra of dyad **2** as well as the isotope pattern are illustrated in **Figures 8.28** and **8.29**, respectively.

Computational studies along with cyclic and square wave voltammetry measurements have been performed in order to investigate the molecular as well as the electronic structures of the final porphyrin-BODIPY dyads. In **Table 4.1** a collection of their redox features is listed along with the electrochemical data of the reference

compounds. As reference compounds we have used the two alkyne-BODIPYs (**BDP**-**O-Triple** and **BDP-Triple**) and the (**Zn**)**DMP-N₃-COOH** (**Zn-Porphyrin**) as well.

<u>**Table 4.1:</u>** Summary of the electrochemical redox data of the final dyads (1 and 2) and the reference compounds (**Zn-Porphyrin**, **BDP-O-Triple** and **BDP-Triple**) measured in THF. All potentials are reported vs. SCE and FcH/FcH⁺ was used as the internal standard ($E_{1/2}Ox$ is 0.55V).</u>

Compound	Reduct	ion (V)	Oxidation (V)		
Compound	E1/2 Red ¹	E _{1/2} Red ²	E _{1/2} Ox ¹	E _{1/2} Ox ²	
Zn-Porphyrin	-1.15	-1.52	1.03	1.38	
BDP-O-Triple	-1.13	-	1.38	-	
BDP-Triple	-1.09	-	1.41	-	
1	-1.18	-1.40	0.98	1.34	
2	-1.11	-1.39	1.03	1.40	

The cyclic and square wave voltammograms for **1** and **2** are presented in **Figure 4.6**. Each of the final porphyrin-BODIPY dyads shows two reversible reduction and two reversible oxidation peaks. Comparing the oxidation data of each dyad with the corresponding reference chromophores we can conclude that the first oxidation wave $(E_{1/2} \text{ Ox}^1)$ is assigned as a porphyrin oxidation peak, whereas the second oxidation $(E_{1/2} \text{ Ox}^2)$ can be assigned as an overlap to both porphyrin and BODIPY oxidation peaks. The fact that the first oxidation wave is located at the porphyrin suggests that an efficient hole trapping process in the porphyrin is expected under device operation conditions. On the contrary, regarding the reduction process we cannot export a similar conclusion, since the first reduction $(E_{1/2} \text{ Red}^1)$ in both dyads is an overlap of the reduction processes in both BODIPY and porphyrin derivatives.


Figure 4.6: Cyclic (CV) and square wave (SQ) voltammograms of 1 (left part) and 2 (right part).

Therefore, in order to determine the nature of the reduction process, DFT calculations have been performed. The gas phase optimized structures of **1** and **2** are illustrated in **Figure 8.29** while their corresponding coordinates are listed in **Table 8.5** and **8.6**, respectively. The observation of their frontier molecular orbitals with the corresponding electronic distribution shed light to the origin of the reduction process. More specifically, as presented in **Figure 4.7** in both dyads the electronic structure of the ground state consists of two LUMO that are located at the porphyrin unit. These findings are consistent with the CV measurements where the first oxidation peak was assigned to the porphyrin moiety. On the other hand the HOMO in both cases is located at the porphyrin ring and the HOMO-1 to the BODIPY moiety. Thus the above energy distributions indicate that the reduction could be assigned to the porphyrin moiety also. This finding suggests that under device operation, charge carrier trapping process possibly occurs at the porphyrin.



Figure 4.7: Frontier molecular orbitals of **1** (left part) and **2** (right part) with the corresponding energy levels.

The photo-physical characterization of the final compounds was performed through absorption and emission spectroscopies. Furthermore, apart from the steady-state measurements, time-resolved spectroscopy was also applied to obtain insight into the energy transfer process in the dyads. The absorption spectra of the reference and the final dyads are presented in **Figure 4.8**. In both cases, the obtain spectrum can be described as a superimposition of the UV-Vis spectra of the **Zn-Porphyrin** and the BODIPY molecule. More specifically, in the absorption spectra of **1** and **2** an intense Soret band at 425 nm, two Q-bands in the 555-600 nm range and one sharp band at 500 nm have appeared.



Figure 4.8: Absorption spectra of **Zn-Porphyrin**, **BDP-O-Triple** and **BDP-Triple** (left part) and **1** and **2** (right part) with their corresponding absorption coefficient number.

The emission and the excitation spectra of the final dyads and the reference compounds are illustrated in **Figure 4.9**. In addition, in **Table 4.2** a collection of the absorption and emission data of each dyad and reference compound along with their absorption coefficient numbers and their fluorescence quantum yields numbers is provided. The steady-state fluorescence and excitation experiments provided the first findings regarding the energy transfer in the dyads. When selectively excite the BODIPY unit in the dyads (490 nm), both the emission spectra showed an intense fluorescence peak at ~515 nm, and two fluorescence peaks at ~610 and 660 nm. The first peak (515 nm) is related to the BODIPY emission, while the peaks at 610 and 660 nm are characteristic features of a typicall zinc-porphyrin derivative (**Figure 4.8**).



Figure 4.8: Emission spectra of **1** and **BDP-O-Triple** (upper left part), **2** and **BDP-Triple** (upper right part) in THF solution upon excitation at 490 nm. Excitation spectra of **1** (lower left part) and **2** (lower right part) in THF solution when monitoring the porphyrin emission (at 660 nm).

The fluorescence peak that is assigned to BODIPY emission was strongly quenched in both dyads compared to the peak that appeared at the BODIPY reference spectra in isoabsorbing solutions. In detail, selective excitation of the BODIPY chromophore in the dyads showed an almost quantitative quenching of the BODIPY emission accompanied by the zinc porphyrin-based emission. Calculating the quantum yield of the fluorescence process revealed that for dyad **1** the quenching was 98%, whereas for dyad **2** 91% (**Table 4.2**). In addition the zinc porphyrin emission was not affected in terms of photoluminescence quantum yields, namely from 4.4% in the reference porphyrin the quantum yields were 4.8 for **1** and 4.3 for **2** (**Table 4.2**). The excitation experiments are in perfect agreement with the above findings since in the excitation spectra of the dyads when monitoring at the porphyrin-based emission (660 nm) a BODIPY absorption feature is observed at 500 nm. This implies that energy transfer occurs from the singlet excited state of the BODIPY unit to the lower lying singlet excited state of zinc porphyrin (**Figure 4.8**).

<u>**Table 4.2:**</u> Photoluminescence features of the BODIPY and Porphyrin reference as well as the dyads **1** and **2**.

	Absorption	Emission		
Compound	$\lambda_{max}/nm^{a} (\epsilon/mM^{-1}cm^{-1})$	Emission ^{a/b} λ _{max} /nm	Ф ^с (%)	Φ ^d (%)
Zn- Porphyrin	424 (368.2); 550 (19.1); 597 (2.8)	607; 657ª/ 660 ^b	-	4.4
BDP-O- Triple	500 (46.9); 359 (4.1); 307 (4.4)	512ª/- ^b	57	-
BDP-Triple	499 (42.8); 361 (3.5); 306 (2.3)	514ª/- ^b	51	-
1	425 (369.3); 500 (46.1); 557 (11.6); 598 (2.9)	514;607;656 ^a / 656 ^b	1.1	4.8
2	426 (379.8); 501 (41.2); 557 (12.3); 598 (2.2)	515;607;655ª/ 659 ^b	4.4	4.3

^aAbsorption and emission maxima measured in THF. ^bEmission maxima of the thin films. ^cPhotoluminescence quantum yields using rhodamine ($\Phi = 49\%$ in ethanol) as standard measured in THF upon excitation at 490 nm. ^dPhotoluminescence quantum yields using ZnTPP ($\Phi = 0.03$ in toluene) as standard measured in THF upon excitation at 550 nm.

To prove the above hypothesis transient absorption measurements were performed in the final dyads 1 and 2 (Figure 4.9 and 8.31) using for comparison reasons BDP-Triple as a reference compound (Figure 8.32). In the transient absorption spectra of **BPD-Triple** we observe a pronounced peak at the 400-600 range, upon photoexcitation at 505 nm. This feature is assigned to the formation of the first excited BODIPY singlet state with a lifetime of 3750 ps. On the other hand photoexcitation of 1 and 2 at the same wavelength (505 nm), results in the bleaching of the aforementioned peak and a weak transient absorption in the NIR region (1100 nm). This transient feature rapidly decays with a lifetime of 82 ps in case of 1 and 60 ps in 2. In addition new transient absorption features are observed maximizing at 455, 535, 585, 690 and 855 nm. Those transient absorption peaks indicate the formation of the first excited singlet state of the porphyrin unit in the dyads. Additionally, the Zn-porphyrin singlet first excited state decays into the corresponding Zn-porphyrin triplet excited state with a lifetime of 2600 ps in 1 and 2800 ps in 2. Generally, in both dyads upon photoexcitation at 505 nm the singlet excited state of the BODIPY is formed which is strongly quenched due to efficient energy transfer to the porphyrin moiety. The energy transfer process is quicker in case of dyad 2, a fact that was expected due to the longer distance of the BOPIDY unit from the porphyrin entity in dyad 1.



Figure 4.9: Femtosecond transient absorption spectra of dyad **1** (left part) and dyad **2** (right part) in argon saturated THF; 1 ps (black), 10 ps (red), 100 ps (green), 1000 ps (blue), and 7500 ps (cyan) after excitation at 505 nm

To examine the behavior of our dyads in solid state, films of both the final compounds and the reference compounds were constructed. Their morphology was investigated using Atomic Force Microscopy (AFM) and as you can clearly observe (**Figure 4.10**) the films of the final dyads were homogenous, with no particular aggregation or phase separation features. In the constructed films of **Zn-Porphyrin** though, we observe aggregation features that could limit the efficiency of a working LEC device due to their potency to act as emission quenchers. The same features are observed in the case of **Zn-Porphyrin/BODIPY-Triple** mixture (1:1 ratio). The latter proves the excellent morphology that dyads possess in thin films comparing to the references or mixtures of them.



Figure 4.10: AFM images of **1** (left), **Zn-Porphyrin** (middle), and 1:1 molar ratio mixture of **Zn-Porphyrin/BODIPY-Triple** films with a thickness of 110 nm.

In addition, we have also performed photoluminescence studies in the formed films which provided similar findings with the solution studies (**Figure 4.11**). Explicitly, in the solid state emission spectra of the final dyad **1** upon excitation at 490 nm we can detect a broad band at around 660 nm, lacking the BODIPY emission. This absence of BODIPY features could be attributed to the poor emission of such chromophore in thin films. However the excitation spectra of the thin film when monitoring at the range that zinc porphyrin emits (660 nm) clearly showed the corresponding absorption peak of BODIPY at 500 nm. Consequently, the energy transfer process for the BODIPY unit to the porphyrin moiety occurs in both solution and solid state.



Figure 4.11: Emission spectra of **1** films upon excitation at 490 nm (left part) and excitation spectra of **1** films when monitoring the emission at 660 nm (right part).

We have used the thin films of the dyads to prepare deep-red lighting sources for LEC devices. In addition, we have also prepared LECs using the reference compounds so as to detect at what degree the use of the final dyads was beneficial for the device performance. The following procedure was followed to create each LEC: the thin film was mixed with an ionic electrolyte matrix to prepare the active layer and afterwards the modified films were deposited onto glass substrates that were coated with indium tin oxide (ITO). The ITO was modified with poly-(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) with a thickness of 100 nm. Lastly, for the succesfull formation of the device, aluminum was used as the top cathode. All the LEC devices were analyzed using electroluminescence measurements (EL) as well as average voltage and irradiance versus time diagrams. In Figure 4.12 the normalized electroluminescence measurements of BODIPY-Triple, Zn-Porphyrin, dyad 1 and dvad 2 are provided along with the average voltage and irradiance vs. time diagram of dyad 1. The devices that were prepared using the reference compounds BODIPY-**Triple** and **Zn-porphyrin** showed green and red emission with EL peaks located at 545, as well as 630 and 660 nm, respectively. Nevertheless, the LEC devices prepared with dyads 1 and 2 showed an EL response that was related to the porphyrin unit only (630 and 670 nm). Notably, the maximum luminous efficacy and the maximum irradiance of device 1 were 5 times greater compared to those of the Zn-Porphyrin device. Thus, in the LEC devices based on the dyads the energy transfer process is advantageous for the device performance highlighting the need for having both chromophores linked. In order to measure the efficiency and stability of the LEC device we applied voltage and an immediate EL response was detected, with a turn-on time on

the sub-second regime. Then, by reducing the applied voltage over time the irradiance continues to increase until it reaches its maximum value. All those experiments as, illustrated in **Figure 4.12** provide great results in terms of efficiency and stability, namely the two LEC devices with **1** and **2** featured lifetimes of around 1000 hours and efficiencies of 0.13 Lm/W. Those values are comparable to the best performing OLED devices based on porphyrin derivatives.^{206, 207}



Figure 4.12: Left part: Normalized electroluminescence spectra of **BODIPY-Triple** (open circles) and **Zn-Porphyrin** (close circles), **1** (open triangles) and **2** (close triangles) devices. Right part: Average voltage (open symbols) and irradiance (full symbols) vs. time of **1** device.

In conclusion, this is the first reported porphyrin derivative that has been applied in a new concept based on LEC devices. In detail, only one active compound mixed with an ionic electrolyte was responsible for charge transport and emission process that led to one of the best porphyrin-based deep-red light emitting device. The synthesized porphyrin-BODIPY dyads **1** and **2** fulfill key merits for an efficient LEC device such as: i) the quantitative energy transfer between the two chromophores both in solution and solid state, ii) the suitable energy alignment of the electronic levels between the BODIPY and the porphyrin units that assists the charge trapping process at the porphyrin, iii) the homogenous film morphology that lack phase separation and aggregation features between the two components iv) the presence of strong porphyrin emission which is considered as one of the best candidates for developing narrow emission deep-red OLEDs.^{196, 206, 207}

²⁰⁶ Fenwick, O.; Sprafke, J.K.; Binas, J.; Kondratuk, D.V.; Stasio, D.; Anderson, H.L.; Cacialli, F., *Nano Lett.*, **2011**, *11*, 2451-2456.

²⁰⁷ Wang, X.; Wang, H.; Yang, Y.; He, Y.; Zhang, L.; Li, Y.; Li, X., *Macromolecules*, **2010**, *43*, 709-715.

Chapter 5: DNA and Porphyrin Assemblies

5.1 Introduction

Natural biological systems are considered as the ideal assemblies for chemists to create supramolecular configurations since possessing the perfect structure enabling them to function in living organisms. To this end, 2'-deoxyribose nucleic acid (DNA), can be considered as an essential construction material for such supramolecular structures due to its key merits. More specifically, such virtues are the DNA's predictable three-dimensional structure that forms the well-known double helix as well as its synthetic availability. The structure of DNA has been studied by many research groups over the years but it was finally clarified in 1953 by Watson and Crick.²⁰⁸ Despite the various known morphologies of DNA, there are three major forms that are illustrated in **Figure 5.1**. In particular, A- and B-form DNA structures are helices with right hand orientation on the contrary to the Z-form DNA left handed helix.^{209, 210}



Figure 5.1: The three forms of DNA a) A-DNA, b) B-DNA and c) Z-DNA.²¹⁰

²⁰⁸ Watson, J. D.; Crick, F.H.C., *Nature*, **1953**, *171*, 737-738.

²⁰⁹ Franklin, R.E.; Gosling, R.G., *Nature*, **1953**, *171*, 740-741.

²¹⁰ Arnott, S., *Trends Biochem. Sci.*, **2006**, *31*, 349-354.

DNA is an ideal scaffold for supramolecular systems; therefore taking advantage the properties of DNA novel supramolecular assemblies with chromophores can be developed. As a template DNA, can be used either as a double or as a single strand, in order to create well-defined and targeted architectures. The basic principle to build DNA architectures is via the ability of complementary strands for selective recognition (**Figure 5.2**). There are many examples of DNA nanostructures, for instance the concept of origami in which DNA sequences of several length are linked together to form designs of certain structures.²¹¹



Figure 5.2: DNA double and single strands (left upper part). The recognition of complementary DNA strands (right part). Two examples of DNA origami structures (left lower part).

Assemblies of DNA with organic chromophores have been studied over the years for various applications in medicinal chemistry, electronics, materials science and more.^{212, 213} Porphyrins are excellent modifiers for developing DNA-porphyrin structures. Not only their chemical and optical properties can easily be tuned, but lipophilic porphyrin derivatives can be used as anchoring molecules into a DNA template, thus transporting it in hydrophobic environments. Even though porphyrin-DNA assemblies have been studied mostly for their optical and structural properties,

²¹¹ Saccà, B.; Niemeyer, C.N., Angew. Chem. Int. Ed., 2012, 51, 58-66.

²¹² Ensslen, P.; Wagenknecht, H.A., Acc. Chem. Res., 2015, 48, 2724-2733.

²¹³ Malinovskii, V.L.; Wenger, D.; Härner, R., Chem. Soc. Rev., **2010**, *39*, 410-422.

many targeted applications regarding such assemblies have been reported. Namely, porphyrins have been used as electrochemical tags for DNA sensing and porphyrin-DNA based lipid bilayers for spanning nanopores. Hence, the creation of new materials based on DNA-porphyrin assemblies is of great importance in many fields of chemistry, such as catalysis, light harvesting schemes, optics and energy/electron transfer systems.^{214, 215} For the preparation of DNA-porphyrin assemblies two approaches have been followed, the covalent attachment and the supramolecular coordination. In the latter, porphyrin units self-assemble via hydrogen bonds with DNA templates. Regarding the covalent approach though, DNA-porphyrin assemblies are formed through sequential attachment of starting building blocks, introducing different porphyrin moieties with a programmed arrangement.

The first porphyrin-DNA structure was reported by Casas et al. in 1993 that described the attachment of a manganese-porphyrin derivative to oligonucleotides.²¹⁶ A few years later, Brault and coworkers created an artificial nuclease with a chlorin moiety on the periphery of the nucleotide strand.²¹⁷ In both studies though the functionalization of the DNA strand with the porphyrin derivative was at the end of the oligonucleotide sequence. As a matter of fact, the first embedded porphyrin in a DNA sequence was published in 1998 by Berlin et al.²¹⁸ Many other reports followed this approach by replacing either a nucleoside or a nucleobase with a modified porphyrin entity.^{219, 220} Finally, numerous arrays have been investigated with porphyrin moieties placed on the periphery of the DNA. The first supramolecular scaffold for porphyrin arrays was presented in 2007 by Stulz and coworkers in which TPP modified with deoxyuridine base was applied for a covalent attachment onto a DNA structure.²²¹ In **Figure 5.3** representative examples of each approach are presented. More specifically, a) the first single end-of-DNA porphyrin attachment,²¹⁷ b) a porphyrin derivative

²¹⁴ Zhao, L. Z.; Qu, R.; Li, A.; Ma, R. J.; Shi, L. Q., Chem. Commun., **2016**, 52, 13543-13555.

²¹⁵ Rioz-Martinez, A.; Roelfes, G., Curr. Opin. Chem. Biol., **2015**, 25, 80-87.

²¹⁶ Casas, C.; Lacey, C.J.; Meunier, B., *Bioconjugate Chem.*, **1993**, *4*, 366-371.

²¹⁷ Boutorine, A.S.; Brault, D.; Takasugi, M.; Delgado, O.; Hélène, C, J. Am. Chem. Soc., **1996**, *118*, 9469-9476.

²¹⁸ Berlin, K.; Jain, R.K.; Simon, M.D.; Richert, C.A., J. Org. Chem., **1998**, 63, 1527-1535.

²¹⁹ Morales-Rojas, H.; Kool, E.T.A., Org. Lett., 2002, 4, 4377-4380.

²²⁰ Vybornyi, M.; Nussbaumer, A.L.; Langenegger, S.M.; Häner, R., *Bioconjugate Chem.*, **2014**, 25, 1785-1793.

²²¹ Fendt, L.A.; Bouamaied, I.; Thöni, S.; Amiot, N.; Stulz, E., J. Am. Chem. Soc., **2007**, *129*, 15319-15329.

inserted in a DNA strand²¹⁸ and c) the first multi-porphyrin array through external incorporation into a DNA scaffold.²²¹



Figure 5.3: Examples of porphyrin attachment on DNA sequence: a) at the end, b) embedded and c) on the periphery. ^{217, 218, 221}

5.2 DNA modification with porphyrin derivatives

5.2.1 Introduction

In this chapter, DNA modification by porphyrin derivatives via three different approaches is discussed. In detail, two different click reactions (copper-catalyzed and copper-free) were probed in order to efficiently attach various azide-porphyrins onto the DNA. In addition, amide coupling reaction between an amino-porphyrin and a properly functionalized DNA strand was studied in order to compare the efficiency of the two click reactions. The comparison between the two synthetic approaches was made in terms of internal as well as terminal DNA modification. Finally, the formed DNA-multi-porphyrin arrays were assembled in supramolecular structures providing an alternative yet efficient route for exciton coupling. Supramolecular porphyrin assemblies are one of the most attractive research field because the formed structures can be used in plenty light harvesting schemes.²²² Particularly, artificial photosynthetic schemes,^{131, 223} catalysis,²²⁴ sensing²²⁵ and molecular electronics²²⁶ are only a few examples of research topics that deal with supramolecular porphyrin assemblies. Porphyrins are ideal building blocks for these applications due to their tunable and diverse properties. Moreover, the use of DNA as a supramolecular template has gained widespread attention in developing multi-chromophore arrays.^{227, 228} Plenty synthetic approaches have been followed to efficiently connect porphyrins with oligonucleotides, including post synthetic modifications as well as solid phase synthesis.^{229, 230}

In this project we used four different functionalized oligonucleotide sequences (**ODNs**) and four porphyrin derivatives (**P-1, P-2, P-3** and **P-4**) to successfully synthesize porphyrin-DNA assemblies through click reactions or through amide coupling. As presented in **Figure 5.4** the oligonucleotides were functionalized with a 5-(octa-1,7-diynyl) sidechain either at the terminal position (**ODN-1**) or with alkyne groups inserted at five positions with variable spacing between the alkynes (**ODN-2**). To probe the post-synthetic modification with click chemistry (copper- and non-copper-based) three azido-porphyrin derivatives were synthesized (**P-1, P-2** and **P3**). Noteworthy, in order to perform the copper-free click reaction **ODN-3** was prepared bearing a cyclooctyne group in a terminal position. In addition, one amino-porphyrin was prepared (**P-4**) to perform amide coupling reaction, for comparison reasons, with the properly functionalized **ODN-4**.

²²² Zhang, C.C.; Chen, P.L.; Dong, H.L.; Zhen, Y.G.; Liu, M.H.; Hu, W.P., *Adv. Mater.*, **2015**, *27*, 5379-5387.

²²³ Yamamoto, M.; Föhlinger, J.; Petersson, J.; Hammarström, L.; Imahori, H., *Angew. Chem. Int. Ed.*, **2017**, *56*, 3329-3333.

²²⁴ Roux, Y.; Ricoux, R.; Avenier, F.; Mahy, J.P., Nat. Commun. 2015, 6, 8509.

²²⁵ Zhang, Z.; Kim, D.D.; Lin, C.Y.; Zhang, H.C.; Lammer, A.D.; Lynch, V.M.; Popov, I.; Miljanic, O.S.; Anslyn, E.V.; Sessler, J.L., *J. Am. Chem. Soc.*, **2015**, *137*, 7769-7774.

²²⁶ Davis, C.M.; Ohkubo, K.; Lammer, A.D.; Kim, D.S.; Kawashima, Y.; Sessler, J.L.; Fukuzumi, S., *Chem. Commun.*, **2015**, *51*, 9789-9792.

²²⁷ Lee, H.; Jeong, Y.H.; Kim, J.H.; Kim, I.; Lee, E.; Jang, W.D., *J. Am. Chem. Soc.*, **2015**, *137*, 12394-12399.

²²⁸ Schreiber, R.; Do, J.; Roller, E.M.; Zhang, T.; Schuller, V.J.; Nickels, P.C.; Feldmann, J.; Liedl, T., *Nat. Nanotechnol.*, **2014**, *9*, 74-78.

²²⁹ Woller, J.G.; Hannestad, J.K.; Albinsson, B., J. Am. Chem. Soc., 2013, 135, 2759-2768.

²³⁰ Borjesson, K.; Woller, J.G.; Parsa, E.; Martensson, J.; Albinsson, B., *Chem. Commun.*, **2012**, *48*, 1793-1795.



Figure 5.4: Structures of the porphyrins and sequences of ODNs including the modifiers for subsequent attachment of the functionalized porphyrin derivatives.

5.2.2 Experimental

This project was conducted in collaboration with University of Southampton (UoS) and Baseclick (GmbH) Company. The synthesis and characterization of **P-1** and **P-4** derivatives, the amide coupling reaction, as well as the purification of the final porphyrin-DNA assemblies through HPLC were carried out in UoS. Whereas, the alkyne modified oligonucleotides were provided by baseclick GmbH along with the oligo-click kit for the successful completion of click reactions. Regarding porphyrins **P-2** and **P-3**, their synthesis and characterization took place in our laboratory, as well as their final attachment to the DNA using the oligo-click kit provided from baseclick. Moreover, the final porphyrin-DNA arrays were characterized after purification through HPLC by MALDI-TOF mass spectrometry in our laboratory as well.

For the preparation of **P-2**, we followed the experimental procedure illustrated in **Figure 5.5**, while **P-3** was synthesized according to an already published procedure.¹²¹ In detail, 5-[4-(aminophenyl)]-10,15,20-triphenyl porphyrinato $zinc^{231}$ was functionalized with 5-bromovaleryl chloride to afford the bromo porphyrin derivative. Subsequently, the bromo-porphyrin was transformed into the azide-derivative **P-2** via sodium azide.



Figure 5.5: The experimental procedure followed for the preparation of P-2.

Synthesis of P-2. To a solution of 5-[4-(aminophenyl)]-10,15,20-triphenyl porphyrinato zinc (50 mg, 0.072 mmol) in dry CH₂Cl₂ (3 mL) and dry Et₃N (0.1 mL), 5-bromovaleryl chloride (45 μ L 0.336 mmol) was added and the reaction mixture was stirred at 40 °C for 3.5 hours. The solvent was removed under reduce pressure and CH₂Cl₂ (40 mL) was added. The organic phase was washed with H₂O (2 x 30 mL) separated and dried over anhydrous Na₂SO₄. The product was diluted in a THF solution (40 mL), an aqueous solution (4 mL) of NaN₃ (325 mg, 5 mmol) was added and the reaction mixture was refluxed for 4 hours. Upon removal of the solvents under reduced pressure, distilled H₂O (30 mL) and CH₂Cl₂ (30 mL) were added and the organic layer was separated and dried over anhydrous Na₂SO₄. Purification of the crude product by column chromatography (silica, CH₂Cl₂/EtOH 99:1) resulted in the isolation of 36 mg of **P-2** (yield: 60%).

¹**H NMR (500 MHz, CDCl₃):** δ = 8.93 (m, 8H), 8.22 (d, *J* = 7.1 Hz, 6H), 8.09 (d, *J* = 7.9 Hz, 2H), 7.75 (m, 10H), 7.52 (d, *J* = 7.7 Hz, 2H), 2.97 (m, 2H), 2.01 (m, 2H), 1.40 (m, 4H). ppm. **HRMS (MALDI-TOF):** calc. for C₄₉H₃₆N₈OZn [M]⁺: 816.2304; found 816.2308.

²³¹ Zervaki, G.E.; Papastamatakis, E.; Angaridis, P.A.; Nikolaou, V.; Singh, M.; Kurchania, R.; Kitsopoulos, T.N.; Sharma, G.D.; Coutsolelos, A.G., *Eur. J. Inorg. Chem.*, **2014**, *2014*, 1020-1033.

Porphyrin DNA coupling reactions

General procedure for the copper catalyzed click reaction using the baseclick oligo-kit:

The oligo-click kit was provided by Baseclick, Germany. This kit contained all required reagents except the porphyrin azide-derivatives (**P-1**, **P-2** and **P-3**) that were synthesized during this project.

The experimental procedure is as follows: To a "reactor" vial that contains the copper catalyst, the "activator" (ligand) solution (5 μ L) was added and thoroughly flushed with argon. Next, the alkyne-modified oligonucleotide (5 nmoles, 1 equiv.) in a solution of water (5 μ L) and the azide-porphyrin (250 nmoles, 50 equiv.) in a solution of DMF (50 μ L) were added. The reactor vial was then sealed under argon and heated to 30°C in the dark for 48 hours. After the completion of the reaction, nanopure water (100 μ L) was added to the reaction mixture and sequentially washed with ethyl acetate (200 μ L) until the organic layer was colorless. The lack of colour suggested the majority of the unreacted porphyrin had been removed from the vial. The porphyrin-modified oligonucleotide that remained in the aqueous layer was isolated by HPLC.

General procedure for the copper-free click reaction

The 5'-cyclooctyne-modified DNA (10 nmoles, 1 equiv.) was dissolved in deionized water (10 μ L) in an argon pursed Eppendorf tube. Next, the azide-porphyrin was added (100 nmoles, 10 equiv.) in a DMF solution (40 μ L). The reaction mixture was heated at 25 °C for 24 hours. In the next step, addition of water (100 μ L) takes place and the reaction mixture was sequentially washed with ethyl acetate (200 μ L) until all excess of unreacted porphyrin had been removed. The porphyrin-modified oligonucleotide that remained in the aqueous layer was isolated by HPLC.

5.2.3 Results and Discussion

To form the porphyrin-DNA arrays solution phase click chemistry was employed using the zinc metallated porphyrins **P-1**, **P-2** and **P-3** in order to avoid copper metallation due to the presence of the copper complex. The click reactions were performed using the oligo-kit from baseclick, using 1 equivalent of alkyne-ODN sequences and 50 equivalent of azide-porphyrin. The conversion of the alkyne-ODN to the mono-porphyrin adduct was achieved after 48 hours.

Upon completion of the copper click reaction, the crude mixture was analyzed via HPLC. As presented in **Figure 5.6**, traces recorded at both 260 nm and 420 nm for ODN and porphyrin, respectively. We can clearly were observe the characteristic new elution peak at around 16 min with identical retention time (Rt) for both wavelengths. The conversion, based on isolated yields, was 75% for **ODN-1/P-1**, 39% for **ODN-1/P-2** and 18% for **ODN-1/P-3**. Noteworthy, **ODN-1** showed degradation only after the optimal 48 h reaction time. In case of **P-3** an additional peak could be seen that seemed to consist of a porphyrin-ODN adduct but it could not be identified though.



Figure 5.6: HPLC traces of the crude reaction mixtures using copper click reaction to synthesize mono-porphyrin ODN adducts. Traces recorded at 260 nm (ODN absorbance) and at 420 nm (porphyrin absorbance) are overlaid. Peaks eluting at < 5 min constitute of unreacted

DNA, at 10-20 min of porphyrin-ODN product, and at higher retention times (>25 min) of unreacted porphyrin.

In case of **ODN-2**, which contains five internal alkyne modifiers, only the starting material was recovered. We would expect to observe at least the mono-addition as well as higher adducts but most likely with concomitant decrease in yield.²³² Strikingly enough, in this case no click reaction could be observed at all, even when increased amount of the catalyst, higher concentration and/or longer reaction time were used. Evidently, the terminal-alkyne position works excellent in copper click reaction compared to the internal-alkyne one, due to the limited accessibility by large porphyrins.

Regarding copper-free click chemistry, we have used the strained bicyclo[6.1.0]nonyne (BCN) as terminal modifier in the oligonucleotide sequence **ODN-3** (Figure 5.4). We have used similar reaction conditions with copper click reaction, namely 1 equivalent of **ODN-3**, 10 equivalents of azide-porphyrin (P-1, P-2 and P-3) in a 1:4 ratio solution of H₂O/DMF (50 µL). The reaction mixtures were heated at 25 °C for 24 h and then purified using HPLC (Figure 5.7). The traces show very little remaining ODN and mainly porphyrin-ODN with Rt around 12 min. Thus, copperfree click reaction is more dependent on the porphyrin structure than the copper click reaction. This could be attributed to the length of the linker which is longer in case of **ODN-3** compared to **ODN-1**. Porphyrins are therefore more exposed and hence capable of showing different interactions with the stationary phase in HPLC. To sum up, the isolated yields of the three different porphyrin adducts are 21% for **ODN-3/P-1**, 62% for ODN-3/P-2 and 48% for ODN-3/P-3.

²³² Gramlich, P.M.E.; Wirges, C.T.; Manetto, A.; Carell, T., *Angew. Chem. Int. Ed.*, **2008**, *47*, 8350-8358.



Figure 5.7: HPLC traces of the crude reaction mixtures using copper-free click reaction to synthesize mono-porphyrin ODN adducts. Traces recorded at 260 nm (ODN absorbance) and at 420 nm (porphyrin absorbance) are overlaid. Peaks eluting at < 5 min constitute of unreacted DNA, at 10-20 min of porphyrin-ODN product, and at higher retention times (>25 min) of unreacted porphyrin.

Consequently, after the isolation of the products via HPLC, MALDI-TOF analysis followed confirming the mono-addition of a porphyrin compound in each case. A collection of the calculated and observed m/z peaks of all porphyrin-ODN click-made products are listed in **Table 5.1** and their MALDI-TOF spectra are illustrated in figure **5.8**.

ODN	Calculated m/z	Observed m/z
ODN1/P-1	7626	7660
ODN1/P-2	7638	7640
ODN1/P-3	7768	7782
ODN3/P-1	9489	9449
ODN3/P-2	9503	9517
ODN3/P-3	9631	9652

Table 5.1: Calculated and observed m/z for the porphyrin-ODNs modified via click chemistry.



Figure 5.8: Upper part: MALDI-TOF spectra of **ODN1/P-1** (left), **ODN1/P-2** (middle) and **ODN1/P-3** (right). Lower part: MALDI-TOF spectra of **ODN3/P-1** (left), **ODN3/P-2** (middle) and **ODN3/P-3** (right).

The successful attachment of porphyrins to ODNs using click chemistry both copper and copper-free was compared to the more frequently used amide coupling approach. Notably, the amino-porphyrin **P-4** was attached to **ODN-4**, yielded the **ODN-4/P-4** in 14%, which is lower than the click reactions performed by **P-1** and **ODN-1** or **ODN-3**. Hence, based on the successful attachment of porphyrins to ODNs via click reaction and amide coupling, we designed a self-assembled supramolecular porphyrin system as presented in **Figure 5.9**. On the contrary to internal-modification, the terminal-one is a possible route to create multi-porphyrin assemblies on a nanoscale.

To this end, we prepared four different strands, namely **ODN-4** to **ODN-7** with a terminal porphyrin on the DNA stand (**P-1** or **P-4**). The DNA strands are designed to assemble with their corresponding complementary strands (**ODN-4**' to **ODN-7**') and therefore to form a linear array of porphyrins. In this array, the staple strands contain a complementary sequence to part of one porphyrin-ODN at the 5'-end, and a complementary sequence to a second porphyrin-ODN at the 3'-end.



Figure 5.9: Design principle of the DNA supramolecular assembly consist of multi-porphyrin arrays. The assembly of **ODN-4 / ODN-4 '** is denoted as **1P**, **ODN-4 / ODN-4 '** / **ODN-5 / ODN-5 / ODN-5 '** as **2P** and so forth.

The multi-porphyrin arrays were observed using native gel electrophoresis (**Figure 5.10**). Despite the fact that the formation of the dimer is clearly visible in the PAGE analysis, the assemblies containing three or four porphyrins are appeared as faint bands. Apparently, under the PAGE conditions the higher assemblies are not stable and thus observable. However, through absorption and emission spectroscopy measurements we were able to prove the formation of the full porphyrin-DNA array (**Figure 5.10**). More specifically, in the absorption spectra we can detect the gradual increase of intensity regarding the formed porphyrin-DNA arrays. In case of **ODN-4**, a relatively broad and partially split Soret band is observed at around 420 nm, due to the intramolecular association of porphyrins. The addition of more strands leads to a less broad Soretband, an indication that suggests reduced intermolecular interactions. On the other hand, in the absorption spectra of the formed **1P**, **2P**, **3P**, and **4P** systems we can clearly observe the consistent broadening of the Soret band which is partially split. This is consistent with the close alignment of all porphyrins and leads to an electronic coupling between the chromophores. According to the exciton coupling model, the interactions

of the lower energy (B_x) and higher energy (B_y) dipoles lead to these split signals.²³³ In detail, the lone porphyrin chromophore has a maximum absorbance at 417 nm, whereas the split Soret bands can be found at $\lambda = 404$ nm (B_y) and at $\lambda = 423$ nm (B_x). These shifts indicate that J-aggregates (404 nm, red shift) and the H-aggregates (423 nm, blue-shift) are present in the formed assays. In addition, due to the observed broadening of the absorption peaks, we can conclude that the orientation of the porphyrins is happening freely (not in strictly fixed positions).The electron interaction in the arrays was also confirmed via emission spectroscopy since associated quenching in fluorescence was observed by increasing the number of porphyrins number



Figure 5.10: Analysis of the supramolecular porphyrin-DNA assemblies. A) PAGE analysis of the assemblies. B) Absorption spectra ODN mixtures indicating hydrophobic interactions of the porphyrins in solution. C) Absorption spectra (left) and fluorescence spectra (right) of the assemblies with increasing number of DNA strands. The assembly of **ODN-4 / ODN-4'** is denoted as **1P**, **ODN-4 / ODN-4' / ODN-5 / ODN-5'** as **2P** and so forth.

²³³ Hwang, I.W.; Park, M.; Ahn, T.K.; Yoon, Z.S.; Ko, D.M.; Kim, D.; Ito, F.; Ishibashi, Y.; Khan, S.R.; Nagasawa, Y.; Miyasaka, H.; Keda, C.; Takahashi, R.; Ogawa, K.; Satake, A.; Kobuke, Y., *Chem. Eur. J.*, **2005**, *11*, 3753-3761.

In summary, we have efficiently attached different azide-porphyrins through copper and copper-free click chemistry reactions in DNA oligonucleotides. The formed ODNs can produce multi-porphyrin arrays and be assembled in a programmed manner. In the tetra-porphyrin array electronic coupling between the units was observed suggesting the formation of a π -stacked array with close contact. This methodology can easily be extended in order to form longer arrays. Thus, providing an elegant and efficient way to create porphyrin wires linked to DNA strands with the purpose of recognition in applications such as DNA based bio-nanotechnology.

Chapter 6: Solar Cells

6.1 Introduction

The worldwide necessity for sustainable energy derived from the utilization of renewable sources is the leading reason for the constant interest of academic research in photovoltaic technologies (PVs). Plenty variations of PVs have been explored over the years by many researchers, but the concept of PVs lies in a basic principle. Light is adsorbed to create photocurrent, which can be described as excited states leading to flow of electrons. Nowadays, the PV devices that are commercially available are silicon-based solar cells. Such devices have been studied and manufactured for many years reaching their theoretical limit concerning the produced cells on the lab scale.²³⁴ Specifically, in the market crystal silicon (Si) solar cells exhibit power conversion efficiencies of about 25%.²³⁵ The great challenge however is to reduce the cost of kilowatt per hour so that solar cells would be a vital solution as a universal energy source. Despite the fact that silicon solar cells offer the optimum yields so far, the toxic manufacturing processes as well as the high cost in purification and the treatment methods needed are major drawbacks to their application. An alternative technology to single crystal silicon photovoltaics is thin film solar cells, which have been widely studied as cost-effective photovoltaic systems. Thin film solar materials are mostly amorphous silicon (powder form), making the constructed cell more flexible and lighter. Silicon and thin film solar cells comprise the first and second generation of photovoltaic devices, respectively.

Organic solar cells (OSCs) represent the third generation of photovoltaic devices and have attracted enormous attention due to their applied materials. In detail, the compounds used in OSCs are easily manufactured, flexible and abundant.^{236, 237} Furthermore, the organic molecules applied in those devices possess tunable electronic and optical properties. OSCs could be constructed in high speed, with low thermal budget (no high temperatures required) and possess the shortest energy payback time

²³⁴ Battaglia, C.; Cuevas, A.; De Wolf, S., *Energy Environ. Sci.*, **2016**, *9*, 1552-1576.

²³⁵ Han, G.; Zhang, S.; Boix, P.P.; Wong, L.H.; Sun, L.; Lien, S.-Y., *Prog. Mater Sci.*, **2017**, 87, 246-291.

²³⁶ Chen, W.; Zhang, Q., J. Mater. Chem. C, 2017, 5, 1275-1302.

²³⁷ Cao, W.R.; Xue, J.G., Energy Environ. Sci., 2014, 7, 2123-2144.

possible.²³⁸ The latter indicates that among all different photovoltaic technologies, OSCs repay the amount of energy invested during their life-time in the minimum period of time. Dye-sensitized solar cells (DSCs), bulk heterojunction cells, quantum dot cells, polymer solar cells belong to the third generation solar cells. Compared to the other types of solar cells, DSCs possess unique features such as the low cost fabrication methods, the variation in colors and their ability to perform under low light conditions.²³⁹ At the moment, such devices are used in indoor environments (on walls and windows) due to their flexibility as devices.^{240, 241} Nonetheless, there is a great need to minimize the cost and maximize the stability of all individual components of DSCs targeting the improvement of overall performance. As a consequence the application of these devices in large-scale production would hopefully be feasible the following years.

The first working DSC based on a chromophore was introduced by Moser J. in 1887,²⁴² improving the idea of Vogel that demonstrated the activity of a silver halide towards solar radiation.²⁴³ The decisive step though that made these systems popular among the research community was the report by O'Regan and Gratzel in 1991.²⁴⁴ They developed the first photovoltaic cell that was created by low-cost processes using a ruthenium (Ru) chromophore onto the surface of a semiconductor (TiO₂), which exhibited a high energy-conversion efficiency of 7.1%. Over the years many research studies provided outstanding results in terms of efficiency that led to the best reported devices so far with conversion yields of 14%.²⁴⁵ The structure of a typical DSC and the operational principle are illustrated in **Figure 6.1**. The main components in such device are: a) a platinum-coated glass substrate that acts as a counter electrode, b) a transparent conductive glass oxide (TCO), c) a semiconductor deposited on the TCO (typically TiO₂), d) a chromophore that is anchored onto the surface of the semiconductor and e) a volatile electrolyte as a redox mediator (usually I'/I₃⁻ redox couple).

²³⁸ Espinosa, N.; Hosel, M.; Jorgensen, M.; Krebs, F.C., *Energy Environ. Sci.*, **2014**, *7*, 855-866.

²³⁹ Gong, J.; Liang, J.; Sumathy, K., Sustain Energy Rev., **2012**, *16*, 5848-5860.

²⁴⁰ Galogero, G.; Sinopoli, A.; Citro, I.; Di Marco, G.; Petrov, V.; Diniz, A.M.; Parola, A.J.; Pina, F., *Photochem. Photobiol. Sci.*, **2013**, *12*, 883-894.

²⁴¹ Hug, H.; Bader, M.; Mair, P. Glatzel, T., Appl. Energy, **2014**, 115, 216-225.

²⁴² Moser J., Mon. Chem., 1887, 8, 373.

²⁴³ Balasingam S.K.; Chem. Commun.; 2013, 49, 1471-1487.

²⁴⁴ O'Regan, B.; Grätzel M., *Nature*, **1991**, 353, 737-740.

²⁴⁵ Kakiage, K.; Aoyama, Y.; Yano, T.; Oya, K.; Fujisawa, J.-I.; Hanaya, M., *Chem. Commun.*, **2015**, *51*, 15894-15897.



Figure 6.1: Schematic illustration and operational principle of a typical DSC.

In a DSC the sensitizer (S) absorbs solar energy (hv, photoexcitation) forming its excited state (S^{*}). Thus, electrons are transferred from the HOMO to the LUMO level of the chromophore and subsequently to the conduction band (CB) of TiO₂. The injected electrons are transported from the working towards the counter electrode through the external circuit until reaching the Pt-coated glass. The electrolyte, which is an I^{-}/I_{3}^{-} redox couple, restores the oxidized dye to its initial neutral state by transferring an electron to its LUMO orbital.

To estimate the power conversion efficiency (PCE or η) of a DSC we need to consider three major parameters. Explicitly, the short circuit photocurrent density (J_{sc}), the open circuit voltage (V_{oc}) and the fill factor (ff). Maximizing one of these terms will lead to enhanced PCE performance of the device, a difficult task considering the various processes that are involved in the operation of the cell. All the above mentioned parameters are obtained via the photocurrent-density (J-V) curve. A representative J-V curve is provided in **Figure 6.2**, density values versus the voltage are presented, during device operation. In addition, the maximum power point (P_{max}) can be extracted from the J-V curve. The current density at maximum power point is the J_{max}, while the voltage at maximum point is the V_{max}.



Figure 6.2: A representative J-V curve of a DSC.

The V_{oc} is the electrical potential between two terminals of a cell when the circuit is open. The V_{oc} in a DSC corresponds to the difference between the energy level of the conduction band of the semiconductor and the redox potential of the electrolyte. On the other hand the J_{sc} represents the photocurrent per unit area which is calculated under short-circuit irradiation. The J_{sc} is associated with essential characteristics of the applied sensitizer, such as its light absorption ability, the electron injection efficiency from the dye to the CB of the semiconductor and its efficient reduction the electrolyte. The fill factor is the third important parameter for defining the performance of a DSC and it correlates to the maximum power of the device ($P_{max} = J_{max}V_{max}$) over the theoretical maximum power, as stated by **equation 6.1**.

$$\mathrm{ff} = \frac{J_{max}V_{max}}{J_{sc}V_{oc}}$$

Equation 6.1: The fill factor of a DSC.

The efficiency of the device, namely the conversion of solar energy into electricity (η) is defined as the ratio of the maximum power output (P_{max}) generated by the solar cell to the power input (P_{in}). The P_{in} stands as the energy of incident sunlight. Thus, the PCE of the device is determined by using V_{oc} , J_{sc} , ff and P_{in} as presented in **equation 6.2** below.

$$\eta = \frac{P_{max}}{P_{in}} = \frac{J_{sc}V_{oc}\ FF}{P_{in}}$$

Equation 6.2: The power conversion efficiency in a DSC.

The role of the sensitized dye is crucial for the device performance since the initial charge separation in the cell is produced via its photo-excitation. The HOMO and LUMO energy levels of the dye must be appropriate in order to perform the two critical processes for the adequate operation of the cell.²⁴⁶ The LUMO level has to be sufficiently higher than the CB level of TiO₂ in order to effectively promote the electron transfer. In addition, the HOMO level should be lower compared to the redox shuttle thus enabling the electrolyte to efficiently regenerate the oxidized dye. The ability of the dye to bind strongly onto the semiconductor surface, along with its high absorption coefficient numbers are two factors that determine the sensitizer's efficiency in DSCs. Hence, these desirable characteristics motivated many researchers towards searching for new families of sensitizers.²⁴⁷ More specifically, dyes that are capable to absorb solar light from the visible to the near-IR region and contain anchoring groups such as carboxylic acid, cyanoacrylic acid, phosphonic acid, pyridine and sulfonic acid have been employed in DSCs.^{248, 249} Last but not least, an efficient dye should present faster electron transfer rate to the CB of TiO₂, rather than decay rate. The most representative examples of the best working dyes regarding the three more extensively studied families (Ru-dyes, Zn-porphyrins and organic molecules) are illustrated in Figure **6.3**. ^{245, 250, 251}

 ²⁴⁶ Hagfeld, A.; Boschloo, G.; Sun, L.; Kloo, L.; Pettersson, H., *Chem. Rev.*, **2010**, *110*, 6595-6663.
²⁴⁷ Al-Alwani, M.A.M.; Mohamad, A.B.; Ludin, N.A.; Kadhum, Abd.A.H.; Sopian, K., *Renew. Sust. Energ. Rev.*, **2016**, *65*, 183-213.

²⁴⁸ Labomenou, K.; Kitsolpoulos, T.N.; Sharma, G.D.; Coutsolelos, A.G., *RSC Adv.*, **2014**, *4*, 21379-21404.

²⁴⁹ Anselmi, C.; Mosconi, E.; Pastore, M.; Ronca, E.; De Angelis, F., *Phys. Chem. Chem. Phys.*, **2012**, *14*, 15963-15974.

 ²⁵⁰ Nazeeruddin, M.; De Angelis, F.; Fantacci, S.; Selloni, A.; Viscardi, G.; Liska, P.; Itso, S.; Takeru, B.; Grätzel, M., *J. Am. Chem. Soc.*, **2005**, *127*, 16835-16847.

²⁵¹ Mathew, S.; Yella, A.; Gao, P.; Humphry-Baker, R.; Curchod, B.F.; Ashari-Astani, N.; Tavernelli, I.; Rothlisberger, U.; Nazeeruddin, M.; Grätzel, M., *Nat. Chem.*, **2014**, *6*, 242-247.



Figure 6.3: Chemical structures of: a) the Ru-dye N719,²⁵⁰ b) the organic dyes ADEKA-1 and LEG-4²⁴⁵ and c) the Zn-porphyrin SM315.²⁵¹

6.2 Porphyrin-fullerene dyads for p-type DSCs

6.2.1 Introduction

Over the last decades n-type DSCs have dominated the scientific interest, however the best photo-conversion efficiency is yet lower than 15%.^{245, 251, 252} In order to improve this conversion efficiency, many researchers have struggled with the synthesis of various chromophores as well as the usage of different electrolytes and semiconductors.²⁵³ However, the most reasonable solution would be to deal with another essential part of the DSC devices. More specifically, the replacement of Ptcathode by a photo-cathode such as NiO would create a tandem cell.²⁵⁴ This type of solar cells (tandem or pn-DSCs) could theoretically reach energy conversion efficiencies of 40%.^{255, 256} Despite the high expectations though, the maximum photo-

²⁵² Yella, A.; Mai, S.-L.; Zakeeruddin, M.; Chang, S.-N.; Hsieh, C.-H.; Yeh, C.-Y.; Grätzel, M., *Angew. Chem. Int. Ed.*, **2014**, *53*, 2973-2977.

²⁵³ Kumaraa, N.T.R.N.; Limb, A.; Lima, C.M.; Petrac, M.I.; Ekanayake, P., *Renew. Sust. Energ. Rev.*, **2017**, 78, 301-317.

²⁵⁴ Nattestad, A.; Perera, I.; Spiccia, L., J. Photochem. Photobiol. C, 2016, 28, 44-71.

²⁵⁵ Odobel, F.; Pellegrin, Y.; Gibson, E.A.; Hagfeldt, A.; Smeigh, A.L.; Hammarstrom, L., *Coord. Chem. Rev.*, **2012**, *256*, 2414-2423.

²⁵⁶ Yu, M.Z.; Draskovic, T.I.; Wu, Y.Y.; Phys. Chem. Chem. Phys., 2014, 16, 5026-5033.

conversion efficiency still remains at only 4.1%.^{257, 258} As presented in **Figure 6.4** a pn-DSC is consisted of an n-type together with a p-type DSC. In detail, on the photo-anode of the cell a photosensitizer (S₁) is excited through solar irradiation and one electron is transferred from the HOMO to the LUMO orbital giving rise to the S₁⁺ form of the sensitizer. Then, an electron from the excited state of the photosensitizer (S₁^{*}) is injected to the conduction band of TiO₂. The electron is transferred to the photo-cathode via the external circuit and the sensitizer that is attached to the NiO surface receives it. Noteworthy, the sensitizer applied on the p-type counterpart of the tandem cell (S₂) has already been excited (S₂^{*}) via photo-excitation and has provided an electron to the redox couple (I⁻/I₃⁻). The reduced form of the sensitizer (S₂⁻) is returned to its ground state by receiving the electron from the valence band of NiO. Finally, the electrolyte transports an electron to the oxidized sensitizer (S₁⁺) of the n-counterpart.



Figure 6.4: Schematic illustration and operational principle of a typical pn-type DSC (tandem cell). The n-type photo-anode and the p-type photo-cathode are combined in a single solar cell.

The inefficient p-type photo-cathode is the limiting factor of such tandem devices. This poor photovoltaic performance of p-type DSCs is due to the low photocurrent produced by the dye that is attached onto the NiO cathode. Thus, the critical step in developing efficient tandem cells is the improvement of the photovoltaic performance

²⁵⁷ Nattestad, A.; Mozer, A.J.; Fischer, M.K.R.; Cheng, Y.B.; Mishra, A.; Bauerle, P.; Bach, U., *Nat. Mater.*, **2010**, *9*, 31-35.

²⁵⁸ Farré, Y.; Raissi, M.; Fihey, A.; Pellegrin, Y.; Blart, E.; Jacquemin D.; Odobel, F., *ChemSusChem*, **2017**, *10*, 2618-2625.

of p-type DSCs. In **Figure 6.5** the schematic representation along with the operation principal of a p-type DSC is illustrated.¹²⁵ The first step is the light excitation of the sensitizer which is adsorbed on the NiO semiconductor surface. Subsequently, the excited state of the sensitizer (S^{*}) is formed, followed by hole injection into the valence band (VB) of the nickel oxide. The reduced dye (S⁻) is then restored to its ground state in presence of the redox shuttle (I₃⁻/ Γ). Lastly the electron is transported to the external circuit through the counter electrode (CE). The observed difference in the potential between the redox couple and the Fermi level of NiO is defined as the maximum voltage of the device (V_{oc}). It is worth mentioning that in the **Figure 6.5** below the dashed arrows represent two recombination processes between: i) the dye and NiO, ii) the redox couple and NiO. On the other hand the straight blue arrows stand for electron transfer processes.



Figure 6.5: Operation principle of a NiO DSC.¹²⁵

To date, the best NiO p-DSC exhibits an overall the power conversion efficiency of 2.51%, with $V_{oc} = 724 \text{ mV}$, $J_{sc} = 4.11 \text{ mA/cm}^2$ and ff = 0.44 when $[\text{Fe}(\text{acac})_3]^{0/1-}$ was applied as the electrolyte.²⁵⁹ The low photovoltaic performances of p-type DSCs, compared to their n-type counterparts, are mainly attributed to three reasons: a) the fast recombination between the electrolyte and the photo-cathode, b) the constricted photon absorption and c) the low electron transport in the p-type semiconductor. Both stability and efficiency of such devices are strongly dependent on the nature of the electrolyte,

²⁵⁹ Perera, I.R.; Daeneke, T.; Makuta, S.; Yu, Z.; Tachibana, Y.; Mishra, A.; Bauerle, P.; Ohlin, C.A.; Bach, U.; Spiccia, L., *Angew. Chem. Int. Ed.*, **2015**, *54*, 3758-3762.

whose main role is to transfer electrons from the counter electrode to the reduced dye. Hence, the great ionic mobility and high solubility are essential requirements for an efficient working electrolyte. The utilized redox shuttle should not only regenerate the reduced dye quantitatively, but also possess energy close enough to the dye's (S^*/S^-) energy level.

As we have previously mentioned porphyrinoids play a decisive role in photosynthesis on account of their sole features.^{132, 260} Since porphyrins and their analogues have been extensively studied in n-type DSCs due to their key merits, it is safe to assume that they could be employed to p-type DSCs as well.^{52, 53} Notably, the first example that stands as the proof of the p-DSC concept was reported by He et al. in 1999.²⁶¹ In this work, a NiO electrode was dyed with a porphyrin, namely Erythrosin (tetrakis(4-carboxyphenyl)porphyrin), generating very low power conversion efficiency of 0.01%. Many years after this report, specifically in 2014 Guldi, Costa and co-workers synthesized three nickel porphycenes as chromophores in p-type DSCs (**Figure 6.6**).^{125, 262} The highest efficiency (0.028%) was found for **P2** which contains two carboxylic acid units at the ethylene bridge, while porphycenes **P1** and **P3** reached $\eta = 0.019$ and 0.021%, respectively.



Figure 6.6: Porphycenes P1, P2 and P3 as chromophores in p-type DSC.^{125, 262}

²⁶⁰ Balaban, T.S., Acc. Chem. Res., 2005, 38, 612-623.

²⁶¹ He, J.J.; Lindstrom, H.; Hagfeldt, A.; Lindquist, S.E., J. Phys. Chem. B, 1999, 103, 8940-8943.

²⁶² Feihl, S.; Costa, R.D.; Brenner, W.; Margraf, J.T.; Casillas, R.; Langmar, O.; Browa, A.; Shubina, T.E.; Clark, T.; Jux, N.; Guldi, D.M., *Chem. Commun.*, **2014**, *50*, 11339-11342.

This type of porphyrinoid (porphycene) is suitable for application in p-type DSCs due to its strong electron accepting ability, on the contrary to zinc-porphyrins that are mainly electron donating dyes.¹³² However, when zinc-porphyrins are linked to an electron acceptor they are ideal for application in p-type DSCs. This was first reported by Tian et. al, where a supramolecular assembly consisted of an electron donor zinc-porphyrin and an electron acceptor fullerene C_{60} was developed.²⁶³ Recently, Odobel, Hammarstrom, Jacquemin and coworkers reported a series of push-pull zinc-porphyrin derivatives as sensitizers in p-DSCs.^{264, 265}

They have used zin-porphyrin derivatives with different electron withdrawing groups. Specifically, nitrophenyl unit (**ZnP-CO₂H-eNO₂**), benzyl-viologen (**ZnP-CO₂H-BV**²⁺) and naphthalene diimide (**ZnP-CO₂H-eNDI**). Moreover, they examined the influence of the spacer to the device performance by introducing an ethynyl unit. In addition to the above mentioned study, they have also synthesized one porphyrin sensitizer bearing a donor unit on its periphery (**ZnP-TPA-NO₂**, **Figure 6.7**). In conclusion, the best performing dye (**ZnP-CO₂H-eNDI**) exhibited an $\eta = 0.056\%$, with $V_{oc} = 127 \text{ mV}$, $J_{sc} = 1.38 \text{ mA/cm}^2$, ff = 0.32 using I⁻/I₃⁻ as electrolyte.

²⁶³ Tian, H.N.; Oscarsson, J.; Gabrielsson, E.; Eriksson, S.K.; Lindblad, R.; Xu, B.; Hao, Y.; Boschloo, G.; Johansson, E.M.J.; Gardner, J.M.; Hagfeldt, A.; Rensmo, H.; Sun, L.C., *Sci. Rep.*, **2014**, *4*, 4282.

²⁶⁴ Maufroy, A.; Favereau, L.; Anne, F.B.; Pellegrin, Y.; Blart, E.; Hissler, M.; Jacquemin, D.; Odobel, F.; *J. Mater. Chem. A*, **2015**, *3*, 3908-3917.

²⁶⁵ Zhang, L.; Favereau, L.; Farre, Y.; Maufroy, A.; Pellegrin, Y.; Blart, E.; Hissler, M.; Jacquemin, D.; Odobel, F.; Hammarstrom, L.; *RSC Adv.*, **2016**, *6*, 77184-77194.



Figure 6.7: Chemical structures of zin-porphyrin derivatives used in p-type DSCs.^{125, 264, 265}

In our project, a series of dyads have been prepared consisting of an electron donor chromophore (zinc-porphyrin) coupled to an electron acceptor (fullerene). All three final compounds (Compounds 1, 2 and 3) as well as the Reference compound contain carboxylic acid groups for their successful binding onto the NiO surface (Figure 6.8). This is the first attempt to develop covalently linked porphyrin-fullerene dyads as sensitizers in p-type DSCs. The distance of the chromophore from the electron acceptor as well as from the surface of the semiconductor determines to a large extent the performance of the devices. In order to examine the effect of the distance and to determine the optimal combination, three different porphyrin-fullerene dyads have been synthesized. These modifications were carried out by introducing a triazole ring as a spacer between the zinc-porphyrin and the two peripheral units (fullerene and anchoring group). The triazole ring increased the distance while also allowing the efficient electron transfer. As presented in Figure 6.8 regarding Compound 1 the spacer was introduced between the fullerene and the porphyrin, while in Compound 3 both the fullerene and the anchoring group are directly attached on the periphery of the porphyrin ring. In case of Compound 2 though, two triazole spacers were inserted between the porphyrin ring and both peripheral units, namely the fullerene as well as the anchoring group. Finally, a **Reference** compound has been prepared, in which the electron acceptor fullerene moiety is absent, in order to compare the device efficiencies and the photo-physical characteristics of our dyads. The performances of the p-DSCs revealed that the optimal complex was **Compound 1** and thus the ideal position of the triazole ring was between the zinc-porphyrin and the fullerene unit.



Figure 6.8: The chemical structures of porphyrin-fullerene dyads (**Compound 1**, **2** and **3**) and **Reference** compound.

6.2.2 Experimental

The synthesis of **Compound 1** is illustrated in **Scheme 6.1**. Porphyrin **1** was the initial derivative from which the preparation of **Compound 1** started and was synthesized following previously published procedures.¹²¹ The formation of the aldehyde-porphyrin **3** was achieved via click reaction between the azide-porphyrin **1** and the ethynyl-benzaldehyde **2**. For the click reaction, CuI complex was used as the catalyst and the solvent mixture was THF/CH₃CN in a 1:1 ratio. The next step involved the hydrolysis of porphyrin **3** that was consequently followed by a Prato reaction using fullerene (**4**). The hydrolysis was performed using an aqueous solution of KOH in a THF/MeOH reaction mixture. Concerning the Prato reaction, toluene was used as solvent and the reaction mixture was refluxed overnight in the presence of sarcosine.

Finally, the desired product (**Compound 1**) was purified through column chromatography.



<u>Scheme 6.1:</u> Synthesis of Compound 1. Reagents and conditions: a) CuI, DIPEA, THF/CH₃CN, RT, 12h, b) THF/MeOH, 10% KOH aqueous solution, 40 °C for 6h, c) Toluene, sarcosine, reflux overnight.

<u>Synthesis of 3.</u> Equimolar amounts of porphyrin 1 (100 mg, 0.116 mmol) and 4ethynylbenzaldehyde (16 mg, 0.116 mmol) were dissolved in a 1:1 mixture of THF/CH₃CN (10 mL) under N₂ atmosphere. In the next step, CuI (22 mg, 0.116 mmol) and DIPEA (20 μ L, 0.124 mmol) were added and the reaction mixture was stirred at room temperature for 12 hours. Upon reaction completion, the volatiles were removed under reduced pressure and the crude solid, was purified by column chromatography (silica gel, CH₂Cl₂/EtOH, 99:1) yielding 84 mg of 1 (0.086 mmol, yield: 73%).

¹**H** NMR (500 MHz, CDCl₃): $\delta = 10.03$ (s, 1H), 8.88 (d, J = 4.6 Hz, 2H), 8.82 (m, 4H), 8.79 (d, J = 4.6 Hz, 2H), 8.61 (s, 1H), 8.42 (m, 4H), 8.33 (d, J = 7.9 Hz, 2H), 8.17 (m, 4H), 8.01 (d, J = 8.2 Hz, 2H) 7.29 (s, 4H), 4.08 (s, 3H), 2.58 (s, 6H), 2.64 (s, 6H), 1.85 (s, 12H) ppm. HRMS (MALDI-TOF): calc. for C₆₁H₄₈N₇O₃ Zn [M + H]⁺: 990.3032; found 990.3040.
Synthesis of Compound 1. Porphyrin **3** (50 mg, 0.050 mmol) was dissolved in a THF/MeOH mixture with 5:2 ratio (20/8 mL) and then 3 mL of a 10% KOH aqueous solution were added. The reaction mixture was heated at 40 °C for 6 h. Upon reaction completion, we added 20 mL of 1 M citric acid aqueous solution and 20 mL of a MeOH/CHCl₃ (1:4 ratio). The mixture was extracted with H₂O (3 x 20 mL) and the organic phase was evaporated under reduced pressure. The crude product was subsequently used as a starting material for the synthesis of Compound 3. In a round bottom flask we added the crude porphyrin, 2-methyl glycine (sarcosine, 110 mg, 1.24 mmol) and C₆₀ (43 mg, 0.060 mmol) and dissolved them in 45 mL of dry toluene. The reaction mixture was refluxed overnight. The purification of Compound 1 was accomplished through silica gel column chromatography. Firstly, we used toluene as eluent to remove the excess of unreacted C₆₀ and then a mixture of CH₂Cl₂/MeOH in a 97:3 ratio. **Compound 1** was produced in a 46% yield (40 mg, 0.023 mmol).

¹**H** NMR (500 MHz, THF-*d*₈): $\delta = 11.66$ (s, 1H), 9.15 (s, 1H), 8.86 (d, J = 4.6 Hz, 2H), 8.78 (d, J = 4.5 Hz, 2H), 8.70 (m, 4H), 8.40 (m, 4H), 8.31 (m, 4H), 8.19 (m, 2H), 8.00 (sb, 2H), 7.30 (s, 4H) 5.09 (s, 1H), 5.05 (d, J = 9.0 Hz, 1H), 4.3 (d, J = 8.9 Hz, 1H), 2.87 (s, 3H), 2.60 (s, 6H), 1.85 (s, 12H) ppm.

¹³C NMR (125 MHz, THF-*d*₈): δ = 167.70, 157.70, 155.22, 154.73, 154.66, 150.57, 150.42, 150.23, 148.70, 148.52, 147.81, 147.64, 147.31, 147.08, 146.77, 146.61, 146.43, 146.37, 146.16, 146.02, 145.84, 145.65, 145.26, 145.12, 144.96, 144.91, 144.44, 144.03, 143.67, 143.49, 143.20, 143.04, 143.01, 142.91, 142.72, 142.63, 142.55, 142.49, 142.36, 142.20, 142.08, 140.66, 140.60, 140.42, 140.35, 140.05, 139.65, 137.98, 137.90, 137.63, 137.55, 137.19, 136.66, 136.47, 136.15, 135.07, 132.36, 132.24, 130.97, 130.74, 128.34, 128.31, 126.57, 119.76, 119.52, 119.27, 119.22, 118.39, 83.98, 78.32, 70.49, 70.13, 39.77, 21.85, 21.39 ppm.

HRMS (MALDI-TOF): calc. for $C_{122}H_{51}N_8O_2Zn [M + H]^+$: 1723.3348; found 1723.3351.

To synthesize **Compound 2** we first had to prepare the di-azide-porphyrin **5** (**Scheme 6.2**). Porphyrin **5** was synthesized following the published procedure of Beletskaya and coworkers with slight deviations in the purification methods.²⁶⁶ More specifically, in column chromatography instead of ethyl acetate we have used MeOH. We have performed two click reactions using the same experimental conditions as previously between porphyrin **5** and compounds **2** and **6**. The desired porphyrin **7** was

²⁶⁶ Polevaya, Y.P.; Tyurin, V.S.; Beletskaya, I.P., J. Porphyr. Phthalocyanines, 2013, 17, 1-15.

purified and separated from the other two formed porphyrin derivatives in a 42% yield. As a final point, to synthesize **Compound 2** we have performed a hydrolysis and a Prato reaction likewise in case of **Compound 1**.



<u>Scheme 6.2</u>: Synthesis of Compound 2. Reagents and conditions: a) CuI, DIPEA, THF/CH₃CN, RT, 12h, b) THF/MeOH, 10% KOH aqueous solution, 40 °C for 6h, c) Toluene, sarcosine, reflux overnight.

Synthesis of 7. Porphyrin 5 (70 mg, 0.083 mmol) and ester 6 (6.6 mg, 0.041 mmol) were dissolved in a 1:1 mixture of THF/CH₃CN (8 mL) under N₂ atmosphere. In the next step, CuI (15.8 mg, 0.083 mmol) and DIPEA (11 μ L, 0.083 mmol) were added and the reaction mixture was stirred at room temperature for 12 hours. Upon reaction completion, the volatiles were removed under reduced pressure and the crude solid, was subsequently was used for another click reaction. Namely, between the newly formed clicked porphyrin derivative and aldehyde 2 (5.3 mg, 0.041 mmol) were added in a Schlenk tube and dissolved in a 1:1 mixture of THF/CH₃CN (8 mL) under N₂ atmosphere. Afterwards, CuI (15.8 mg, 0.083 mmol) and DIPEA (11 μ L, 0.083 mmol) were added and the reaction mixture was stirred at room temperature for 12 hours. Then, the volatiles were removed under reduced pressure and the crude solid was purified by column chromatography (silica gel, CH₂Cl₂/EtOH, 99:1) yielding 40 mg of 7 (0.035 mmol, yield: 42%).

¹**H NMR (500 MHz, CDCl₃):** δ = 10.07 (s, 1H), 8.90 (d, *J* = 4.6 Hz, 4H), 8.83 (d, *J* = 4.6 Hz, 4H), 8.61 (s, 1H), 8.57 (s, 1H), 8.43 (m, 4H), 8.19 (m, 8H), 8.08 (d, *J* = 8.1 Hz, 2H), 8.03 (d, *J* = 8.0 Hz, 2H), 7.30 (s, 4H), 3.97 (s, 3H), 2.64 (s, 6H), 1.85 (s, 12H) ppm.

HRMS (MALDI-TOF): calc. for Chemical Formula: $C_{69}H_{53}N_{10}O_3Zn [M + H]^+$: 1133.3515; found 1133.3519.

Synthesis of Compound 2. Porphyrin **7** (35 mg, 0.030 mmol) was dissolved in a THF/MeOH mixture with 5:2 ratio (15/6 mL) and then 2 mL of a 10% KOH aqueous solution were added. The reaction mixture was heated at 40°C for 6 h. Upon reaction completion, we added 15 mL of 1 M citric acid aqueous solution and 15 mL of a MeOH/CHCl₃ mixture (1:4 ratio). The mixture was extracted with H₂O (3 x 15 mL) and the organic phase was evaporated under reduced pressure. The crude product was subsequently used as a starting material for the synthesis of Compound 2. In a round bottom flask we added the crude porphyrin, 2-methyl glycine (sarcosine, 75 mg, 0.84 mmol) and C₆₀ (29 mg, 0.040 mmol) and dissolved them in 35 mL of dry toluene. The reaction mixture was refluxed overnight. The purification of Compound 2 was accomplished through silica gel column chromatography. Firstly, we used toluene as eluent to remove the excess of unreacted C60 and then a mixture of CH2Cl2/MeOH in a 97:3 ratio providing **Compound 2** in a 40% yield (22 mg, 0.012 mmol).

¹**H NMR (300 MHz, THF-***d*₈**):** δ = 11.42 (s, 1H), 9.23 (s, 1H), 9.16 (s, 1H), 8.86 (m, 4H), 8.71 (m, 4H), 8.37 (m, 8H), 8.18 (s, 6H), 8.04 (m, 2H), 7.30 (s, 4H), 5.11 (s, 1H), 5.06 (s, 1H), 4.34 (d, *J* = 9.4, 1H), 2.88 (s, 3H), 2.60 (s, 6H), 1.85 (s, 12H) ppm.

¹³C NMR (75 MHz, THF-*d*₈): δ = 167.30, 157.95, 155.48, 154.98, 150.77, 150.64, 148.68, 148.19, 148.06, 147.89, 147.57, 147.31, 146.99, 146.86, 146.67, 146.59, 146.26, 146.01, 145.50, 145.36, 145.21, 144.74, 144.58, 143.82, 143.44, 143.30, 143.14, 142.94, 142.80, 142.59, 142.44, 142.31, 140.89, 140.65, 140.53, 140.27, 139.82, 138.20, 138.10, 137.86, 137.67, 137.41, 136.90, 136.71, 136.35, 136.10, 132.57, 132.42, 131.33, 131.17, 130.83, 128.55, 126.73, 126.11, 120.20, 119.73, 119.41, 118.64, 84.15, 78.55, 70.66, 70.36, 39.94, 22.03, 21.57 ppm.

HRMS (MALDI-TOF): calc. for $C_{130}H_{55}N_{11}O_2Zn [M + H]^+$: 1866.3832; found 1866.3836.

The experimental approach regarding **Compound 3** is illustrated in **Scheme 6.3**. First, dipyrromethane **8** and mesityl-aldehyde **9** were combined following a new acidcatalyzed condensation reaction reported by Balaban, Gryko and coworkers.²⁶⁷ The formed porphyrin **10** was then transformed to the corresponding di-bromo-porphyrin **11** using N-Bromosuccinimide (NBS). To successfully synthesize the porphyrin derivative **14**, which contains an ester and an aldehyde functional group, we had to perform two Suzuki coupling reactions using the relevant boronic acid derivatives **12** and **13**. The mixed Suzuki coupling was carried out using a mixture of THF/H₂O under argon atmosphere which was degassed according to the freeze-pump-thaw technic. Then, the addition of Pd(PPh₃)₄ took place and the reaction was heated at 80°C overnight. The formed porphyrin **14** after its purification with column chromatography, was firstly metallated with zinc and then hydrolyzed to the corresponding carboxylic acid derivative. The crude product was finally used for the formation of **Compound 3** via a Prato reaction with fullerene (**4**).



Scheme 6.3: Synthesis of Compound 3. Reagents and conditions: a) EtOH, HCl/H₂O 16h RT, p-chloranil, 1h under reflux; b) CHCl₃, 0°C, NBS, pyridine, acetone; c) THF/H₂O, Pd(PPh₃)₄, Ba(OH)₂, d) Zn(CH₃COO)₂·2H₂O, MeOH, CH₂Cl₂; e) THF/MeOH, 10% KOH aqueous solution, 40 °C for 6 h, f) Toluene, sarcosine, reflux overnight.

²⁶⁷ Nowak-Król, A.; Plamont, R.; Canard, G.; Edzang, J.A.; Gryko1, D.T.; Balaban, T.S., *Chem. Eur. J.*, **2015**, *21*, 1488-1498.

Synthesis of 10. Dippyrromethane **8** (1 g, 6.8 mmol) and mesityl-aldehyde **9** (1 mL, 6.8 mmol) were dissolved in 200 mL EtOH under argon atmosphere. After 10 min of constant stirring, 50 mL of a HCl/H₂O solution (in 1:50 ratio) were added to the reaction mixture and afterwards stirring continued for 16h under dark conditions. Then, extraction with CHCl₃ (200 mL), H₂O (3 x 100 mL) and aqueous solution of NaHCO₃ (1 x 100 mL) took place. The organic layer was dried over anhydrous MgSO₄ and hereupon oxidized using p-chloranil (2.5 g, 10.2 mmol) for 1h, under reflux. Upon reaction completion, the porphyrin mixture was filtrated using a short silica gel plug. Subsequently, column chromatography (silica gel, CH₂Cl₂/Hexane, 70:30) was performed to obtain 380 mg of the desired porphyrin derivative **10** in a 21% yield (0.035 mmol).

¹**H NMR (500 MHz, CDCl₃):** δ = 10.23 (s, 2H), 9.33 (d, *J* = 4.5 Hz, 4H), 8.89 (d, *J* = 4.6 Hz, 4H), 7.34 (s, 4H), 2.68 (s, 6H), 1.86 (s, 12H), -3.05 (s, 2H) ppm.

HRMS (MALDI-TOF): calc. for Chemical Formula: $C_{38}H_{35}N_4$ [M + H] ⁺: 547.2783; found 547.2786.

Synthesis of 11. Porphyrin **10** (50 mg, 0.092 mmol) was dissolved in 25 mL of CHCl₃ at 0°C. Then, 100 μ L of pyridine and NBS (33 mg, 0.18 mmol) were added and the reaction mixture was stirred while checking the reaction progress via TLC every few minutes. Upon reaction completion (almost 25 min), 2 mL of acetone were added and the volatiles were removed under reduced pressure. The crude solid was purified by column chromatography (silica gel, CH₂Cl₂/Hexane, 60:40) yielding 53 mg of **11** (0.075 mmol, yield: 82%).

¹H NMR (500 MHz, CDCl₃): δ = 9.55 (d, J = 4.3 Hz, 4H), 8.69 (d, J = 4.1 Hz, 4H), 7.30 (s, 4H), 2.64 (s, 6H), 1.82 (s, 12H), -2.54 (s, 2H) ppm.

HRMS (MALDI-TOF): calc. for Chemical Formula: C₃₈H₃₃N₄Br₂ [M + H]⁺: 703,0994; found 703.0998.

<u>Synthesis of 14.</u> To a sealed tube containing porphyrin **11** (100 mg, 0.14 mmol), boronic acid **12** (12.6 mg, 0.07 mmol), barium hydroxide (48 mg, 0.28 mmol) and a mixture of THF/H₂O (8 mL, in 3:1 ratio) were added under argon atmosphere. The solution was degassed using the freeze-pump-thaw technic, prior to the addition of $Pd(PPh_3)_4$ (4 mg, 3.14 µmol) and the reaction was heated at 80°C overnight. Then, the mixrure was cooled down to room temperature and filtrated over celite. The solvents

were evaporated under reduced pressure and the crude product was subsequently used for a second Suzuki reaction with boronic acid **13** (10.5 mg, 0.07 mmol). For the successful preparation of porphyrin **14** the same experimental procedure was followed using barium hydroxide (48 mg, 0.28 mmol) and a THF/H₂O solvent mixture (8 mL, in 3:1 ratio) under argon atmosphere. Prior to the addition of Pd(PPh₃)₄ (4 mg, 3.14 µmol) the solution was degassed using the freeze-pump-thaw technic and the reaction mixure was heated at 80°C overnight. The desired compound (porphyrin **14**) was purified through silica gel chromatography using CH₂Cl₂ as eluent yielding 31% (35 mg, 0.045 mmol).

¹**H** NMR (500 MHz, CDCl₃): $\delta = 10.42$ (s, 1H), 8.76 (m, 8H), 8.46 (m, 4H), 8.36 (m, 4H), 7.32 (s, 4H), 4.14 (s, 3H), 2.66 (s, 6H), 1.87 (s, 12H), -2.60 (s, 2H) ppm.

HRMS (MALDI-TOF): calc. for Chemical Formula: $C_{69}H_{52}N_{10}O_3Zn [M + H]^+$: 1133.3515; found 1133.3519.

Synthesis of Compound 3. To a CH₂Cl₂ solution (20 mL) of 14 (50 mg, 0.064 mmol, a MeOH (3 mL) solution containing Zn(CH₃COO)₂·2H₂O (219 mg, 1 mmol) was added and the reaction mixture was stirred at room temperature overnight. The volatiles were evaporated, the porphyrin was diluted in 25 mL of CHCl₃ and extracted with H₂O (3 x 25 mL). The solvent was removed under reduced pressure and the produced porphyrin was hydrolyzed to the corresponding acid porphyrin using the below mentioned experimental procedure. In detail, the crude product was dissolved in a THF/MeOH mixture with 5:2 ratio (20/8 mL) and then 3 mL of a 10% KOH aqueous solution were added. The reaction mixture was heated at 40 °C for 6h. Upon reaction completion, we added 20 mL of 1 M citric acid aqueous solution and 20 mL of a MeOH/CHCl₃ mixture (1:4 ratio). The mixture was extracted with H₂O (3 x 20 mL) and the organic phase was evaporated under reduced pressure. The produced porphyrin was subsequently used as a starting material for the synthesis of Compound 3. In a round bottom flask we added the crude porphyrin, 2-methyl glycine (sarcosine, 75 mg, 0.84 mmol) and C_{60} (29 mg, 0.040 mmol) and dissolved them in 35 mL of dry toluene. The reaction mixture was refluxed overnight. The purification of Compound 3 was accomplished through silica gel column chromatography. The first column was performed with toluene to remove the excess of unreacted C₆₀ and the second one with CH₂Cl₂/MeOH in a 97:3 ratio providing **Compound 3** in a 35% yield (22 mg, 0.012 mmol).

¹**H NMR (500 MHz, THF-***d*₈**):** δ = 11.64 (s, 1H), 8.69 (m, 8H), 8.39 (d, *J* = 8.0 Hz, 4H), 8.28 (d, *J* = 8.0 Hz, 4H), 7.29 (m, 4H), 5.39 (s, 1H), 5.18 (d, *J* = 8.8 Hz, 1H), 4.48 (d, *J* = 8.8 Hz, 1H), 3.13 (s, 3H), 2.60 (m, 6H), 1.84 (m, 12H) ppm.

¹³C NMR (125 MHz, THF- d_8): $\delta = 167.89, 158.00, 155.04, 150.65, 150.33, 148.94, 148.17, 147.77, 147.66, 147.07, 146.93, 146.78, 146.71, 146.48, 146.34, 146.24, 146.14, 145.67, 145.60, 145.30, 144.73, 144.04, 143.83, 143.42, 143.30, 143.01, 142.87, 142.56, 140.96, 140.85, 140.57, 140.24, 139.82, 138.09, 137.92, 137.49, 137.04, 135.94, 135.24, 132.64, 132.40, 131.00, 130.85, 130.78, 128.49, 128.44, 120.50, 119.68, 119.51, 84.17, 78.90, 70.83, 70.44, 40.17, 21.96, 21.56 ppm.$

HRMS (**MALDI-TOF**): calc. for C₁₁₄H₄₆N₅O₂Zn [M + H] ⁺: 1579.2865; found 1866.2870.

The synthesis of the **Reference** compound is presented in **Scheme 6.4**. Porphyrin **16** was synthesized as discussed in a previous chapter of this thesis (page 45).¹²³ For the preparation of **Reference** compound a click reaction between porphyrin **16** and the alkyne-derivative **17** was performed, using the same experimental conditions as previously stated.



<u>Scheme 6.4</u>: Synthesis of the **Reference** compound. Reagents and conditions: a) CuI, DIPEA, THF/CH₃CN.

<u>Synthesis of reference.</u> Equimolar amounts of porphyrin **16** (30 mg, 0.035 mmol) and derivative **17** (3.6 mg, 0.035 mmol) were dissolved in a 1:1 mixture of THF/CH₃CN (4 mL) under N₂ atmosphere. Afterwards, CuI (6.7 mg, 0.035 mmol) and DIPEA (7 μ L, 0.04 mmol) were added and the reaction mixture was stirred at room temperature for 12 hours. Then, the volatiles were removed under reduced pressure and the crude solid,

was purified by column chromatography (silica gel, CH₂Cl₂/EtOH, 98:2) yielding 29 mg of **Reference** compound (0.031 mmol, yield: 89%).

¹**H NMR (500 MHz, DMSO-** d_6 **):** δ = 13.19 (s, 1H), 9.65 (s, 1H), 8.82 (m, 2H), 8.73 (m, 2H), 8.60 (m, 2H), 8.41 (m, 8H), 8.08 (d, J = 7.4 Hz, 2H), 7.57 (m, 2H), 7.44 (m, 1H), 7.31 (s, 4H), 2.57 (s, 6H), 2.46 (s, 6H), 1.79 (s, 12H) ppm.

HRMS (**MALDI-TOF**): calc. for C₅₉H₄₅N₇O₂Zn [M] ⁺: 947.2926; found 947.2932.

6.2.3 Results and Discussion

The successful formation of the three porphyrin-fullerene dyads (Compound 1, 2 and 3) as well as the **Reference** compound was verified through NMR spectroscopy (¹H and ¹³C) and via MALDI-TOF mass spectrometry. In addition all the intermediate porphyrin derivatives were characterized through ¹H NMR spectroscopy and Maldi-TOF spectrometry. In the appendix of this thesis and specifically in Figures 8.33-8.60 all these ¹H and ¹³C NMR spectra are presented with the relevant assignment of each peak to the corresponding proton or carbon, respectively. In the ¹H NMR spectra of the final dyads, the characteristic proton signal of the formed triazole ring appeared at 9.15 ppm for Compound 1 (Figure 8.36) and at 9.16 and 9.28 for Compound 2 (Figure **8.44**). Moreover, in the 13 C NMR spectra the peak that corresponds to the carbon of the formed triazole ring was detected at 119.27 ppm for Compound 1 (Figure 8.40) and at 119.41 and 119.73 for Compound 2 (Figure 8.46). In addition, we observe the proton signal concerning the carboxylic acid unit at 11.66 (Figure 8.35), 11.42 (Figure 8.43) and 11.64 ppm (Figure 8.54) for Compound 1, 2 and 3, respectively. Furthermore, the relevant carbon peaks regarding the carboxylate unit in the ¹³C NMR spectra can be detected at 167.71 (Figure 8.37), 167.30 (Figure 8.47) and 167.88 ppm (Figure 8.58) for Compound 1, 2 and 3, respectively. The covalent attachment of the fullerene moiety to the porphyrin macrocycle can also be verified through ¹H NMR spectroscopy. More precisely, the proton peaks of the formed pyrolidine ring can be located in the range of 5.4-4.3 ppm as illustrated in Figure 8.35, Figure 8.44 and Figure 8.55 for Compound 1, 2 and 3, respectively. Finally, as shown in Figure 8.60, where the ¹H NMR spectrum of the **Reference** compound is provided, the characteristic proton signal of the carboxylate unit as well as that of the triazole ring are detected at 13.19 and 9.65 ppm, respectively.

The photo-physical investigation concerning **Compound 1**, **2** and **3** as well as the **Reference** porphyrin was performed via UV-Vis absorption measurements, emission and excitation fluorescence experiments. In **Figure 6.8** the absorption spectra of the **Reference** porphyrin and the final dyads are presented, which can be described as a superimposition of the UV-Vis spectra of the Zn-Porphyrin and the fullerene molecule. More specifically, in the absorption spectra of **Compound 1**, **2** and **3** an intense Soret band at approximately 425 nm is appeared together with two Q-bands in the 556-598 nm range. The only difference in the UV-Vis spectra between the final dyads and the **Reference** porphyrin is the appearance of a broad peak in the 390-300 nm range in the spectra of all three dyads which is assigned to the fullerene moiety. The above described behavior in the absorption measurements of the final dyads implies that there is negligible interaction in the ground state among the two chromophores.



Figure 6.9: Absorption spectra of **Compound 1**, **2**, **3** (red, blue and magenta, respectively) and **Reference** (black) with their corresponding absorption coefficient number.

Nonetheless, to determine if there is any interaction between the fullerene unit and the porphyrin chromophore fluorescence experiments were performed. The emission spectra of the final dyads and the **Reference** porphyrin are illustrated in **Figure 6.10**. In addition, in **Table 6.1** a collection of the absorption and emission data of **Compound 1**, **2** and **3** as well as the **Reference** compound along with their absorption coefficient numbers is provided. In the emission spectra of all compounds we observe the two

characteristic peaks of the Zn-porphyrin around 607 and 657 nm. Concerning the porphyrin-fullerene dyads though we can clearly detect that the observed emission is strongly quenched due to the fullerene moiety. In detail, selective excitation of the porphyrin chromophore in the dyads showed an almost quantitative quenched emission implying that electron or energy transfer occurs from the Zn-porphyrin to the fullerene unit in all cases. To prove this hypothesis and understand the exact process that take place in the porphyrin-fullerene dyad, transient absorption spectroscopy will be carried out. This is an ongoing investigation that will be performed both in solution (THF) and in NiO films as well to make sure that the behavior of the porphyrin-fullerene dyads is the same under device operation conditions.



Figure 6.10: Emission spectra of **Compound 1**, **2**, **3** (red, blue and magenta, respectively) and **Reference** (black) in THF solution upon excitation at the porphyrin absorption peak (550 nm).

<u>**Table 6.1:**</u> Absorption and Emission features of **Compound 1**, **2**, **3** and **Reference** in THF solution.

	Absorption	Fluorescence	
Dye	λ_{max} (s)/nm (mM ⁻¹ cm ⁻¹)	Emission	
		λ _{max} / nm	
Reference	425 (429.2); 556 (16.7); 597 (4.5)	606; 658	
Compound 1	425 (416.0); 557 (15.7); 597 (4.9)	607; 656	
Compound 2	426 (477.7); 556 (17.2); 598 (5.5)	607; 655	
Compound 3	425 (366.6); 556 (19.1); 597 (8.5)	607; 655	

Computational studies using DFT calculations have been performed in order to investigate the molecular as well as the electronic structure of all final porphyrinfullerene dyads. The gas phase optimized structures of **Compound 1**, **2** and **3** are illustrated in **Figure 8.61** while their corresponding coordinates are listed in **Tables 8.7**, **8.8** and **8.9**, respectively. In **Figure 6.11** the HOMO and LUMO orbitals of **Compound 1**, **2** and **3** are provided. In all porphyrin-fullerene dyads the HOMO is located on the porphyrin ring, while the LUMO is positioned on the fullerene moiety. These distributions suggest that in all porphyrin-fullerene dyads a donor-acceptor system exists, in which the Zn-porphyrin acts as the electron donor unit and on the other hand the fullerene entity as an electron acceptor.



Figure 6.11: HOMO and LUMO calculated molecular orbitals of Compound 1, 2 and 3.

The results regarding the photovoltaic performances of **Compound 1**, **2**, **3** and the **Reference** porphyrin in the developed p-type DSC devices are listed in **Table 6.2**. We have used all the above mentioned porphyrin derivatives as sensitizers in NiO-based photo-cathodes using either iodide/triiodide or a cobalt complex (Co^{II} (dtb-bpy)₃,(2ClO₄-)) as redox shuttle. For all prepared solar cells the photovoltaic parameters were recorded, namely the short circuit photocurrent density (J_{sc}), the open circuit voltage (V_{oc}), the fill factor (ff) and the power conversion efficiency (PCE). All porphyrin derivatives performed better when iodide was used as an electrolyte, on the contrary to the results recorded using the cobalt redox suttle. Interestingly, **Compound**

1 gave the following characteristics: $J_{sc} = 1.86 \text{ mA/cm}^2$, $V_{oc} = 109 \text{ mV}$, ff = 37.2%, and PCE = 0.076%. These results revealed that the optimal complex is **Compound 1** and thus the ideal position of the triazole ring is between the zinc-porphyrin and the fullerene moiety. Noteworthy, this porphyrin-fullerene dyad (**Compound 1**) provided the best results so far regarding covalently linked porphyrin derivatives in p-type DSCs.^{262, 264, 265}

<u>**Table 6.2:**</u> Photovoltaic characteristics of the solar cells made with mesoporous NiO electrodes sensitized with **Compound 1, 2, 3** and **Reference** porphyrin dyes.

Dye-Electrolyte	J _{sc} (mA/cm ²)	V _{oc} (mV)	ff (%)	PCE (%)
Reference-Iodide	0.69	68	33.3	0.015
Reference-Cobalt	0.22	48	24.1	0.002
Compound 1-Iodide	1.86	109	37.2	0.076
Compound 1-Cobalt	0.63	244	35.0	0.054
Compound 2-Iodide	0.91	101	38	0.034
Compound 2-Cobalt	0.20	175	31	0.011
Compound 3-Iodide	1.68	103	36.8	0.063
Compound 3-Cobalt	0.71	175	28.0	0.035

6.3 Porphyrin derivatives for n-type DSCs

6.3.1 Introduction

The severe environmental issues derived from growing global energy consumption directed the scientific community in investigating clean and renewable energy sources. Photovoltaic technology is one of these sources and its universal application could lead into the development of a sustainable society.¹⁶ During the last decades, DSCs have drawn tremendous attention as a promising photovoltaic technology due to their easy

processing and inexpensive materials.^{268, 269} Porphyrins and their analogues have comprehensively been studied as sensitizers in DSCs and proven to be ideal candidates since they have produced the most efficient results so far, concerning a sole chromophore.

Among the various porphyrin derivatives that have been studied over the years, push-pull type porphyrins demonstrated the most efficient results. The first highly efficient push-pull porphyrin based photosensitizer was reported in 2011 achieving an efficiency of 12.3%²⁷⁰ and a few years later the porphyrin dye SM315 was reported, with an efficiency at the range of 13%.^{251, 252} Although these push-pull porphyrins are highly efficient, multistep synthetic approaches have to be applied for the successful preparation of such derivatives.^{271, 272} What is more, the synthetic procedures followed are governed of low overall yields which is quite challenging in large scale applications. On the other hand, the synthesis of tetraarylporphyrins by condensation of dipyrromethane or pyrrole with an aryl aldehyde require fewer synthetic steps with relatively higher yields.^{273, 274} Moreover, the use of an efficient and facile method for the successful preparation of porphyrin derivatives is of immense importance. As we have already mentioned click reaction suffices the above requirements and as a consequence, has been employed for the successful preparation of plenty porphyrinic derivatives in numerous applications.¹²⁸

Even though porphyrins that contain carboxylic acid unist as anchoring groups have shown remarkable performance in DSCs, the incorporation of an additional electron withdrawing group proved to positively affect the device performance. Such groups are quinoxaline, benzothiadiazole and benzotriazole, which are able to decrease the HOMO-LUMO gap, extend the absorption range of the dye and result in increased

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²⁶⁹ Sharifi, N.; Tajabadi, F.; Taghavinia, N., ChemPhysChem, **2014**, *15*, 3902-3927.

²⁷⁰ Yella, A.; Lee, H.W.; Tsao, H.N.; Yi, C.; Chandiran, A.K.; Nazeeruddin, M.K.; Diau, E.W.-G.; Yeh, C.Y.; Zakeeruddin, S.M.; Grätzel, M., *Science*, **2011**, *334*, 629-634.

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²⁷³ Lindsey, J.S.; *Acc. Chem. Res.*, **2010**, *43*, 300-311.

²⁷⁴ Biroli, O.A.; Tessore, F.; Vece, V.; Di Carlo, G.; Mussini, P.R.; Trifiletti, V.; De Marco, L.; Giannuzzi, R.; Manca, M.; Pizzotti, M., *J. Mater. Chem. A*, **2015**, *3*, 2954-2959.

photovoltaic performance.^{252, 275, 276} Lately, the importance of the insertion of a spacer between the porphyrin macrocycle and the anchoring group has been implemented by Diau, Wand and coworkers.²⁷⁷ Thus, the nature of the anchoring group along with the incorporation of a spacer between the chromophore and the anchoring group significantly affects the device performance. As a result, introduction of an acceptor unit in the periphery of the porphyrin ring together with a spacer that promotes the electron transfer process could be considered as an effective strategy for enhancing the performance of simple aryl porphyrins in DSCs.

To this end, we have synthesized two novel zinc-porphyrin derivatives (Zn-3DoHclick-CNCOOH and Zn-3DoH-click-COOH) and two reference compounds (Zn-**3DoH-CNCOOH** and **Zn-3DoH-COOH**) as sensitizers in n-DSCs (Figure 6.12).¹²⁶ The photo-physical and electrochemical measurements along with the computational studies suggest that the four synthesized porphyrin derivatives exhibit appropriate light absorption characteristics as well as suitable molecular orbital levels for their use as sensitizers in DSCs. All the modified zinc-porphyrin complexes bear hexyloxy chains at the ortho-positions of their three phenyl rings and contain either a carboxylic or a cyanoacrylic acid as anchoring group. Noteworthy, long alkyl chains at these certain positions of a porphyrin entity have been proved to almost eliminate the film-based aggregation.²⁷⁸ In the zinc-porphyrin derivatives **Zn-3DoH-click-CNCOOH** and **Zn-**3DoH-click-COOH, a spacer with an electron withdrawing unit was incorporated between the porphyrin ring and each anchoring group. More specifically, the triazole ring was used as a spacer since it is considered to be a highly efficient electron transfer bridge. In addition, the tetrafluoro-phenyl ring was selected due to its strong electron withdrawing ability in both final derivatives (Zn-3DoH-click-CNCOOH and Zn-**3DoH-click-COOH**). Following this strategy, four-fold and eight-fold increase of the device performance was observed regarding Zn-3DoH-click-CNCOOH and Zn-3DoH-click-COOH, respectively, when compared to the efficiencies achieved with the two reference compounds (Zn-3DoH-COOH and Zn-3DoH-CNCOOH).

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²⁷⁷ Lu, J.F.; Li, H.; Liu, S.S.; Chang, Y.C.; Wu, H.P.; Cheng, Y.B.; Diau, E.W.E.; Wang, M.K., *Phys. Chem. Chem. Phys.*, **2016**, *18*, 6885-6892.

²⁷⁸ Splan, K.E.; Hupp, J.T., Langmuir, 2004, 20, 10560-10566.



Figure 6.12: The chemical structures of **Zn-3DoH-click-CNCOOH**, **Zn-3DoH-click-COOH** and the reference compounds **Zn-3DoH-CNCOOH** and **Zn-3DoH-COOH**.¹²⁶

6.3.2 Experimental



<u>Scheme 6.5:</u> Synthesis of Zn-3DoH-click-COOH. Reagents and conditions: a) CHCl₃, BF₃OEt₂, 24h in RT, DDQ, 20h in RT; b) DMF, NaN₃; c) Zn(CH₃COO)₂·2H₂O, MeOH, CH₂Cl₂; d) CuI, DIPEA, THF/CH₃CN, RT, 12h.

Synthesis of 4: In a two-neck round bottom flask, 2,6-bishexyloxybenzaldehyde **1** (363 mg, 1.18 mmol), dipyrromethane **2** (1 g, 2.37 mmol) and pentafluorobenzaldehyde **3** (232 mg, 1.183 mmol) were dissolved in 250 mL of CHCl₃. The reaction mixture was subsequently bubbled under N₂ for 15 min and after the addition of BF₃OEt₂ (95 μ L) was stirred for 24h. Then, 400 mg of DDQ were added and the mixture was left stirring additionally for 20h. The resulting product was filtered through silica pad and afterwards purified via column chromatography (silica gel, petroleum ether/CH₂Cl₂ in 1:1 ratio) providing 295 mg of porphyrin **4** (yield = 19%).

¹**H** NMR (500 MHz, CDCl₃): $\delta = 8.84$ (d, J = 4.7 Hz, 2H), 8.72 (s, 4H), 8.62 (d, J = 4.6 Hz, 2H), 7.68 (m, 3H), 6.98 (m, 6H), 3.80 (m, 12H), 0.95 (m, 12H), 0.61 (m, 24H), 0.52 (m, 12H), 0.30 (m, 18H), -2.59 (s, 2H) ppm.

<u>Synthesis of 5:</u> In a schlenk tube porphyrin 4 was dissolved in a dry DMF solution (5 mL) under N₂ atmosphere and NaN₃ (56 mg, 0.86 mmol) was added. The reaction mixture was heated up to 60°C for 2h. Upon reaction completion, the solvent was removed under reduced pressure and the produced porphyrin was purified via silica gel column chromatography using Hexane/CH₂Cl₂ as eluent in a 7:3 ratio. The desired porphyrin **5** was collected as purple solid (0.23 g, yield = 81%).

¹**H** NMR (500 MHz, CDCl₃): $\delta = 8.83$ (d, J = 4.7 Hz, 2H), 8.71 (s, 4H), 8.64 (d, J = 4.6 Hz, 2H), 7.67 (m, 3H), 6.97 (m, 6H), 3.79 (m, 12H), 0.94 (m, 12H), 0.61 (m, 24H), 0.50 (m, 12H), 0.29 (m, 18H), -2.59 (s, 2H) ppm.

<u>Synthesis of 6:</u> To a 40 mL CH₂Cl₂ solution of 5 (210 mg, 0.15 mmol), a MeOH (6 mL) solution containing Zn(CH₃COO)₂·2H₂O (341 mg, 1.51 mmol) was added and the reaction mixture was stirred at RT overnight. The solvents were evaporated under reduced pressure and the resulting residue was purified through column chromatography (silica gel, using Hexane/CH₂Cl₂ as eluent in a 6:4 ratio). The formed metallated porphyrin derivative **6** was produced in quantitatively yield, namely 94% (0.2 g).

¹**H NMR (500 MHz, CDCl₃):** δ = 8.91 (sb, 2H), 8.80 (s, 4H), 8.73 (sb, 2H), 7.67 (m, 3H), 6.99 (m, 6H), 3.80 (m, 12H), 0.91 (m, 12H), 0.56 (m, 24H), 0.45 (m, 12H), 0.26 (m, 18H) ppm.

Synthesis of Zn-3DoH-click-COOH: In a schlenk tube porphyrin **6** (70 mg, 0.05 mmol) and 4-ethynylbenzoic acid **7** (11 mg, 0.076 mmol) were dissolved in a 1:1 mixture of THF/CH₃CN (5 mL) under N₂ atmosphere. In the next step, DIPEA (9 μ L, 0.05 mmol) and CuI (0.96 mg, 0.005 mmol) were added and the reaction mixture was stirred at room temperature for 12 hours. Upon reaction completion, the volatiles were removed under reduced pressure and the crude solid, was purified by column chromatography (silica gel, CH₂Cl₂) yielding 55 mg of **Zn-3DoH-click-COOH** (yield: 71%).

¹**H NMR (500 MHz, CDCl₃):** δ = 8.96 (d, *J* = 4.0 Hz, 2H), 8.80 (m, 6H), 8.57 (s, 1H), 8.29 (d, J = 8.2 Hz, 2H), 8.18 (d, J = 8.3, 2H) 7.69 (m, 3H), 6.70 (m, 6H), 3.80 (m, 12H), 0.93 (m, 12H), 0.62 (m, 24H), 0.50 (m, 12H), 0.33 (m, 18H) ppm.

¹³C NMR (75 MHz, CDCl₃): δ = 170.60, 160.10, 150.98, 150.59, 150.22, 147.75, 147.21, 142.33, 142.19, 140.29, 140.15, 134.61, 132.21, 131.43, 131.12, 131.08, 130.70, 129.58, 128.22, 127.42, 126.04, 123.24, 131.78, 121.57, 113.95, 113.28, 105.26, 105.16, 68.53, 65.47, 30.84, 30.82, 28.52, 28.46, 24.84, 24.73, 23.93, 22.02, 13.58, 13.55 ppm.



HRMS (MALDI-TOF): calc. for C₈₉H₁₀₂F₄N₇O₈Zn [M + H] ⁺: 1535.6939; found 1535.6942.

Scheme 6.6: Synthesis of **Zn-3DoH-click-CNCOOH**. Reagents and conditions: a) CuI, DIPEA, THF/CH₃CN, RT, 12 h; b) THF, Piperidine, 65°C, 24h.

<u>Synthesis of 9:</u> Porphyrin 6 (70 mg, 0.050 mmol) and 4-ethylynbenzaldehyde 8 (11 mg, 0.076 mmol) were dissolved in a schlenk tube under N₂ atmosphere, using a 1:1 mixture of THF/CH₃CN (5 mL). In the next step, DIPEA (9 μ L, 0.05 mmol) and CuI (0.96 mg, 0.005 mmol) were added and the reaction mixture was stirred at room temperature for 12 hours. Upon reaction completion, the solvents were distilled under vacuum and the resulting residue was purified by column chromatography (silica gel, CH₂Cl₂/Hexane 6:4) yielding 55 mg of **9** (yield: 72%).

¹**H NMR (500 MHz, CDCl₃):** $\delta = 10.09$ (s, 1H), 8.96 (sb, 2H), 8.81 (sb, 6H), 8.54 (s, 1H), 8.21 (d, J = 8.2 Hz, 2H), 8.04 (d, J = 8.2 Hz, 2H) 7.68 (m, 3H), 6.99 (sb, 6H), 3.81 (m, 12H), 0.94 (m, 12H), 0.58 (m, 24H), 0.47 (m, 12H), 0.28 (m, 18H) ppm.

Synthesis of Zn-3DoH-click-CNCOOH: Porphyrin **9** (40 mg, 0,026 mmol) and 2cyanoacetic acid **10** (10 mg, 0.11 mmol) were dissolved in a THF solution (5 mL). Then, piperidine (8 μ L) was added and the reaction mixture was heated at 65°C for 24h under N₂. The resulting solution was evaporated to dryness under vacuum. Finally, the crude residue was purified by column chromatography over silica gel using CH₂Cl₂/MeOH as an eluent (in a 93:7 ratio) to obtain **Zn-3DoH-click-CNCOOH** in 73% yield (30mg). ¹**H NMR (500 MHz, CDCl₃):** $\delta = 8.97$ (d, J = 4.6 Hz, 2H), 8.82 (m, 4H), 8.79 (d, J = 4.6 Hz, 2H), 8.46 (s, 1H), 8.01 (d, J = 4.1, 2H) 7.68 (m, 3H), 7.47 (d, J = 4.1 Hz, 2H), 6.99 (m, 6H), 3.80 (m, 12H), 0.95 (m, 12H), 0.57 (m, 24H), 0.45 (m, 12H), 0.26 (m, 18H) ppm.

¹³C NMR (75 MHz, CDCl₃): δ = 160.16, 151.17, 150.78, 150.42, 148.39, 147.96, 147.43, 145.11, 143.22, 142.49, 139.53, 138.52, 132.47, 131.70, 131.43, 130.48, 129.81, 128.51, 127.69, 127.28, 125.44, 122.62, 121.63, 121.44, 116.93, 114.27, 113.67, 105.31, 77.58, 77.16, 76.74, 68.66, 38.64, 30.90, 29.85, 28.57, 24.91, 24.83, 23.67, 22.08, 13.63 ppm.

HRMS (MALDI-TOF): calc. for C₉₂H₁₀₃F₄N₈O₈Zn [M + H] ⁺: 1586.7048; found 1586.7050.



Scheme 6.7: Synthesis of **Zn-3DoH-COOH**. Reagents and conditions: a) CHCl₃, BF₃OEt₂, 24h in RT, DDQ, 20h in RT; b) Zn(CH₃COO)₂·2H₂O, MeOH, CH₂Cl₂; c) LiOH·H₂O, THF, H₂O reflux, overnight.

<u>Synthesis of 12</u>: In a two-neck round bottom flask, 2,6-bishexyloxybenzaldehyde 1 (363 mg, 1.18 mmol), dipyrromethane 2 (1 g, 2.37 mmol) and methyl-4-formylbenzoate 11 (194 mg, 1.18 mmol) were dissolved in 250 mL of CHCl₃. The reaction mixture was subsequently bubbled under N₂ for 15 min and after the addition of BF₃OEt₂ (95 μ L) was stirred for 24h. Then, 400 mg of DDQ were added and the mixture was additionally left stirring for 20 h. The resulting product was filtered through silica pad and

afterwards purified via column chromatography (silica gel, petroleum ether/ CH_2Cl_2 in 1:1 ratio) providing 210 mg of porphyrin **12** (yield: 14%).

¹**H NMR (500 MHz, CDCl₃):** δ = 8.78 (d, *J* = 4.7 Hz, 2H), 8.71 (s, 4H), 8.65 (d, *J* = 4.7 Hz, 2H), 8.40 (d, *J* = 2.8 Hz, 2H), 8.27 (d, *J* = 2.8 Hz, 2H), 7.66 (m, 3H), 6.97 (m, 6H), 4.11 (s, 3H), 3.79 (m, 12H), 0.94 (m, 12H), 0.63 (m, 24H), 0.51 (m, 12H), 0.23 (m, 18H), -2.59 (s, 2H) ppm.

<u>Synthesis of 13</u>: To a 20 mL CH₂Cl₂ solution of **12** (60 mg, 0.047 mmol) a MeOH (3 mL) solution containing $Zn(CH_3COO)_2$ ·2H₂O (105 mg, 0.48 mmol) was added and the reaction mixture was stirred at RT overnight. The solvents were evaporated under reduced pressure and the resulting residue was purified through column chromatography (silica gel, using CH₂Cl₂/Hexane as eluent in a 6:4 ratio). The formed metallated porphyrin derivative **13** was produced in quantitatively yield, namely 98% (62 mg).

¹**H NMR (500 MHz, CDCl₃):** δ = 8.85 (sb, 2H), 8.80 (sb, 4H), 8.74 (sb, 2H), 8.38 (sb, 2H), 8.28 (sb, 2H), 7.66 (m, 3H), 6.98 (m, 6H), 4.11 (s, 3H), 3.80 (m, 12H), 0.93 (m, 12H), 0.48 (m, 36H), 0.25 (m, 18H) ppm.

Synthesis of Zn-3DoH-COOH: Porphyrin **13** (40 mg, 0.03 mmol) and LiOH·H₂O (50 mg, 1.19 mmol) were dissolved in THF (30 mL) and H₂O (4 mL) under N₂ and the mixture was refluxed overnight. Then, the solvent was removed in vacuum, the resulting residue was dissolved in THF and subsequently the precipitate was filtered off. Finally, the filtrate was concentrated under reduced pressure to afford the crude product, which was purified by column chromatography (silica gel, CH₂Cl₂/EtOH in a 98:2 ratio) to successfully obtain porphyrin **Zn-3DoH-COOH** (32 mg, yield: 81%). ¹H NMR (500 MHz, CDCl₃): δ = 8.87 (d, *J* = 3.6 Hz, 2H), 8.81 (sb, 4H), 8.77 (d, *J* = 3.9 Hz, 2H), 8.48 (d, *J* = 7.2 Hz, 2H), 8.34 (d, *J* = 7.0 Hz, 2H), 7.68 (m, 3H), 6.99 (m, 6H), 3.80 (m, 12H), 0.94 (m, 12H), 0.56 (m, 24H), 0.44 (m, 12H), 0.27 (m, 18H) ppm. HRMS (MALDI-TOF): calc. for C₈₁H₁₀₁N₄O₈Zn [M + H] +: 1321.6833; found 1321.6840.



Scheme 6.8: Synthesis of **Zn-3DoH-CNCOOH**. Reagents and conditions: CHCl₃, BF₃OEt₂, 24h in RT, DDQ, 20h in RT; b) Zn(CH₃COO)₂⁻²H₂O, MeOH, CH₂Cl₂; c) DMSO, NaHCO₃, 1.5h, 160°C; d) THF, Piperidine, 65 °C, 24h.

Synthesis of 15: In a two-neck round bottom flask, 2,6-bishexyloxybenzaldehyde **1** (363 mg, 1.18 mmol), dipyrromethane **2** (1 g, 2.37 mmol) and 4-bromomethylbenzaldehyde **14** (232 mg, 1.18 mmol) were dissolved in 250 mL of CHCl₃. The reaction mixture was subsequently bubbled under N₂ for 15 min and after the addition of BF₃OEt₂ (95 μ L) was stirred for 24h. Then, 400 mg of DDQ were added and the mixture was additionally left stirring for 20h. The resulting product was filtered through silica pad and afterwards purified via column chromatography (silica gel, petroleum ether/CH₂Cl₂ in 1:1 ratio) providing 210 mg of porphyrin **15** (yield: 14%). ¹**H NMR (500 MHz, CDCl₃):** δ = 8.76 (d, *J* = 4.6 Hz, 2H), 8.70 (sb, 6H), 8.17 (d, *J* = 8.0 Hz, 2H), 7.74 (d, *J* = 7.9 Hz, 2H), 7.66 (m, 3H), 6.97 (m, 6H), 3.78 (m, 12H), 0.94 (m, 12H), 0.63 (m, 24H), 0.52 (m, 12H), 0.32 (m, 18H), -2.59 (s, 2H) ppm.

Synthesis of 16: To a 20 mL CH₂Cl₂ solution of 15 (60 mg, 0.048 mmol) a MeOH (3 mL) solution containing Zn(CH₃COO)₂·2H₂O (105 mg, 0.48 mmol) was added and the

reaction mixture was stirred at RT overnight. The solvents were evaporated under reduced pressure and the resulting residue was purified through column chromatography (silica gel, using CH₂Cl₂/Hexane as eluent in a 6:4 ratio). The formed metallated porphyrin derivative was subsequently dissolved in DMSO (4.7 mL), then sodium bicarbonate (NaHCO₃) (12.2 mg, 0.145 mmol) was added and the reaction mixture was heated at 160°C for 1.5h. After reaction completion, the mixture was poured into an ice-water bath. Consequently, the resulting aqueous mixture was dissolved in CH₂Cl₂ and dried over magnesium sulfate (MgSO₄). The desired porphyrin **16** was purified through silica gel column chromatography using CH₂Cl₂/Hexane (in a 6:4 ratio) as eluent (42 mg, 89%).

¹**H** NMR (500 MHz, CDCl₃): $\delta = 10.38$ (s, 1H), 8.87 (d, J = 4.4 Hz, 2H), 8.81 (sb, 4H), 8.73 (d, J = 4.4 Hz, 2H), 8.38 (d, J = 7.6 Hz, 2H), 8.24 (d, J = 7.6 Hz, 2H), 7.67 (m, 3H), 6.98 (m, 6H), 3.80 (m, 12H), 0.93 (m, 12H), 0.55 (m, 24H), 0.43 (m, 12H), 0.26 (m, 18H) ppm.

Synthesis of Zn-3DoH-CNCOOH: Porphyrin 16 (40 mg, 0,026 mmol) and 2cyanoacetic acid 10 (10 mg, 0.11 mmol) were dissolved in a THF solution (5 mL). Then, piperidine (8 μ L) was added and the reaction mixture was heated at 65°C for 24h under N₂. The resulting solution was evaporated to dryness under vacuum. Finally, the crude residue was purified by column chromatography over silica gel using CH₂Cl₂/MeOH as an eluent (in a 98:2 ratio) to obtain Zn-3DoH-CNCOOH in 78% yield (28mg).

¹**H NMR (500 MHz, CDCl₃):** δ = 8.83 (d, *J* = 3.7 Hz, 2H), 8.78 (sb, 4H), 8.72 (d, *J* = 4.2 Hz, 2H), 8.24 (d, *J* = 6.9 Hz, 2H), 7.64 (m, 5H), 6.97 (m, 6H), 3.79 (m, 12H), 0.92 (m, 12H), 0.50 (m, 36H), 0.27 (m, 18H) ppm.

HRMS (**MALDI-TOF**): calc. for C₈₄H₁₀₂N₅O₈Zn [M + H] ⁺: 1372.6942; found 1372.6946.

6.3.3 Results and Discussion

The successful preparation of all intermediate porphyrin derivatives as well as the final compounds was confirmed through ¹H NMR spectroscopy. Moreover, the zinc-porphyrin dyes **Zn-3DoH-click-COOH** and **Zn-3DoH-click-CNCOOH** were characterized via NMR spectroscopy (¹H and ¹³C), MALDI-TOF mass spectrometry and through photo-physical studies (absorption and emission measurements). In

addition, theoretical calculations along with cyclic and square wave measurements have been performed regarding the final **ZnP-3DoH-click-COOH** and **ZnP-3DoH-click-CNCOOH** porphyrins for realizing their molecular structure and their electronic properties as well.

The ¹H and ¹³C NMR spectra of all synthesized porphyrin compounds are presented in **Figures 8.61-8.77**. In the ¹H NMR spectra of the final dyads, the characteristic proton signal of the formed triazole ring appeared at 8.57 ppm for **Zn-3DoH-click-COOH** (**Figure 8.65**) and 8.46 for **Zn-3DoH-click-CNCOOH** (**Figure 8.69**). Moreover, the characteristic proton peaks regarding the hexyloxy chains appear in both cases at the range of 3.9-0.28 ppm (**Figure 8.64** for **Zn-3DoH-click-COOH** and **Figure 8.68** for **Zn-3DoH-click-CNCOOH**). The characteristic carbon peak regarding the carboxylic acid unit of **Zn-3DoH-click-COOH** can be observed at its ¹³C NMR spectrum (**Figure 8.66**) at 170.60 ppm. On the other hand, the relevant peak of the carboxylate unit reagarding the cyanoacrylic acid unit of **Zn-3DoH-click-CNCOOH** can be detected at 163.09 ppm (**Figure 8.70**).

The photo-physical characterization of the final compounds and the reference porphyrins was performed via absorption and emission spectroscopies. The absorption spectra of the reference and the final dyes are presented in **Figure 6.13**. Similar features, typical for zinc-porphyrin derivatives, are observed for both final compounds as well as the reference derivatives. More specifically, an intense Soret band at 422 nm in all cases and one Q-band at approximately 550 nm are appeared. The only worth mentioning finding derived from these studies is the higher coefficient absorption number of the two carboxylate derivatives, namely **Zn-3DoH-click-COOH** and **Zn-3DoH-COOH**, compared to their cyanoacrylate analogues (**Zn-3DoH-click-CNCOOH** and **Zn-3DoH-CNCOOH**, respectively). A collection of the absorption and emission data of the reference and final porphyrin sensitizers along with their absorption coefficient numbers and their fluorescence quantum yields is provided in the following **Table 6.3**.



Figure 6.13: Absorption spectra of **Zn-3DoH-click-COOH** (black), **Zn-3DoH-click-CNCOOH** (red), **Zn-3DoH-COOH** (blue) and **Zn-3DoH-CNCOOH** (magenta).

Compound	Absorption	Emission		
e ompound	$\lambda_{max}/nm (\epsilon/mM^{-1} cm^{-1})$	λ_{max}/nm	Φ	τ/ns
Zn-3DoH-COOH	422 (513.2), 550 (20.5)	600, 647	0.036	2.89
Zn-3DoH-CNCOOH	422 (399.7), 550 (16.6) 598, 6		0.031	2.91
Zn-3DoH-click- COOH	422 (385.2), 549 (19.8)	598, 647	0.032	2.6
Zn-3DoH-click- CNCOOH	422 (317.2), 549 (15.1)	598, 647	0.039	2.5

<u>Table 6.3:</u> Absorption and emission data of compounds **Zn-3DoH-click-COOH**, **Zn-3DoH-click-CNCOOH**, **Zn-3DoH-COOH** and **Zn-3DoH-CNCOOH**.

Moving onto the studies regarding the emission properties of the synthesized porphyrin dyes, the fluorescence spectra of all reported compounds are illustrated in **Figure 6.14**. Upon excitation at $\lambda = 550$ nm the emission features of all porphyrin derivatives are nearly identical. More precisely, in all cases the observed emission spectra display two bands approximately at $\lambda = 600$ and $\lambda = 647$ nm, which are characteristic signals for a zinc-metallated porphyrin based chromophore. The

calculated quantum yield (Φ) of **Zn-3DoH-click-CNCOOH** is 0.039, which is slightly higher than **Zn-3DoH-click-COOH** ($\Phi = 0.032$). Additionally, the time-resolved fluorescence measurements of **Zn-3DoH-click-COOH** and **Zn-3DoH-click-CNCOOH** in THF solution at RT exhibit single exponential decay with lifetimes of ca. 2.6 and 2.5 ns, respectively, corresponding to the singlet excited state of the porphyrin moiety.



Figure 6.14: Emission spectra of **Zn-3DoH-click-COOH** (black), **Zn-3DoH-click-CNCOOH** (red), **Zn-3DoH-COOH** (blue) and **Zn-3DoH-CNCOOH** (magenta).

Computational studies at the B3LYP/6-31G(d) level of theory were employed in order to gain insight into the electronic and molecular structure of the two porphyrin sensitizers **Zn-3DoH-click-COOH** and **Zn-3DoH-click-CNCOOH**. In **Figure 6.15** their gas phase optimized structures are presented while their corresponding coordinates are listed in **Tables 8.10** and **8.11** for **Zn-3DoH-click-COOH** and **Zn-3DoH-click-CNCOOH**, respectively. From the optimized structures we observe that in both cases the triazole ring is almost co-planar to both the porphyrin plane and the phenyl ring bearing the anchoring group. On the contrary, all four phenyl rings of each porphyrin macrocycle are nearly perpendicular to the porphyrin ring and as a consequence to the triazole ring. The hexyloxy groups of the three phenyl rings in both porphyrin derivatives are extended above and under the porphyrin plane, reducing the probability of π - π stacking with another porphyrin ring and as a result dye aggregation. The frontier molecular orbitals and the analogue energy distribution are depicted in **Figures 8.78** and **8.79** for **Zn-3DoH-click-COOH** and **Zn-3DoH-click-CNCOOH**.

respectively. In both porphyrin derivatives, the electron densities of the HOMOs are predominantly located on the porphyrin unit, with some additional contributions on the phenyl group bearing the hexyloxy units. In addition, electron density distribution regarding the LUMOs is localized on the porphyrin macrocycle and on the anchoring groups, namely on the carboxylate and cyanoacrylic acid unit for Zn-3DoH-click-COOH and Zn-3DoH-click-CNCOOH, respectively. Consequently, both porphyrin sensitizers can be described as "push-pull" D- π -A systems with potential to act as sensitizers in DSCs. Where D stand for donor, A for acceptor and π for conjugated bridge. The electron density distributions clearly favor intramolecular electron transfer from the donor porphyrin ring and hexyloxy chains to each acceptor (phenyl group with carboxylic or cyanoacrylic acid) via the triazole π -conjugated spacer. The successful electron injection from each dye to the TiO₂ conduction band is supported by the fact that the LUMO orbitals (LUMO+2 for Zn-3DoH-click-COOH and LUMO for Zn-**3DoH-click-CNCOOH**) are located on the anchoring groups. In **Table 6.4** the HOMO and LUMO energies, the HOMO-LUMO gap (HL) and the calculated dipole moment for Zn-3DoH-click-COOH and Zn-3DoH-click-CNCOOH are presented. The HL theoretical gap was calculated in THF solution and is in agreement with the HL electrochemical gap observed from the electrochemistry experiments.



Figure 6.15: Different view perspectives of the gas phase geometry optimized structure of Zn-3DoH-click-COOH (left part) and Zn-3DoH-click-CNCOOH (right part). Carbon,

nitrogen, hydrogen, oxygen, fluoro and zinc correspond to grey, blue, white, red, light blue and green, respectively.

<u>**Table 6.4:</u>** Summary of the calculated HOMO and LUMO values, the HOMO-LUMO gap (HL) and the dipole moments (μ) regarding **Zn-3DoH-click-COOH** and **Zn-3DoH-click-COOH**.</u>

Compound	HOMO (eV)	LUMO (eV)	HL (eV)	μ (D)
Zn-3DoH-click- COOH	-4.866	-2.050	2.816	11.11
Zn3-DoH-click- CNCOOH	-4.872	-2.743	2.129	14.80

The electrochemical properties of Zn-3DoH-click-COOH, Zn-3DoH-click-CNCOOH as well as the reference compounds Zn-3DoH-COOH and Zn-3DoH-**CNCOOH** were examined through cyclic and square wave voltammetry. All the presented studies were performed in dry and degassed THF solution using tetrabutylammonium hexafluorophosphate (0.1 M) as the supporting electrolyte and ferrocene as internal standard. The cyclic and the square wave voltammograms regarding Zn-3DoH-click-COOH, Zn-3DoH-click-CNCOOH, Zn-3DoH-COOH and Zn-3DoH-CNCOOH are illustrated in Figures 8.80, 8.81, 8.82 and 8.83, respectively. In all cases there are two reversible oxidations and one reversible reduction process. The first reduction process corresponds to the LUMO orbital and it is essential for a sensitizer to be more negative than the reduction potential of TiO₂, so that electron injection from the photo-induced dye to the conduction band (CB) of the semiconductor occurs under device operation. The redox potentials of all porphyrin sensitizers are summarized in **Table 6.5**, noticing that all reduction processes are more negative than -1.4 V. Therefore, there is sufficient driving force for all porphyrin sensitizers to inject electrons into the CB of TiO₂. On the contrary, the HOMO orbital which corresponds to the first oxidation potential should be more positive than the redox potential of the electrolyte applied in the DSC. Noteworthy, the first oxidation potential of all porphyrin derivatives is over 0.8 V, which is indeed more positive than the redox potential of the I^{-}/I_{3}^{-} couple. This implies that the regeneration of the oxidized photo-sensitizer is feasible from the energetic point of view in the DSC devices (Figure **6.16**).

<u>Table 6.5:</u> Summary of the electrochemical redox data of **Zn-3DoH-click-COOH**, **Zn-3DoHclick-CNCOOH**, **Zn-3DoH-COOH** and **Zn-3DoH-CNCOOH** in THF. All potentials are reported vs. SCE and FcH/FcH⁺ was used as the internal standard ($E_{1/2}Ox$ is 0.63V).

Compound	Reduction (V)	Oxidation (V)		
Compound	E _{1/2} Red ¹	E _{1/2} Ox ¹	E _{1/2} Ox ²	
Zn-3DoH-click-COOH	-1.47	0.90	1.44	
Zn-3DoH-click-CNCOOH	-1.48	0.92	1.43	
Zn-3DoH-COOH	-1.60	0.85	1.39	
Zn-3DoH-CNCOOH	-1.60	0.81	1.37	



Figure 6.16: Electrochemical potential diagram showing the electron flow in the **Zn-3DoH-click-COOH** and **Zn-3DoH-click-CNCOOH** based DSCs.

For the porphyrin sensitizers **Zn-3DoH-click-CNCOOH** and **Zn-3DoH-click-COOH**, photovoltaic devices were developed and their results were compared to the reference n-DSC constructed using the **Zn-3DoH-COOH** dye. For all prepared n-type DSCs the photovoltaic parameters were recorded and are listed in **Table 6.6**. In detail, the short circuit photocurrent density (J_{sc}), the open circuit voltage (V_{oc}), the fill factor (ff) and the power conversion efficiency (PCE) were measured. Interestingly, **Zn-3DoH-click-CNCOOH** and **Zn-3DoH-click-COOH** performed four and eight times better than the reference device with **Zn-3DoH-COOH**. These results revealed that the

optimal complex is the carboxylate porphyrin **Zn-3DoH-click-COOH** and thus the incorporation of an electron withdrawing group along with the presence of an electron transfer bridge has detrimental effects in the efficiency of the device. The 8-fold increase in the efficiency indicates that using tetrafluoro-phenyl electron withdrawing unit along with a triazole spacer between the chromophore and the anchoring group is an efficient way to drastically increase the device performance.

<u>**Table 6.6:</u>** Photovoltaic characteristics of the solar cells made with **Zn-3DoH-click-COOH**, **Zn-3DoH-click-CNCOOH** and the reference **Zn-3DoH-COOH**.</u>

Compound	J _{sc} (mA/cm ²)	Voc (V)	ff	PCE (%)
Zn3DoH-click-COOH	0.93	0.52	0.54	0.26
Zn3DoH-click-CNCOOH	0.47	0.45	0.53	0.11
Zn3DoH-COOH	0.23	0.28	0.46	0.03

In summary, a new series of porphyrin compounds as sensitizers in DSCs is reported. We have incorporated a new electron withdrawing triazole spacer between the porphyrin core and the anchoring unit, examining the influence of this modification on the device performance. The functionalized porphyrin derivatives **ZnP-3DoH-click-COOH** and **ZnP-3DoH-click-CNCOOH** performed eight and four times better, respectively, compared to the reference compounds **ZnP-3DoH-COOH** and **ZnP-3DoH-CNCOOH**. In addition, the carboxylate unit has been proven more efficient anchoring group than the cyanoacrylate when combined with the tetrafluoro-phenyl triazole unit. We have also demonstrated that the introduction of this auxiliary spacer enhances the electron transfer/injection ability in the modified porphyrin derivatives providing relatively higher PCE, J_{SC} and V_{OC} values. Particularly, in the case of **ZnP-3DoH-click-COOH** the best photovoltaic parameters along with the highest overall efficiency were recorded.

Overall, the work presented herein provides insights regarding the molecular design of the efficient porphyrin derivatives as sensitizers in DSCs. In particular, these findings suggest an alternative way to design and develop efficient sensitizers consisted of an auxiliary electron withdrawing spacer between the porphyrin core and the anchoring unit. Thus, such bridging moieties could be used along with an efficient electron donor unit (e.g., triphenylamine) in both electron transfer schemes and DSC applications.

Chapter 7: Perspectives and Future Directions

This dissertation provided insights regarding the development of porphyrin derivatives as photosensitizers in solar-based harnessing applications. The prepared porphyrin entities have been studied as light-harvesters in DSCs, in energy/electron transfer schemes, in LEC devices and DNA supramolecular assemblies. The obtained results from this thesis could be valuable in designing novel porphyrin moieties concerning those applications. In this chapter, suggestions regarding the synthesis and the application of novel porphyrin hybrids will be presented.

More specifically, as illustrated in **Figure 7.1**, the preparation of a supramolecular entity (**(BDP)**₂**-Porphyrin-Corrole**) consisted of one porphyrin moiety, two BODIPY molecules and one corrole unit is proposed in order to act as photosensitizer in electron/energy transfer schemes.



Figure 7.1: The chemical structure of the proposed supramolecular (**BDP**)₂-**Porphyrin-Corrole** compound.

From the studies presented in chapter 3 we are aware that: a) intramolecular energy transfer occurs among porphyrin and BODIPY molecules and b) electron transfer takes place when a porphyrin is covalently attached to a corrole unit. Therefore, we propose the synthesis of this supramolecular system in which two BODIPY chromophores will be axially coordinated to a tin-porphyrin derivative that bears a corrole moiety. Tin-porphyrin was selected instead of indium-porphyrin due to the greater stability of the

formed bond between the porphyrin and the BODIPY molecule.^{124, 279} In this porphyrin hybrid, the selective excitation of the BODIPY molecules will possibly lead to an energy transfer process towards the porphyrin macrocycle. Subsequently, the excited porphyrin unit could probably transport an electron to the corrole moiety forming a charge separated state between the two chromophores (Porphyrin⁺-Corrole⁻). Hence, combining the two separate projects presented in chapter 3 of this dissertation we could prepare a supramolecular entity that efficiently performs as an antenna complex causing charge separation between its components.

In addition to the work presented in the first part of chapter 6 (6.1), we propose the synthesis of an improved porphyrin-fullerene dyad. The results obtained from the DSC measurements suggested that the ideal position of the spacer (triazole bridge) is between the porphyrin macrocycle and the fullerene moiety. Thus, we designed a novel porphyrin-fullerene dyad (**Porphyrin-oPV-C**₆₀, **Figure 7.2**) in which the triazole bridge is replaced by a more efficient electron transfer spacer, namely an oligo(*p*-phenylenevinylene) (**oPPV**). The enhanced electron transfer efficiency of the **oPPV** wire compared to the triazole ring is attributed to its greater length and its chemical nature (extended conjugation) as reported by previous studies in the literature.²⁸⁰



Figure 7.2: The chemical structure of the proposed porphyrin-fullerene dyad (**Porphyrin-oPPV-C**₆₀).

Lastly, we suggest the preparation of a push-pull porphyrin derivative for n-type DSC devices based on the results presented in the second part of chapter 6 (6.2). As we concluded in this part, the synthesized porhyrin derivative **Zn-3DoH-click-COOH** has

²⁷⁹ Lazarides, T.; Kuhri, S.; Charalambidis, G.; Panda, M.K.; Guldi, D.M.; Coutsolelos, A.G., *Inorg. Chem.*, **2012**, *51*, 4193-4204.

²⁸⁰ Stangel, C.; Schubert, C.; Kuhri, S.; Rotas, G.; Margraf, J.T.; Regulska, E.; Clark, T.; Torres, T.; Tagmatarchis, N.; Coutsolelos, A.G.; Guldi, D.M., *Nanoscale*, **2015**, *7*, 2597-2608.

performed eight times greater than the reference compound **Zn-3DoH-COOH**. This behavior was attributed to the modification with an electron withdrawing spacer unit, namely the penta-fluoro-triazole unit. Therefore, we suggest the synthesis of a similar porphyrin moiety which will contain a strong donor unit such as the phenyl-amine group on one end of the porphyrin macrocycle and the penta-fluoro-triazole unit between the porphyrin ring and the anchoring group. The chemical structure of the porphyrin derivative (**Ph**)₂**N-Porphyrin-click-COOH** is presented in **Figure 7.3**.



Figure 7.3: The chemical structure of the proposed donor-acceptor porphyrin derivative (**Ph**)₂**N-Porphyrin-click-COOH**.

Chapter 8: Appendix



Figure 8.1: ¹H NMR spectrum of **2** (500MHz, DMSO- d_6).



Figure 8.2: ¹H NMR spectrum of **4** (500MHz, DMSO-*d*₆).



165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 ppm

Figure 8.3: ¹³C NMR spectrum of 4 (500MHz, DMSO- d_6).



Figure 8.4: Zoom on the aromatic region of 13 C NMR spectrum of **4** (500MHz, DMSO- $d_6{}^6$).



Figure 8.5: ¹⁹F NMR spectrum of 4 (500MHz, DMSO- d_6).



Figure 8.6: Maldi-TOF spectrum of 4.


Figure 8.7: Gas phase geometry optimized structure of **4** (upper part) and a different view perspective of the gas phase geometry optimized structure of **4**. Carbon, nitrogen, hydrogen, oxygen, fluoro, zinc and copper atoms correspond to grey, blue, white, red, light blue, green and orange spheres, respectively.

Table 8.1: Coordinates of gas phase geometry optimized structure of 4 calculated by DFT	at
the B3LYP / 6-31G(d) level. E = - 5588.2265805 Hartree / particle.	

	X	У	Z
С	-4.522786000	-0.715040000	0.218792000
С	-2.207990000	-5.057277000	0.105398000
С	1.691551000	-2.629074000	1.871184000
С	-1.557748000	0.759244000	1.494739000
С	-2.286837000	1.971400000	1.266860000
С	-3.534429000	1.608436000	0.802652000
С	-3.571396000	0.168815000	0.736887000
Ν	-2.376436000	-0.294926000	1.238029000
С	-4.278928000	-2.112222000	0.066750000
С	-5.277726000	-3.123667000	-0.131062000
С	-4.639635000	-4.336558000	-0.157599000
С	-3.235339000	-4.086513000	0.014753000
Ν	-3.042997000	-2.720853000	0.118045000
С	-0.889252000	-4.782288000	0.541932000
С	0.255386000	-5.640279000	0.407917000
С	1.336344000	-4.961019000	0.906680000
С	0.875829000	-3.674409000	1.345522000
Ν	-0.486064000	-3.604121000	1.144074000
С	1.257976000	-1.303107000	1.964279000
С	1.827538000	-0.151479000	2.617941000
С	0.905137000	0.871369000	2.536239000

С	-0.227938000	0.355354000	1.827387000
Ν	0.045389000	-0.918270000	1.438875000
С	3.068644000	-2.965216000	2.315504000
С	-2.535401000	-6.452936000	-0.281549000
С	-5.855532000	-0.185300000	-0.168734000
С	4.195784000	-2.342186000	1.760782000
С	5.489085000	-2.647919000	2.177712000
С	5.685191000	-3.600272000	3.174857000
С	4.587601000	-4.239509000	3.747151000
С	3.303003000	-3.918003000	3.317651000
С	-2.257722000	-7.533728000	0.581097000
С	-2.571652000	-8.836750000	0.225392000
С	-3.164791000	-9.108069000	-1.018687000
C	-3.438759000	-8.050435000	-1.896195000
С	-3.130976000	-6.742678000	-1.518789000
C	-6.348928000	-0.324404000	-1.474131000
Ĉ	-7.592968000	0.173244000	-1.852190000
Ĉ	-8.383397000	0.835430000	-0.915452000
Ĉ	-7.924530000	0.991685000	0.390182000
Č	-6.677735000	0.484769000	0.748528000
F	4 055853000	-1 436745000	0 784306000
F	6 542271000	-2.040911000	1 619848000
F	6 920681000	-3 899404000	3 581366000
F	4.773453000	-5.147207000	4.711765000
F	2 274762000	-4 539601000	3 908104000
F	-8 027660000	0.029796000	-3 109031000
F	-5 612240000	-0.936065000	-2 409719000
F	-9 576797000	1 318188000	-1 267677000
F	-8 687287000	1.617080000	1 293555000
F	-6 287111000	0.638506000	2.020004000
$\hat{0}$	-3 431397000	-10 419435000	-1 271032000
Č	-4 045411000	-10 760116000	-2 520262000
C	-4 248675000	-12 237340000	-2 563347000
C	-5.050303000	-13 046378000	-1 788276000
N	-4 843304000	-14 299445000	-2.274386000
N	-3 956310000	-14 262431000	-3 308626000
N	-3 601332000	-13 023485000	-3 474624000
C	-5 421240000	-15 532246000	-1 861144000
Ċ	-5 514137000	-16 586338000	-2.775001000
C	-6.087457000	-17 789905000	-2.374328000
C	-6 588022000	-17 966233000	-1 073539000
C	-6 478935000	-16 894143000	-0 174349000
C	-5 894128000	-15 687872000	-0 555337000
C	-4 955550000	-20 394490000	-0.840428000
C	-4 517966000	-21 673679000	-0 669257000
C	-5 668809000	-22,473289000	-0 311401000
N	-6 785004000	-21 670126000	-0 274350000
C	-6 383714000	-20 395980000	-0 598177000
Č	-10.717114000	-18.473120000	-0.131352000
č	-9.460856000	-18.079213000	-0.483619000
Č	-8.602188000	-19.240421000	-0.373412000
Ň	-9 352772000	-20 318777000	0.030497000
C	-10 648137000	-19 882345000	0 185798000
Č	-7.219499000	-19.259536000	-0.660903000
č	-12.428668000	-24.135224000	1.353404000
-			

С	-12.864412000	-22.854241000	1.191963000
С	-11.712337000	-22.053499000	0.840956000
Ν	-10.596847000	-22.857571000	0.800217000
C	-10 999923000	-24 133629000	1 114377000
Č	-11 752053000	-20 670963000	0 568942000
C	-6 66/86/000	-26.05/1568000	0.658271000
C	7 022106000	-20.034308000	0.000270000
C	-7.923100000	-20.431080000	0.999279000
	-8./81340000	-25.289198000	0.889518000
N	-8.028/15000	-24.208199000	0.496614000
C	-6./32542000	-24.643909000	0.346226000
C	-5.627980000	-23.854823000	-0.033/15000
С	-10.165473000	-25.271877000	1.170083000
С	-10.801973000	-26.570149000	1.558900000
С	-11.326664000	-26.755838000	2.849288000
С	-11.918940000	-27.961923000	3.215559000
С	-11.999535000	-29.013003000	2.291686000
С	-11.480104000	-28.838633000	1.001841000
С	-10.888727000	-27.632205000	0.641592000
Cu	-1.485606000	-1.971857000	0.960814000
Zn	-8.690793000	-22.264081000	0.263229000
C	-12 619618000	-30 321004000	2 625315000
õ	-12 711423000	-31 263369000	1 863169000
0	-12.711423000	-30 37759/000	3 897770000
U U	1 01/006000	-30.377394000	1 417277000
11	-1.914090000	2.970243000	0.472048000
п	-4.521197000	2.275554000	0.4/2048000
H	-6.342040000	-2.9444/9000	-0.200/33000
H	-5.092155000	-5.313907000	-0.243236000
Н	0.2510/4000	-6.619390000	-0.049007000
Η	2.363459000	-5.298684000	0.932941000
Н	2.774452000	-0.129728000	3.140668000
Η	1.001483000	1.870253000	2.941513000
Η	-1.808050000	-7.338282000	1.549871000
Η	-2.371704000	-9.666598000	0.895824000
Η	-3.877378000	-8.229054000	-2.870958000
Η	-3.338548000	-5.931915000	-2.210609000
Н	-3.401188000	-10.471695000	-3.359267000
Н	-5.000143000	-10.224015000	-2.612688000
Н	-5.732902000	-12.833770000	-0.981366000
Н	-5 142638000	-16 450752000	-3 783748000
Н	-6 166054000	-18 604524000	-3 087919000
н	-6 840562000	-17.013461000	0.842464000
н	-5.7865/13000	-1/.015401000	0.042404000
	-3.780343000	10 527782000	1.005645000
п	-4.303203000	-19.327783000	-1.093043000
п	-5.30/990000	-22.040028000	-0./03499000
H	-11.615168000	-1/.8/2343000	-0.099186000
H	-9.14/10/000	-17.095075000	-0./99986000
H	-13.021869000	-25.003627000	1.600175000
Η	-13.874188000	-22.480934000	1.288961000
Η	-5.766639000	-26.655112000	0.628241000
Η	-8.239332000	-27.437365000	1.306252000
Η	-11.258869000	-25.946793000	3.570575000
Η	-12.314257000	-28.094180000	4.216655000
Η	-11.554196000	-29.658391000	0.294770000
Н	-10.495349000	-27.499760000	-0.361936000
Н	-13.469149000	-31.271496000	3.996981000

С	-13.085735000	-19,982045000	0.688272000
С	-13.937861000	-19.887784000	-0.432857000
С	-13.483830000	-19.426480000	1.922808000
С	-15.171155000	-19.240893000	-0.297115000
С	-14.725986000	-18.788499000	2.013303000
Н	-15.823039000	-19.167777000	-1.165695000
Н	-15.026432000	-18.358803000	2.967095000
С	-15.587181000	-18.687253000	0.917185000
С	-4.293162000	-24.542590000	-0.146267000
С	-3.444286000	-24.629699000	0.978331000
С	-3.886714000	-25.095770000	-1.378709000
С	-2.206817000	-25.268790000	0.848122000
С	-2.639955000	-25.726250000	-1.463573000
Η	-1.554666000	-25.330106000	1.717449000
Η	-2.329981000	-26.148259000	-2.417651000
С	-1.785380000	-25.826898000	-0.362683000
С	-4.771162000	-25.013921000	-2.603365000
Η	-4.296361000	-25.501110000	-3.460616000
Н	-5.740030000	-25.498129000	-2.433324000
Н	-4.981388000	-23.973894000	-2.879773000
С	-3.849033000	-24.041766000	2.312257000
Η	-4.774463000	-24.494332000	2.687855000
Η	-3.067601000	-24.201437000	3.061628000
Η	-4.031077000	-22.962971000	2.238842000
С	-0.456143000	-26.538313000	-0.469030000
Η	0.307303000	-26.057625000	0.152720000
Η	-0.534986000	-27.581628000	-0.134774000
Η	-0.091465000	-26.554168000	-1.501503000
С	-16.937921000	-18.021611000	1.046730000
Н	-17.244741000	-17.550124000	0.106771000
Н	-17.716438000	-18.749196000	1.313430000
H	-16.932887000	-17.252340000	1.826405000
C	-12.591145000	-19.507797000	3.141520000
H	-13.059439000	-19.018851000	4.001400000
H	-12.381003000	-20.54/93/000	3.417537000
H	-11.622365000	-19.025955000	2.964401000
C	-13.538623000	-20.469383000	-1.7/1200000
H	-12.612404000	-20.018558000	-2.146866000
H	-13.360548000	-21.549202000	-1./03905000
Н	-14.321484000	-20.302986000	-2.51/598000



Figure 8.8: Normalized absorption spectra of 2 (red) and 3 (black) in THF.



Figure 8.9: Fluorescence spectra of 2 (red) and 4 (blue) in THF.



Figure 8.10: ¹H NMR spectrum of (TPP)In-O-BDP in CDCl₃.



Figure 8.11: ¹H NMR spectrum of (TPP)In-OOC-BDP in CDCl₃.



Figure 8.12: ¹H NMR spectrum of (TPP)In-O-Ph in C₆D₆.



Figure 8.13: ¹H NMR spectrum of (TPP)In-OOC-Ph in C₆D₆.



Figure 8.14: ¹³C NMR spectrum of (TPP)In-O-BDP in C₆D₆.



Figure 8.15: ¹³C NMR spectrum of (TPP)In-OOC-BDP in C₆D₆.

Table 8.2: TDDFT calculated singlet electronic transitions of (TPP)In-O-BDP and (TPP)In-

C 1	Theoretical	Oscillator		
Compound	(λ_{max}, nm)	strength	Frontier orbital contributions	
			HOMO-3→LUMO+1 (39%)	
	551.2	0.035	HOMO-2→LUMO (59%)	
			HOMO-1→LUMO+1 (4%)	
			HOMO-3→LUMO (39%)	
	550.2	0.027	HOMO-2→LUMO+1 (59%)	
			HOMO-1→LUMO (4%)	
(TPP)In_O_RDP	420.9	0 349	HOMO \rightarrow LUMO+2 (69%)	
(111)11-0-001	120.9	0.5 17	HOMO-4 \rightarrow LUMO+2 (3%)	
			HOMO-3→LUMO+1 (43%)	
	397.9	1.49	HOMO-2 \rightarrow LUMO (20%)	
			HOMO-18→LUMO (3%)	
			HOMO-3→LUMO (42%)	
	396.7	1.67	HOMO-2→LUMO+1 (20%)	
			HOMO-18 \rightarrow LUMO+1 (3%)	
	551 1	0.031	HOMO-2 → LUMO+1 (41%)	
	551.1	0.051	HOMO→LUMO (60%)	
	550.0	0.022	HOMO-2→LUMO (42%)	
	550.0	0.022	HOMO→LUMO+1 (60%)	
	122 1	0 422	HOMO-1→LUMO+2 (69%)	
(TPP)In-OOC-BDP	722.7	0.422	HOMO-3 \rightarrow LUMO+2 (4%)	
	397.2	1 45	HOMO-2→LUMO (40%)	
	571.2	1.45	HOMO \rightarrow LUMO+1 (21%)	
			HOMO-2→LUMO+1 (40%)	
	396.8	8 1.65	HOMO→LUMO (20%)	
			HOMO-2→LUMO (2%)	

OOC-BDP. Computed wavelengths, oscillator strengths and major orbital contributions.



Figure 8.16: Gas phase DFT (B3LYP/6-31G^{*}) optimized geometry of (**TPP**)**In-O-BDP** (left part) and (**TPP**)**In-OOC-BDP** (right part).

Table 8.3: Gas phase geometry optimized (B3LYP/LANL2DZ/6-31G*) coordinates of	of
(TPP) In-O-BDP . E = 83235.736097406 eV/particle.	

	X	У	Z
In	2.09013	0.01598	0.29074
Ν	3.32224	1.64869	0.39161
Ν	1.58646	1.305	1.94635
С	4.14583	1.60092	1.49569
С	4.43666	2.94947	1.92217
Н	5.05092	3.21494	2.76978
С	3.79236	3.79327	1.06746
Н	-3.7847	4.87293	1.09028
С	3.09559	2.9769	0.10161
С	2.30995	3.47107	0.96062
С	1.64012	2.68239	1.91943
С	0.93378	3.20002	3.06667
Н	0.82676	4.24684	3.30982
С	0.45944	2.13188	3.76849
Н	0.11448	2.14856	4.68301
С	-0.8813	0.93908	3.07331
С	4.62713	0.43166	2.12093
С	2.19291	4.95924	1.09886
С	0.97338	5.60374	0.83808
Н	0.11669	5.01301	0.52578
С	0.85914	6.98897	0.96585
Н	0.09098	7.47218	0.75443
С	1.96139	7.75113	1.35845
С	3.17894	7.12046	1.62265
Н	4.04022	7.70554	1.9341
С	3.29399	5.73537	1.49353
Н	4.24028	5.24582	1.70684
С	5.51376	0.60359	3.31724
С	5.06276	0.23714	4.59526
Н	4.05968	0.16432	4.70897
С	5.88451	0.39436	5.71239
Н	5.51686	0.11068	-6.6949
С	7.17087	0.91866	5.56947
С	7.63096	1.28486	4.30287
Н	8.63275	1.68852	-4.182
С	6.80895	1.12885	3.18562
Н	7.17207	1.40706	2.20004
Ν	1.80042	1.60706	1.67948
Ν	-3.5379	1.26081	0.66139
С	1.09363	1.55154	2.86138
С	0.95978	2.88825	3.38947
Н	-0.4728	3.14256	4.3193
С	1.58874	3.73204	2.52302
Н	1.70971	4.80123	2.61616
С	2.12193	2.92778	1.44972
С	2.90913	3.42278	0.38888
С	3.57818	2.63533	0.57115
С	4.44418	3.14703	1.60692

Н	4.66267	4.19104	1.77572
С	4.92988	2.07548	2.29533
Н	5.62506	2.08466	3.12182
С	-4.3553	0.88928	1.70622
С	0.62759	0.38212	3.49982
С	3.07732	4.91021	0.30475
С	4.30789	5.51646	0.60293
Н	5.14766	4.89549	0.9025
С	4.45503	-6.9025	0.52866
Н	5.41341	-7.3557	0.76787
С	3.37428	7.70403	0.15497
С	2.14514	-7.112	-0.1425
Н	1.29977	7.72802	0.43718
С	1.99715	5.72612	0.06661
Н	1.04148	5.26677	0.30341
С	0.16708	-0.5642	4.75789
С	-0.3626	-0.196	6.00497
Н	1.36439	0.22173	6.05442
С	0.37912	0.37214	7.1741
Н	0.04874	0.08566	8.13113
С	1.66244	0.91959	7.11534
С	2.19882	1.29199	5.88108
Н	3.19806	1.71539	5.82551
С	1.45653	1.11746	4.71206
Н	1.87841	-1.4049	3.75288
В	8.06201	-0.0697	-1.547
Ν	7.11233	1.30199	1.56489
Ν	7.1464	1.18101	1.41216
С	0.70715	0.00886	1.06983
С	1.36347	0.09804	2.31773
Н	0.75207	0.18142	3.21149
С	2.75156	0.08163	2.40348
Н	3.22982	0.15315	3.37768
С	3.54774	0.02536	1.25246
С	2.90378	-0.1154	0.01157
Н	3.50073	0.19705	0.89409
С	1.51322	0.10003	0.08367
Н	1.0407	0.17172	1.05956
С	5.03775	0.04023	1.34841
С	5.74903	1.17201	1.31696
С	5.3094	2.53218	-1.1971
С	6.46235	3.31074	1.22595
Н	6.50884	4.39052	1.15919
С	7.57578	2.45692	1.35874
С	7.5058	2.58561	1.67813
С	6.36828	3.41754	1.66203
Н	6.38422	4.49759	1.73784
С	5.23717	-2.6169	1.53517
С	5.71532	1.26593	1.47238
С	3.91696	3.0754	-1.0618
Н	3.95288	4.16776	0.99126

Н	3.28385	2.80875	1.91457
Η	3.40987	2.6915	0.17009
С	9.02276	2.82376	1.43497
Η	9.46176	2.46497	2.37215
Η	9.14719	3.90807	1.37123
Η	9.58357	2.34785	0.62335
С	3.8286	3.13217	1.48492
Η	3.83183	4.22446	1.56445
Η	3.32152	2.85843	0.55371
Η	3.21411	2.73239	-2.2985
С	8.94264	2.97947	1.79848
Η	9.51339	2.62016	0.93551
Η	9.03824	4.06646	1.86658
Η	9.394	2.52174	2.68535
0	0.62345	0.03029	1.04236
F	8.93026	0.14799	0.45636
F	8.78881	0.00709	2.73691
Η	1.87207	8.82946	1.45827
Η	7.81072	1.04078	6.43919
Η	3.48912	8.78299	0.09691
Η	2.24039	1.05583	8.0253

<u>Table 8.4</u>: Gas phase geometry optimized (B3LYP/LANL2DZ/6-31G*) coordinates of (**TPP)In-O-BDP**. E = 86320.457541844 eV/ particle

	X	У	Z
In	-2.461634	0.029006	0.044659
Ν	-3.068535	1.596326	1.295853
Ν	-2.953137	1.427211	1.619625
С	-3.104279	1.459183	2.665812
С	-3.115047	2.770189	3.268224
Η	-3.140169	2.964092	4.330547
С	-3.090476	3.682352	2.255356
Η	-3.087674	4.759046	-2.33932
С	-3.060861	2.945099	-1.01366
С	-3.014456	3.518753	0.273413
С	-2.985178	2.798981	1.487075
С	-3.02395	3.395656	2.80075
Η	-3.072352	4.455931	3.000501
С	-3.00472	2.379506	3.709306
Η	-3.024816	2.460269	4.785971
С	-2.977095	1.14108	2.968197
С	-3.134468	0.244063	3.375442
С	-3.014776	5.014979	0.362848
С	-1.876088	5.705001	0.808034
Η	-0.987481	5.142209	1.080189
С	-1.874928	7.098129	0.893295
Η	-0.982438	7.615559	1.235081
С	-3.012781	7.824438	0.535836
С	-4.152004	7.149186	0.092825
Н	-5.043826	7.706022	0.182433

С	-4.152838	5.756087	0.007017
Н	-5.042913	5.23234	-0.33057
С	-3.059635	0.317812	4.871532
С	-1.836421	0.059271	5.509493
Н	-0.968261	0.178692	4.900955
С	-1.738925	0.122854	-6.90039
Н	-0.785624	-0.07603	7.383034
С	-2.859773	0.444324	7.669784
С	-4.079835	0.703895	-7.0423
Н	-4.956326	0.952624	-7.63496
С	-4.179503	0.641392	5.650506
Н	-5.130171	0.839347	5.162392
Ν	-3.032403	1.503033	1.456662
Ν	-3.16269	1.334295	1.458088
С	-3.078574	1.360846	2.826628
С	-3.293145	2.656418	3.425458
Н	-3.39688	2.841568	4.484478
С	-3.380322	3.562857	2.410933
Н	-3.568545	4.623443	2.489976
С	-3.216909	2.839267	1.172859
С	-3.297876	3.415461	0.112914
С	-3.280406	2.700941	1.328133
С	-3.385439	3.287836	2.643555
Н	-3.488355	4.343478	2.846789
С	-3.335652	2.268183	-3.54715
Н	-3.399394	2.335996	4.623371
С	-3.193236	1.040771	2.802481
С	-3.009761	0.146883	3.542113
С	-3.441755	4.905315	0.186742
С	-4.63954	5.493335	0.623561
Н	-5.472502	4.855121	0.905242
С	-4.770313	6.881518	0.687534
Н	-5.706776	7.318999	1.023383
С	-3.705247	7.704764	0.316196
С	-2.509304	7.131601	0.120967
Н	-1.673936	7.764607	0.408313
С	-2.379168	-5.74351	0.186516
Н	-1.445736	5.299588	0.521161
С	-3.021044	0.239529	5.038565
С	-4.138847	0.172944	5.781071
Н	-5.009001	0.561425	5.259131
С	-4.143886	0.078242	7.173647
Н	-5.019927	0.398031	7.731721
С	-3.031264	0.430912	7.846686
С	-1.914626	0.846957	7.118756
Н	-1.043477	1.242306	7.63439
С	-1.910236	0.753253	5.726124
Н	-1.0388	1.073282	5.16164
В	9.051902	0.117401	0.23738
Ν	8.113934	-1.35237	0.098527
Ν	8.135464	1.1362	0.124955

С	1.772955	0.040684	-0.65054
С	2.617066	0.041101	1.767823
Н	2.167187	0.027677	2.755025
С	4.000854	-0.05707	1.607515
Н	4.652274	0.056695	2.477412
С	4.565497	0.072573	0.323505
С	3.719105	0.072852	0.794299
Н	4.151867	0.084664	1.791076
С	2.33435	0.057002	0.632105
Н	1.675379	0.056022	1.493337
С	6.049789	0.087512	0.146362
С	6.746192	1.128864	0.049857
С	6.302733	2.493524	0.097389
С	7.445708	3.271326	0.051532
Н	7.487586	4.35313	0.062547
С	8.557048	2.413973	0.186464
С	8.513378	2.638217	0.1345
С	7.387289	3.473321	0.016577
С	7.410464	4.555695	0.026869
С	6.257897	2.672986	0.149311
С	6.72498	1.317538	0.075216
С	4.916622	3.042313	-0.27141
Н	4.949981	4.13647	0.265371
Н	4.460723	2.722921	1.214598
Н	4.239825	2.719862	0.527154
С	9.994347	2.779843	0.368954
Н	10.599698	2.381137	-0.45226
Н	10.111884	3.865921	0.408381
Н	10.388127	2.339962	1.291397
С	4.862356	3.194066	0.332942
Н	4.875705	4.288654	0.340744
Н	4.189741	2.869389	0.468185
Н	4.414301	2.854745	1.273034
С	9.943996	3.032394	0.31011
Н	10.340188	2.631739	1.249393
Н	10.044681	4.120881	0.311954
Н	10.559175	2.614196	0.493774
С	0.283561	0.019564	0.860288
0	-0.197684	0.004769	1.995157
0	-0.431915	-0.01649	0.239109
F	9.687685	0.136377	1.478681
F	9.995096	0.114388	0.789749
Н	-3.011843	8.909059	0.602256
Н	-3.806785	8.785494	0.366551
Н	-2.782677	0.492861	8.752757
Н	-3.035025	0.504173	8.930858



Figure 8.17: Room temperature emission spectra of isoabsorbing (A = 0.1) solution of (**TPP)In-OOC-Ph**(orange), (**TPP)In-O-Ph** (green), (**TPP)In-OOC-BDP** (blue) and (**TPP)In-O-Ph** (blue) when exciting at porphyrin chromophore (563 nm).



Figure 8.17: Cyclic voltammogram (black) and Square Wave (blue) of (**TPP)In-O-Ph** and (**TPP)In-OOC-Ph** in dry degassed CH₂Cl₂.



Figure 8.18: ¹H NMR spectrum of **1** (500 MHz, DMSO-*d*₆).



Figure 8.19: Zoom on the aromatic region of ¹H NMR spectrum of **1** (500 MHz, DMSO- d_6).



Figure 8.20: ¹H NMR spectrum of **2** (500 MHz, DMSO-*d*₆).



Figure 8.21: Zoom on the aromatic region of ¹H NMR spectrum of **2** (500 MHz, DMSO- d_6).



Figure 8.22: ¹³C NMR spectrum of **1** (500 MHz, DMSO- d_6).



Figure 8.23: Zoom on the aromatic region of 13 C NMR spectrum of **1** (500 MHz, DMSO- d_6).



Figure 8.24: ¹³C NMR spectrum of **2** (500 MHz, DMSO-*d*₆).



Figure 8.25: Zoom on the aromatic region of ¹³C NMR spectrum of 2 (500 MHz, DMSO-d⁶).



Figure 8.26: Maldi-TOF spectrum of 1.



Figure 8.27: Isotope pattern of the mass peak of MALDI-TOF spectrum for **1**, experimental (blue line), theoretical (red line).



Figure 8.28: Maldi-TOF spectrum of 2.



Figure 8.29: Isotope pattern of the mass peak of MALDI-TOF spectrum for **2**, experimental (blue line), theoretical (red line).



Figure 8.30: Gas phase geometry optimized structure of **1** (upper part) and **2** (lower part). Carbon, nitrogen, hydrogen, oxygen, fluoro, zinc and boron atoms correspond to grey, blue, white, red, light blue, green and yellow spheres, respectively.

<u>Table 8.5</u>: Coordinates of gas phase geometry optimized structure of **1** calculated by DFT at the B3LYP/LANL2DG/6-31G* level with energy E = -3826.71253198 Hartree/particle.

	X	y	Z
С	-3.841126000	-2.097396000	3.472486000
С	-2.807861000	-2.748323000	4.077336000
С	-3.374976000	-3.856581000	4.813437000
С	-4.740324000	-3.861077000	4.645004000
С	-5.055547000	-2.803754000	3.825251000
С	-9.753430000	-3.583857000	3.940933000
С	-8.877331000	-2.731593000	3.337926000
С	-7.550926000	-3.084788000	3.800088000
Ν	-7.643363000	-4.152577000	4.660733000
С	-8.975460000	-4.478571000	4.768933000
С	-6.355777000	-2.441165000	3.409863000
С	-8.310692000	-8.135029000	7.737383000
С	-9.345118000	-7.472927000	7.147041000
С	-8.770482000	-6.429464000	6.326959000
Ν	-7.399365000	-6.475110000	6.430513000
С	-7.086747000	-7.510454000	7.278782000
С	-9.516374000	-5.519389000	5.550919000
С	-2.379802000	-6.811547000	7.057268000

С	-3.253465000	-7.682007000	7.636854000
С	-4.588344000	-7.253282000	7.272483000
Ν	-4.501052000	-6.142712000	6.467279000
С	-3.165671000	-5.846150000	6.321033000
С	-2.627703000	-4.777704000	5.575221000
С	-5.783886000	-7.893091000	7.667864000
С	-11.014638000	-5.670131000	5.558429000
С	-5.660354000	-9.076383000	8.576655000
С	-1.131970000	-4.604926000	5.596560000
С	-6.475782000	-1.279228000	2.473616000
С	-11.645430000	-6.527904000	4.631121000
С	-13.038137000	-6.653406000	4.658674000
C	-13.826542000	-5.953178000	5,577359000
C	-13.181449000	-5.113316000	6.488468000
C	-11.790331000	-4.956266000	6,495686000
Ċ	-6.031061000	-10.360365000	8.139596000
Č	-5.917551000	-11.460821000	8.982788000
Č	-5.430080000	-11.303351000	10.287174000
Č	-5.057282000	-10.028471000	10.735080000
Ċ	-5 172305000	-8 930267000	9 886474000
C	-0 334008000	-5 209637000	4 601728000
C	1 053315000	-5.032878000	4 641619000
C	1 674817000	-4 275600000	5 639011000
C	0.865370000	-3 681970000	6 611245000
C	-0 525878000	-3 833470000	6 610752000
C	-5 962932000	-1 349520000	1 167462000
C	-6 077436000	-0 280414000	0 283549000
C	-6 704342000	0.896255000	0.705428000
C	-7 209690000	0.997333000	2 004545000
C	-7 100205000	-0.087388000	2 872718000
Zn	-6 070797000	-5 158913000	5 549848000
C	-15 332002000	-6 086877000	5 568181000
C	-11 145402000	-4 032479000	7 505421000
c	-10 841185000	-7 310511000	3 616228000
C	-0.952720000	-6.039817000	3 4986220000
C	-1 352971000	-3 166158000	7 687831000
C	-6 822296000	1 987676000	-0 198441000
N	-5 949384000	2 125759000	-1 231666000
N	-6 286266000	3 196994000	-1 889864000
C	-7 376173000	3 765440000	-1 296457000
C	-7 733718000	3.002307000	-0.210712000
C	-11 571508000	11 374900000	-1 333319000
C	-10 344076000	11.748122000	-0.688030000
C	-10.414181000	13 123901000	-0.500050000
C	-11 644860000	13 584022000	-1.013821000
N	-12 332183000	12 537151000	-1 509/156000
C	-12.332103000	10.796560000	-3 179/87000
C	15 238085000	Q 103021000	3 305867000
C	-12 030/37000	8 80813000	-2.22007000
C	-14.032437000	10 025460000	-2.200232000 -2 38160000
U N	-13.322033000 -14.114227000	11 1636///000	-2.381090000 -2 57/072000
C	-14.114227000	10 131000000	-2.374072000
C	11 2251/2000	8 00/115000	1 565052000
C	11 358580000	8 120574000	-1.303733000
C	-11.336369000	0.1373/4000	-0.374327000 0.200365000
U	-10.363613000	1.001213000	-0.200303000

C C C C B	-9.531947000 10.316415000 -9.184108000 12.173383000 13.643396000 16.333589000	7.348475000 8.491753000 10.892151000 14.981402000 7.451157000	-2.353795000 -2.534819000 -0.270161000 -1.041472000 -2.955402000
C - C - C - C - B -	10.316415000 -9.184108000 12.173383000 13.643396000 16.333589000	8.491753000 10.892151000 14.981402000 7.451157000	-2.534819000 -0.270161000 -1.041472000 -2.955402000
C - C - C - B -	-9.184108000 12.173383000 13.643396000 16.333589000	10.892151000 14.981402000 7.451157000	-0.270161000 -1.041472000 -2.955402000
C - C - C - B -	12.173383000 13.643396000 16.333589000	14.981402000 7.451157000	-1.041472000
C - C - B -	13.643396000 16.333589000	7.451157000	-2.955402000
C - B -	16.333589000		
B -		11.773796000	-3.533500000
-	13.744761000	12.618717000	-2.159913000
F -	13.707255000	13.440937000	-3.284614000
F -	14.669032000	13.102339000	-1.234462000
С	3.178121000	-4.124602000	5.677867000
C ·	-8.003627000	5.006085000	-1.847232000
0	-8.952675000	5.469778000	-0.892995000
C ·	-5.330245000	-12.510521000	11.147045000
0	-5.642923000	-13.635241000	10.808423000
0	-4.843588000	-12.242956000	12.386832000
H	-3.786710000	-1.213655000	2.853463000
H	-1.756464000	-2.500310000	4.039163000
н -	10.828170000	-3.616548000	3.830046000
Н	-9.107302000	-1.942708000	2.636625000
Н	-8.371149000	-8.963883000	8.427574000
н -	10.403195000	-7.663129000	7.259633000
H	-1.300288000	-6.822934000	7.110281000
Н	-3.015858000	-8.541386000	8.246722000
н -	13.518585000	-7.318434000	3.943246000
н -	13.774749000	-4.564174000	7.217095000
Н	-6.402028000	-10.489163000	7.127134000
Н	-6.197023000	-12.454141000	8.647187000
Н	-4.685136000	-9.901041000	11.745651000
Н	-4.890742000	-7.942822000	10.240116000
Н	1.663133000	-5.499726000	3.870277000
Н	1.326867000	-3.081506000	7.392910000
Н	-5 481467000	-2.264402000	0.835436000
Н	-5.691575000	-0.344859000	-0.726859000
Н	-7 662421000	1 921730000	2 348958000
Н	-7 488153000	-0.002164000	3 883272000
н -	15 642157000	-7 121347000	5 382036000
н -	15.782297000	-5.468850000	4.779763000
н -	15 768215000	-5 769263000	6 520977000
н -	11 897467000	-3 594042000	8 168693000
н -	10.609021000	-3.211495000	7.014674000
н -	10.413385000	-4.561662000	8.126679000
н -	10.141988000	-8.001215000	4.102332000
н -	10 241766000	-6 648395000	2,980406000
н -	11 498404000	-7 897518000	2.967278000
Н	-1.648652000	-5.448903000	2.891443000
Н	-1 523238000	-6 884846000	3 902004000
	-0.181467000	-6.440222000	2.833488000
Н		0.504155000	9.260762000
H H	-0.716126000	-2.594177000	8.309/0/000
H H H	-0.716126000	-2.59417/000 -3.901035000	8.282186000
H H H H	-0.716126000 -1.908865000 -2.093264000	-2.594177000 -3.901035000 -2.479501000	8.282186000 7.260580000
H H H H	-0.716126000 -1.908865000 -2.093264000 -8.537709000	-2.594177000 -3.901035000 -2.479501000 3.089772000	8.369762000 8.282186000 7.260580000 0.500254000
H H H H H	-0.716126000 -1.908865000 -2.093264000 -8.537709000 -9.658335000	-2.594177000 -3.901035000 -2.479501000 3.089772000 13.747461000	8.369762000 8.282186000 7.260580000 0.500254000 -0.040513000
H H H H H H	-0.716126000 -1.908865000 -2.093264000 -8.537709000 -9.658335000 16.030554000	-2.594177000 -3.901035000 -2.479501000 3.089772000 13.747461000 8.833121000	8.369762000 8.282186000 7.260580000 0.500254000 -0.040513000 -3.865786000

Η	-10.676480000	6.407901000	0.704142000
Η	-8.828271000	7.061151000	-3.126372000
Η	-10.206044000	9.070491000	-3.447835000
Η	-9.478645000	10.113814000	0.441990000
Η	-8.419917000	11.514221000	0.206635000
Η	-8.720102000	10.379409000	-1.119652000
Η	-11.462814000	15.669481000	-0.576211000
Η	-13.131312000	15.039796000	-0.513870000
Η	-12.362386000	15.300971000	-2.071980000
Η	-14.440041000	6.866498000	-3.426413000
Η	-13.464768000	7.036479000	-1.957463000
Η	-12.723889000	7.292672000	-3.529255000
Η	-17.183738000	11.260919000	-3.990721000
Η	-15.952106000	12.528999000	-4.229281000
Η	-16.672330000	12.311155000	-2.641436000
Η	3.606394000	-4.110391000	4.669635000
Η	3.648195000	-4.957945000	6.217453000
Η	3.475291000	-3.200695000	6.185373000
Η	-8.500583000	4.796318000	-2.805857000
Η	-7.232510000	5.766578000	-2.033175000
Η	-4.825936000	-13.100433000	12.851118000

Table 8.6: Coordinates of gas phase geometry optimized structure of **2** calculated by DFT at the B3LYP/LANL2DG/6-31G* level with energy E = -3712.19862069 Hartree/particle.

	Х	У	Z
С	-1.695180000	0.219894000	-0.794216000
С	-0.743634000	-0.720705000	-1.053218000
С	0.543251000	-0.088653000	-0.862396000
7	0.353634000	1.221478000	-0.488349000
С	-1.002335000	1.439052000	-0.430994000
С	-0.628057000	6.020225000	0.821065000
С	-1.610458000	5.101270000	0.601828000
С	-0.961259000	3.866300000	0.213118000
7	0.400458000	4.052907000	0.216182000
С	0.635209000	5.358307000	0.581265000
С	-1.627605000	2.659967000	-0.095639000
С	5.376488000	5.045694000	0.365087000
С	4.425284000	5.985556000	0.627300000
С	3.139444000	5.332069000	0.519229000
7	3.329605000	4.007879000	0.198586000
С	4.684970000	3.800181000	0.102844000
С	1.898110000	5.971175000	0.712559000
С	4.312736000	-0.808448000	-1.042734000
С	5.295259000	0.107757000	-0.814475000
С	4.644110000	1.369902000	-0.529276000
7	3.281605000	1.195463000	-0.577359000
С	3.047929000	-0.123493000	-0.890554000
С	1.785131000	-0.731706000	-1.040265000
С	5.310566000	2.577257000	-0.225062000
С	1.922416000	7.429036000	1.088732000
С	6.807557000	2.559293000	-0.253442000
С	1.760797000	-2.188942000	-1.418656000
С	-3.124412000	2.676217000	-0.062182000

С	1.976432000	7.808312000	2.447147000
С	1.998758000	9.168814000	2.772932000
С	1.967566000	10.165467000	1.793140000
С	1.918791000	9.767440000	0.454228000
С	1.893783000	8.418421000	0.082992000
С	7.552501000	2.736222000	0.925758000
C	8.943234000	2.718386000	0.899349000
C	9 624078000	2 524538000	-0 310112000
C	8 892701000	2 348115000	-1 492805000
C	7 500481000	2 365136000	-1 460415000
C	1 728077000	-3 179049000	-0.414055000
C	1 703225000	-4 527564000	-0 788002000
C	1 711579000	-4 923888000	-2 127983000
C	1 739604000	-3 926140000	-3 107078000
C	1.766273000	-2 566578000	-2 778831000
C	-3 83/578000	1 942676000	0.90287/000
C	-5 22563/000	1.942070000	0.902874000
C	5 935860000	2 712210000	0.049809000
C	5 253501000	2.712210000	0.003790000
C	-3.233301000	2 422526000	-0.971702000
C 7n	-3.800232000	3.422320000 2.610010000	-0.993304000
	1.641050000	2.019010000	-0.101/94000
C	1.901570000	11.028/01000	2.1/1589000
C	1.843208000	8.043720000	-1.381920000
C	2.012851000	6.//1905000	3.548628000
C	1.717524000	-2.806446000	1.052207000
C	1.794134000	-1.529043000	-3.8/9538000
N	-7.356582000	2.731798000	0.059/04000
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C	-8.223613000	3.6/29/0000	-0.4030/0000
С	-15.253820000	6.355504000	-0.013943000
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С	-16.770644000	7.773152000	0.808704000
Ν	-16.524467000	6.913399000	-0.198356000
С	-17.288922000	5.013299000	-3.391666000
С	-16.349213000	4.112201000	-3.934033000
С	-15.226408000	4.097832000	-3.114418000
С	-15.504721000	5.019062000	-2.048539000
Ν	-16.780867000	5.552156000	-2.266648000
С	-14.750465000	5.419215000	-0.932774000
С	-13.388230000	4.842633000	-0.720135000
С	-12.256644000	5.472351000	-1.256127000
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С	-13.214597000	3.664738000	0.019913000
С	-13.371075000	6.659469000	1.837323000
С	-18.046375000	8.543555000	0.915872000
С	-14.005281000	3.260347000	-3.359608000

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В	-17.502140000	6.600933000	-1.369709000
F	-18.690310000	6.068882000	-0.871681000
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С	11.109306000	2.514546000	-0.282926000
0	11.789124000	2.665332000	0.713293000
0	11.663214000	2.315759000	-1.507282000
Η	-2.767384000	0.101335000	-0.853304000
Н	-0.892858000	-1.747848000	-1.355093000
Н	-0.741082000	7.050435000	1.128178000
Η	-2.676421000	5.243470000	0.704945000
Η	6.447610000	5.184505000	0.342826000
Η	4.573788000	7.029761000	0.864004000
Η	4.426911000	-1.856151000	-1.282810000
Η	6.362748000	-0.057606000	-0.827887000
Η	2.043211000	9.455894000	3.821893000
Η	1.901075000	10.526184000	-0.325893000
Η	7.030074000	2.879364000	1.867043000
Η	9.521704000	2.848252000	1.808165000
Η	9.415248000	2.203582000	-2.431963000
Η	6.937235000	2.235225000	-2.379824000
Η	1.675255000	-5.286971000	-0.008940000
Η	1.739307000	-4.211806000	-4.157420000
Η	-3.285222000	1.363156000	1.638672000
Η	-5.767759000	1.403040000	1.704751000
Η	-5.800028000	3.990423000	-1.729448000
Η	-3.334109000	3.982908000	-1.762391000
Η	2.513735000	11.805029000	3.101060000
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Η	2.410960000	12.247565000	1.387553000
Η	1.819537000	8.937741000	-2.012747000
Η	0.955889000	7.442759000	-1.613044000
Η	2.714760000	7.446502000	-1.675461000
Η	2.890795000	6.120932000	3.460803000
Η	1.131529000	6.120349000	3.517717000
Η	2.044739000	7.249782000	4.532663000
Η	0.843536000	-2.195132000	1.306216000
Η	2.603400000	-2.220802000	1.325135000
Η	1.697738000	-3.701249000	1.681974000
Η	1.782489000	-2.005652000	-4.864668000
Η	2.691067000	-0.901245000	-3.818854000
Η	0.931425000	-0.854896000	-3.820079000
Η	-7.890968000	4.586234000	-0.868386000
Η	-15.579150000	8.394546000	2.573707000
Н	-16.490016000	3.533516000	-4.838140000
Н	-12.375308000	6.384438000	-1.834577000
Н	-10.126487000	5.444232000	-1.488565000
Н	-11.816274000	2.219530000	0.797233000
Н	-14.083047000	3.165466000	0.440935000
Н	-13.243770000	5.608119000	2.116964000

Η	-13.283993000	7.263183000	2.746200000
Η	-12.531043000	6.913003000	1.181611000
Н	-18.902269000	7.862475000	0.971490000
Η	-18.196454000	9.163620000	0.025630000
Η	-18.035799000	9.182463000	1.802710000
Η	-14.134863000	2.679697000	-4.278407000
Η	-13.812823000	2.557994000	-2.541435000
Η	-13.100993000	3.868677000	-3.469211000
Η	-19.416112000	5.119027000	-3.178771000
Η	-18.847638000	4.833580000	-4.845398000
Η	-18.715074000	6.446020000	-4.092229000
Н	1.271417000	-7.006638000	-1.722851000
Η	2.737365000	-6.752350000	-2.674566000
Н	1.155958000	-6.561337000	-3.434803000
Н	12.627718000	2.330192000	-1.363331000



Figure 8.31: Corresponding time absorption profiles at 485 nm (black) and 1100 nm (red) for dyad **1** (left part) and for dyad **2** (right part).



Figure 8.32: Left part: Femtosecond transient absorption spectra of **BODIPY-Triple** in argon saturated THF; 1 ps (black), 10 ps (red), 100 ps (green), 1000 ps (blue), and 7500 ps (cyan) after excitation at 505 nm. Right part: Corresponding time absorption profiles at 485 nm (black) and 1100 nm (red).



Figure 8.33: ¹H NMR spectrum of 3 (500 MHz, CDCl₃).



Figure 8.34: Zoom on the aromatic region of ¹H NMR spectrum of 3 (500 MHz, CDCl₃).



Figure 8.35: ¹H NMR spectrum of Compound 1 (500 MHz, THF-*d*₈).



Figure 8.36: Zoom on the aromatic region of ¹H NMR spectrum of **Compound 1** (500 MHz, THF- d_8).



Figure 8.37: ¹³C NMR spectrum of Compound 1 (125 MHz, THF-*d*₈).



Figure 8.38: Zoom on the ¹³C NMR spectrum of Compound 1 (125 MHz, THF-*d*₈).



Figure 8.39: Zoom on the ¹³C NMR spectrum of Compound 1 (125 MHz, THF-*d*₈).



Figure 8.40: Zoom on the ¹³C NMR spectrum of Compound 1 (125 MHz, THF-*d*₈).







Figure 8.42: Zoom on the aromatic region of ¹H NMR spectrum of 7 (500 MHz, CDCl₃).



Figure 8.43: ¹H NMR spectrum of Compound 2 (300 MHz, THF-*d*₈).



Figure 8.44: Zoom on the ¹H NMR spectrum of Compound 2 (300 MHz, THF-*d*₈).



Figure 8.45: ¹³C NMR spectrum of Compound 2 (75 MHz, THF-*d*₈).



Figure 8.46: Zoom on the ¹³C NMR spectrum of Compound 2 (75 MHz, THF-*d*₈).



Figure 8.47: Zoom on the ¹³C NMR spectrum of **Compound 2** (75 MHz, THF- d_8).



Figure 8.48: ¹H NMR spectrum of 10 (500 MHz, CDCl₃).


Figure 8.50: ¹H NMR spectrum of 11 (500 MHz, CDCl₃).



Figure 8.51: Zoom on the aromatic region of ¹H NMR spectrum of 11 (500 MHz, CDCl₃).



Figure 8.52: ¹H NMR spectrum of 14 (500 MHz, CDCl₃).



Figure 8.53: Zoom on the aromatic region of ¹H NMR spectrum of 14 (500 MHz, CDCl₃).



Figure 8.54: ¹H NMR spectrum of Compound 3 (500 MHz, THF-*d*₈).







Figure 8.56: ¹³C NMR spectrum of Compound 3 (125 MHz, THF-*d*₈).



Figure 8.57: Zoom on the ¹³C NMR spectrum of Compound 3 (125 MHz, THF-*d*₈).



Figure 8.58: Zoom on the ¹³C NMR spectrum of Compound 3 (125 MHz, THF-*d*₈).



Figure 8.59: ¹H NMR spectrum of **reference** compound (500 MHz, DMSO-*d*₆).



Figure 8.60: Zoom on the ¹H NMR spectrum of reference compound (500 MHz, DMSO-*d*₆).



Figure 8.60: Gas phase geometry optimized structure of **Compound 1** (upper left part), **Compound 2** (lower part) and **Compound 3** (upper right). Carbon, nitrogen, hydrogen, oxygen and zinc correspond to grey, blue, white, red and green, respectively.

<u>**Table 8.7:**</u> Coordinates of gas phase geometry optimized structure of **Compound 1** calculated by DFT at the B3LYP/LANL2DG/6-31G* level with energy E = -5332.9185836 Hartree/particle.

X	У	Z
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1.127243000	-1.401949000	-2.015134000
2.399663000	-0.715337000	-2.040760000
2.271605000	0.500468000	-1.409807000
0.968895000	0.605825000	-0.983776000
1.516305000	4.939560000	0.917872000
0.541179000	3.994818000	0.800487000
1.100052000	2.895138000	0.041231000
2.406015000	3.184801000	-0.275278000
2.688592000	4.426928000	0.244531000
0.412716000	1.707227000	-0.295578000
7.234421000	4.486519000	-1.152068000
6.355163000	5.298291000	-0.500031000
5.088134000	4.602652000	-0.452874000
5.216032000	3.384867000	-1.080287000
6.513808000	3.285488000	-1.521227000
3.922559000	5.103711000	0.160759000
5.987863000	-1.075011000	-3.365918000
6.961972000	-0.129123000	-3.251416000
6.392967000	0.982491000	-2.517115000
	x 0.244219000 1.127243000 2.399663000 2.271605000 0.968895000 1.516305000 0.541179000 1.100052000 2.406015000 2.406015000 2.688592000 0.412716000 6.355163000 6.355163000 5.088134000 5.216032000 6.513808000 3.922559000 5.987863000 6.961972000 6.392967000	xy0.244219000-0.5868400001.127243000-1.4019490002.399663000-0.7153370002.2716050000.5004680000.9688950000.6058250001.5163050004.9395600000.5411790003.9948180001.1000520002.8951380002.4060150003.1848010002.6885920004.4269280000.4127160001.7072270007.2344210004.4865190006.3551630005.2982910005.0881340003.2854880003.9225590005.1037110006.961972000-0.1291230006.3929670000.982491000

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С	7.071919000	2.178834000	-2.198423000
С	4.004035000	6.470948000	0.786850000
С	8.506396000	2.283807000	-2.614039000
С	3.491171000	-2.594962000	-3.257264000
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Č	4.386860000	6.610858000	2.136514000
C	4,454094000	7.893472000	2.695391000
Č	4.153265000	9.039462000	1.956494000
С	3.777867000	8.877624000	0.618274000
C	3.696679000	7.616882000	0.020155000
Č	9.489176000	1.459610000	-2.038285000
Ċ	10.821167000	1.555141000	-2.427806000
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Η	6.053166000	-2.036531000	-3.855265000
Η	7.969959000	-0.176187000	-3.637310000
Η	4.750936000	7.995779000	3.737280000
Η	3.541142000	9.756857000	0.021556000
Η	9.199249000	0.743029000	-1.275450000
Η	11.579172000	0.914896000	-1.988762000
Η	10.496043000	4.003161000	-4.778948000
Η	8.153840000	3.831066000	-4.071258000
Η	3.935911000	-5.877406000	-2.473231000
Н	2.774367000	-4.130581000	-6.210880000
Н	-0.720767000	-0.044555000	1.462644000
Η	-3.103984000	-0.200383000	2.146397000
Н	-4.060830000	3.053427000	-0.493339000
Н	-1.685394000	3.226438000	-1.147064000
Η	4.647151000	10.378112000	3.586416000
Η	3.222046000	10.866083000	2.658912000
Η	4.832580000	11.098024000	1.978818000
Η	3.091095000	8.486440000	-1.862203000
Η	2.373760000	6.897953000	-1.542767000
Н	4.060171000	7.012902000	-2.032909000
Н	5.562058000	4.836676000	2.562113000
Η	3.877309000	4.712679000	3.056877000
Η	5.000619000	5.706415000	3.999941000
Н	3.403477000	-3.121267000	-0.435162000
Η	5.095869000	-3.016894000	-0.908075000
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Н	2.537196000	-1.841838000	-6.488045000
Η	3.654058000	-0.849643000	-5.535563000
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Η	-5.793596000	3.350319000	1.166739000
Η	-9.314000000	0.281844000	2.599607000

Η	-11.562126000	1.154102000	3.167365000
Η	-10.211096000	5.153255000	2.398320000
Η	-7.976107000	4.290222000	1.812990000
Η	-14.892181000	4.779628000	3.029159000
Η	-14.260178000	6.440925000	2.921636000
Η	-13.140297000	2.923127000	3.106009000
Η	-13.365393000	5.679907000	0.641443000
Η	-13.868391000	3.990201000	0.911868000
Η	-12.154187000	4.383996000	0.615976000
Η	12.420778000	4.359262000	-4.342279000

<u>**Table 8.8:**</u> Coordinates of gas phase geometry optimized structure of **Compound 2** calculated by DFT at the B3LYP/LANL2DG/6-31G* level with energy E = -5804.9985093 Hartree/particle.

	Х	У	Z
С	-3.912320000	4.993706000	-1.561323000
С	-3.506678000	3.699098000	-1.689087000
С	-2.065376000	3.690175000	-1.566502000
Ν	-1.619955000	4.975547000	-1.361881000
С	-2.724081000	5.794095000	-1.346836000
С	-0.248041000	9.805235000	-0.661168000
С	-1.550058000	9.418329000	-0.772643000
С	-1.552517000	7.989133000	-1.007218000
Ν	-0.256145000	7.532526000	-1.020801000
С	0.563553000	8.618187000	-0.815491000
С	-2.709088000	7.195307000	-1.172242000
С	4.628980000	6.155490000	-0.985753000
С	4.222948000	7.448733000	-0.844226000
С	2.776813000	7.446238000	-0.869325000
Ν	2.328640000	6.154410000	-1.020922000
С	3.435125000	5.341955000	-1.088847000
С	1.972015000	8.598232000	-0.758307000
С	0.951737000	1.312949000	-1.627135000
С	2.253892000	1.699116000	-1.515509000
С	2.262441000	3.142997000	-1.400080000
Ν	0.968579000	3.605621000	-1.431337000
С	0.145431000	2.512412000	-1.572400000
С	-1.261872000	2.534980000	-1.651230000
С	3.419164000	3.939829000	-1.255476000
С	2.674682000	9.915791000	-0.562949000
С	4.741820000	3.238028000	-1.283942000
С	-1.963929000	1.216731000	-1.843507000
С	-4.030195000	7.899715000	-1.162920000
С	2.980165000	10.368265000	0.740090000
С	3.635024000	11.593001000	0.898226000
С	3.998472000	12.385660000	-0.196212000
С	3.686495000	11.919409000	-1.474852000
С	3.030447000	10.698938000	-1.679773000
С	5.551027000	3.167903000	-0.137752000
С	6.785062000	2.523723000	-0.158982000
С	7.225823000	1.923357000	-1.342384000
С	6.433294000	1.966141000	-2.492715000
С	5.206688000	2.626437000	-2.458428000
С	-2.393134000	0.474516000	-0.722188000

С	-3.046652000	-0.745790000	-0.923882000
С	-3.286755000	-1.254265000	-2.203951000
С	-2.857703000	-0.500598000	-3.299862000
С	-2.198919000	0.724347000	-3.144631000
С	-4.957699000	7.690378000	-0.128810000
С	-6.183537000	8.349732000	-0.108193000
С	-6.508290000	9.231035000	-1.144713000
С	-5.609092000	9.443935000	-2.193687000
С	-4.379831000	8.787968000	-2.191746000
С	4.705546000	13.705960000	0.007464000
С	2.718872000	10.242048000	-3.087975000
С	2.609578000	9.551468000	1.958440000
С	-2.160563000	0.978502000	0.685180000
С	-1.756641000	1.498747000	-4.366822000
С	-3.967412000	-2.590113000	-2.394539000
Ν	-7.758215000	9.906091000	-1.122278000
Zn	0.354788000	5.566424000	-1.207111000
Ν	-8.813328000	9.388286000	-0.432911000
Ν	-9.813006000	10.200856000	-0.580028000
С	-9.440544000	11.264054000	-1.365679000
C	-8.116594000	11.077543000	-1.715832000
Ċ	-10.369479000	12.348963000	-1.699061000
Č	-9.990725000	13.409219000	-2.539063000
Ċ	-10.882512000	14.432054000	-2.846098000
Č	-12.181059000	14.432697000	-2.316429000
Č	-12.555754000	13.379324000	-1.473106000
Ċ	-11 669805000	12.348601000	-1 170116000
C	-13 617684000	17 691667000	-3 366659000
C	-13 172388000	15 523944000	-2 659401000
N	-12 567557000	16 848044000	-2 814203000
C	-11 999115000	17 394086000	-1 588344000
N	8 486741000	1 265664000	-1 363739000
N	9.015760000	0 744425000	-0 220422000
N	10 156091000	0.209985000	-0 525668000
C	10 400618000	0.365901000	-1 867556000
C	9 326328000	1 046948000	-2 410374000
C	11 625039000	-0 138986000	-2 494573000
C	12 583318000	-0.815187000	-1 717666000
C	13 747501000	-1 301612000	-2.297484000
C	14 001849000	-1 110739000	-3 663548000
C	13.042552000	-0 447581000	-4 443284000
C	11 869562000	0.029484000	-3 867214000
C	-17 611231000	17 597952000	-6.062399000
C	-16 225386000	17.947934000	-5 817077000
C	-15 395757000	18 253694000	-6.882461000
C	-17 242624000	17 873986000	-8.482885000
C	-18 114118000	17.578953000	-7 367445000
C	-15,732244000	17.1/3159000	-1.507445000
C	-13.732244000 -14.019128000	17.145155000	-6 895182000
C	-14.019120000	16 983085000	-0.099102000
C	-18 085382000	16/73006000	-7.304207000 _7.771518000
C	-17 0/70/1000	16 55/720000	-7.771310000
C	-17.747041000 16 572740000	16.778016000	-5.125707000
C	15 18/250000	16 822688000	10.400924000
C	-13.104239000	16 848224000	-10.100239000
U	-14.200209000	10.040224000	-4.4741/1000

С	-13.706402000	17.377816000	-8.262131000
С	-13.543721000	16.961909000	-5.843587000
С	-18.660492000	16.116849000	-9.142501000
С	-19.317929000	15.471858000	-6.852822000
С	-18.781431000	15.519060000	-5.509499000
С	-16.748578000	16.291651000	-4.303207000
С	-19.355966000	14.080036000	-7.271601000
С	-18.495508000	14.137765000	-5.089118000
С	-16.466844000	14.935206000	-3.890763000
С	-18.690549000	14.780875000	-9.541049000
С	-12.771657000	15.787630000	-6.123604000
С	-18.860270000	13.258591000	-6.178897000
С	-17.388479000	13.859519000	-4.304448000
С	-15.172329000	14.443398000	-3.875399000
С	-15.213821000	13.051251000	-4.325757000
С	-12.453205000	14.076751000	-7.876992000
С	-16.595436000	12.683416000	-4.567501000
C	-16.931340000	11.830286000	-5.624367000
Ċ	-15.887805000	11.307967000	-6.485087000
Č	-18 087081000	12.123249000	-6 447286000
C	-17 644876000	14 252727000	-10 403474000
C	-12 824654000	13.092663000	-6 957564000
C	-19 052018000	13 741401000	-8 590055000
C	-18 234663000	12 571127000	-8 868691000
C	-13 138965000	13 445824000	-5 594004000
C	-12 961170000	14 027295000	-9 236287000
c	-13 809773000	12 989664000	-9 625871000
C	-14 218647000	12 548974000	-5 146300000
C	-14 557494000	11 669788000	-6 250648000
C	-17 765550000	11.777437000	-7 822397000
C	-16 399541000	11 274225000	-7 846676000
C	-13 691577000	11.274223000	-7 367933000
C	-17 363855000	12 891570000	-9.989188000
C	-14 971830000	13 272277000	-10 446792000
C	-14.176820000	11.950666000	-8 67/15/2000
C	16 053338000	12 /00270000	10 012623000
C	15 563078000	11.58/510000	-10.012023000 8 017563000
C	-12/30508000	15 / 5/139000	-7.452804000
C	12.450508000	16 268/156000	8 544082000
C	13 2/318/000	15 302830000	0.651874000
C	13 04604000	15.392830000	4 021374000
C	13.000012000	14.763305000	5 171801000
C	15 006308000	18 208655000	-5.171891000 8 240454000
C	-13.900398000	17 67362000	-8.240434000
C	-14.001/30000	17.073020000	-9.094434000
C	-14.302333000	15.003074000	-10.440338000
C	-10.003344000 15 242254000	13.064206000	-10.827209000
C	-13.245254000	14.38/408000	-10.847340000
C	15.275720000	-1.004380000	-4.223203000
0	13.918143000	-2.334043000	-3.0832/8000
U II	13.70/114000	-1.13/041000	-3.403838000
п	-4.922438000	J.J/2904000	-1.010230000
Н II	-4.121340000	2.820313000	-1.800149000
н U	0.133896000	10.800044000	-0.4/9//9000
Н II	-2.4288/9000	10.041282000	-0.091/28000
н	3.0439/0000	3.787309000	-1.024364000

Η	4.841161000	8.329415000	-0.741194000
Η	0.564787000	0.308564000	-1.726307000
Н	3.127279000	1.063362000	-1.499848000
Н	3.867843000	11.936519000	1.904641000
Η	3.960053000	12.519092000	-2.340750000
Η	5.206737000	3.627102000	0.783999000
Η	7.405725000	2.472063000	0.727731000
Η	6.758240000	1.475270000	-3.404717000
Η	4.595630000	2.663679000	-3.355154000
Η	-3.377772000	-1.312629000	-0.055731000
Η	-3.040716000	-0.873458000	-4.305855000
Η	-4.705576000	7.011855000	0.680630000
Η	-6.889857000	8.194134000	0.698536000
Η	-5.872120000	10.094986000	-3.021304000
Η	-3.687241000	8.952121000	-3.011782000
Η	5.644723000	13.576090000	0.559495000
Η	4.088831000	14.405414000	0.585963000
Η	4.943429000	14.183955000	-0.948130000
Η	3.183999000	9.274148000	-3.309213000
Η	1.640393000	10.117118000	-3.241568000
Η	3.082316000	10.967120000	-3.822765000
Η	2.915857000	10.060992000	2.877247000
Η	3.088526000	8.565335000	1.943440000
Η	1.528478000	9.377150000	2.012918000
Η	-2.536043000	0.262585000	1.422796000
Η	-1.094574000	1.140926000	0.883649000
Η	-2.664510000	1.936867000	0.858465000
Η	-2.047457000	0.978120000	-5.284462000
Η	-0.668535000	1.633563000	-4.385885000
Η	-2.200240000	2.501029000	-4.391516000
Η	-4.713441000	-2.775527000	-1.614010000
Η	-3.243462000	-3.415148000	-2.352520000
Η	-4.470725000	-2.648911000	-3.365421000
Η	-7.422105000	11.673057000	-2.285009000
Η	-8.990202000	13.436207000	-2.963252000
Η	-10.576108000	15.247318000	-3.493780000
Η	-13.556018000	13.365385000	-1.046246000
Η	-11.970484000	11.537041000	-0.516201000
Η	-14.389001000	17.937675000	-2.610632000
Η	-13.205441000	18.633021000	-3.745372000
Η	-13.949067000	15.541512000	-1.868512000
Η	-11.562027000	18.375995000	-1.798132000
Η	-11.207330000	16.737061000	-1.219607000
Η	-12.752894000	17.515462000	-0.786988000
Η	9.113947000	1.404538000	-3.404606000
Н	12.394340000	-0.953296000	-0.658699000
Н	14.482977000	-1.835520000	-1.704944000
Н	13.178045000	-0.332161000	-5.516610000
Н	11.137168000	0.529321000	-4.494994000
Η	15.186762000	-0.348932000	-5.626470000

<u>**Table 8.9:**</u> Coordinates of gas phase geometry optimized structure of **Compound 3** calculated by DFT at the B3LYP/LANL2DG/6-31G* level with energy E = -4860.8372509 Hartree/particle.

	X	У	Z
С	-0.799311000	-0.140756000	-0.326703000
С	0.250422000	-0.998944000	-0.187957000
С	1.457885000	-0.204259000	-0.227985000
Ν	1.123467000	1.120064000	-0.391354000
C	-0.247477000	1.191250000	-0.464050000
C	-0.382638000	5 928933000	-0.937590000
C	-1 255006000	4 882243000	-0.92/862000
C	-1.233000000	4.882243000	-0.924802000
C N	-0.477479000	3.060193000	-0.703244000
N	0.852017000	4.010432000	-0.002820000
C	0.941484000	5.382229000	-0./4111/000
C	-1.006056000	2.3/1984000	-0.62/654000
C	5.687738000	5.564998000	-0.489/43000
С	4.637175000	6.424311000	-0.611200000
С	3.430187000	5.627593000	-0.588361000
Ν	3.765437000	4.301117000	-0.444215000
С	5.136500000	4.229992000	-0.377994000
С	2.126448000	6.146102000	-0.720373000
С	5.278467000	-0.512804000	0.037624000
С	6.151714000	0.532688000	0.000882000
С	5.368253000	1.737027000	-0.182837000
Ν	4.036347000	1.403526000	-0.245195000
C	3.949149000	0.036751000	-0.113550000
Ĉ	2 762920000	-0 724385000	-0 108262000
C	5 895071000	3 045473000	-0.252664000
C	1 987188000	7 638671000	-0.252004000
C	7 38/281000	3 188782000	0.101272000
C	2.002508000	2 216251000	-0.191373000
C	2.902398000	-2.210231000	0.041854000
C	1.826479000	8.444463000	0.283168000
C	1.689983000	9.828441000	0.129252000
C	1./10/85000	10.438/11000	-1.128106000
С	1.867660000	9.621469000	-2.251286000
С	2.007958000	8.233381000	-2.143817000
С	8.004127000	3.816156000	0.903578000
С	9.387494000	3.951912000	0.957753000
С	10.186424000	3.463033000	-0.084757000
С	9.580489000	2.834748000	-1.181567000
С	8.195184000	2.700557000	-1.230035000
С	2.912842000	-2.801760000	1.326133000
С	3.048599000	-4.189548000	1.440310000
С	3.177515000	-5.015397000	0.319540000
С	3.158976000	-4.415346000	-0.942496000
С	3.025092000	-3.031579000	-1.103162000
Ċ	1.592541000	11.939038000	-1.267382000
C	2 173345000	7 396558000	-3 393283000
C	1 795114000	7.836399000	1 668125000
č	2 776385000	-1 955557000	2 572785000
C	2.1160000	-1.233337000	2.272703000
C	2 257102000	-2.433331000 6 509475000	-2.473020000
	3.33/180000 2.444097000	-0.3084/3000	0.4/0213000
	2.44408/000	2.710870000	-0.4187/2000
C	-2.490491000	2.225018000	-0./51/0/000
C	-3.363456000	2.776112000	0.198185000
C	-4.745279000	2.660231000	0.051537000
С	-5.312507000	1.988980000	-1.041247000
С	-4.437051000	1.424871000	-1.982491000

С	-3.055704000	1.542009000	-1.840364000
С	-8.859521000	0.862613000	-1.170315000
С	-6.823209000	1.926821000	-1.146599000
Ν	-7.456099000	0.635778000	-0.893604000
C	-6.888981000	-0.564984000	-1.505003000
Ċ	-8.656222000	5.280564000	-8.856744000
Ċ	-9.625859000	6.257892000	-8.385862000
Č	-9 265940000	7 174034000	-7 394901000
Č	-6.991526000	6.217994000	-7.293057000
Č	-7.367078000	5.262157000	-8.324714000
Ċ	-10.927044000	5.617750000	-8.345381000
Č	-10.192263000	7.483507000	-6.322792000
Č	-6.117727000	5.536644000	-6.350133000
C	-6.727193000	3.995231000	-8.011116000
Č	-9 362958000	4 033631000	-9 103829000
Č	-6 222898000	5 807300000	-4 982158000
C	-7 197250000	6 775699000	-4 511417000
C	-11 822442000	5 917344000	-7 316071000
c	-9 429046000	7 651109000	-5 100185000
c	-11 449189000	6 865648000	-6 283815000
C	-5 957069000	4 166412000	-6 794859000
C	-7 413449000	2 796540000	-8 235693000
C	-8 754820000	2.1790940000	-8 796867000
C	-10 768046000	4 241913000	-8 791329000
C	-7 358495000	1 738391000	-7 249336000
C	-9 528976000	1.756417000	-8 170558000
C	-11 512810000	3 223474000	-8 196674000
C	-5 9072/17000	3 1337/1000	-5 852246000
C	-11 98528/000	6 393502000	-5.022240000
C	-8 676629000	1 089415000	-7 209235000
C	-10.88/1153000	1.009415000	-7 8829/7000
C	-12 446502000	3 535/09000	-7.12/3/5000
C	12 301056000	2 450602000	6 155058000
C	-11 182659000	2.430092000 5.478474000	-2 876/13000
C	-11.102057000	1 474716000	-6 626519000
C	-10 595983000	0.823974000	-5 709475000
C	-10.684487000	1 119681000	-4 291660000
C	-9 196454000	0.637813000	-6.007006000
C	-6.013703000	3 418300000	-4 434552000
C	-11 842466000	4 273416000	-3 127217000
C	-6 628090000	1 906469000	-6.083852000
C	-7.157973000	1.451035000	-4 787451000
C	-12 622752000	4 106944000	-4 343178000
C	-9 846891000	5 445351000	-2 331882000
C	-9.228353000	4 206399000	-2.056366000
C	-12 473722000	2 732995000	-4 788576000
C	-11 611339000	2.732773000	-3 844349000
C	-8 448391000	0.811556000	-4 749616000
C	-0.440371000	1 072387000	-3 718099000
C	-11 200826000	3 013703000	-3.710099000
C	-6 7657/18000	2 336375000	-2.007013000
C	-7 837866000	2.330373000 4 012047000	-3.771343000
C	-7.03200000	-+.0120+/000 2 075021000	-2.5550+2000
C	-7.530024000	2.373301000	-2.200149000
C	-7.302093000 8 068097000	2.323021000	-2.472094000
C	-0.20002/000	1.002014000	-2.434103000

С	-11.252433000	6.558651000	-3.844504000
С	-9.947552000	7.200379000	-3.885232000
С	-9.086913000	6.509927000	-2.941584000
С	-12.595986000	4.852521000	-6.693515000
С	-12.689521000	5.145017000	-5.272260000
С	-7.920992000	7.151678000	-6.838437000
С	-8.024196000	7.440422000	-5.416938000
С	-7.744072000	6.289659000	-3.255071000
С	-6.157044000	4.729065000	-4.012753000
С	-7.114859000	5.028758000	-2.936056000
С	11.657792000	3.635474000	0.021825000
0	12.231553000	4.173077000	0.948849000
0	12.332804000	3.124377000	-1.040704000
Η	-1.851606000	-0.384678000	-0.324800000
Н	0.216659000	-2.071852000	-0.060494000
Н	-0.607385000	6.976514000	-1.080704000
Н	-2.325394000	4.919221000	-1.064469000
H	6.739650000	5.810914000	-0.486109000
Н	4.669979000	7.499465000	-0.717914000
Н	5 506266000	-1 561720000	0 165298000
Н	7 226774000	0 493821000	0 100154000
Н	1 562265000	10 444497000	1 017396000
Н	1 879649000	10 074222000	-3 240970000
Н	7 390333000	4 190568000	1 717525000
н	9 870025000	4 430398000	1 803725000
Н	10 193997000	2 459514000	-1 993245000
н	7 728555000	2 220496000	-2 085157000
н	3 053147000	-4 635423000	2 433234000
н	3 250753000	-5 039369000	-1 829503000
н	1 121010000	12 218109000	-2 215895000
н	1 000347000	12.372091000	-0.453981000
н	2 579548000	12.420531000	-1 241944000
н	2 165014000	8 026439000	-4 288239000
Н	1 369559000	6 657489000	-3 492711000
н	3 117081000	6 838535000	-3 381545000
н	2 720585000	7 291765000	1 889534000
н	0.972876000	7.118887000	1 774534000
Н	1 668472000	8 610625000	2 431246000
н	1.836125000	-1 391611000	2 575582000
н	2 798685000	-2 579317000	3 471793000
н	3 586395000	-1 220790000	2 651246000
Н	3 116954000	-3 216082000	-3 253569000
н	3 828531000	-1 717224000	-2 631453000
н	2 078567000	-1.894823000	-2.691152000
н	2.878367600	-6 892527000	1 340764000
Н	4 415121000	-6 770148000	0.607613000
н	3 0022/9000	-7.046419000	-0.415319000
н	-2 95/858000	3 200508000	1 057697000
Н	-5 396134000	3 0991 59000	0.803920000
Н	-4 829707000	0 907043000	-2 849954000
Н	-2 402203000	1 112285000	-2 594029000
Н	-2.+02203000	1 39555000	
Н	-9.310707000	-0 07950/000	-1 309867000
н	-7.394010000	2 500/01/01/00	-1.309007000
H	-7.213074000	-0 565821000	-0.304471000
11	-0.073302000	0.505021000	-2.003002000





Figure 8.62: ¹H NMR spectrum of 5 (500 MHz, CDCl₃).



Figure 8.63: ¹H NMR spectrum of 6 (500 MHz, CDCl₃).



Figure 8.64: ¹H NMR spectrum of Zn-3DoH-click-COOH (500 MHz, CDCl₃).



Figure 8.65: Zoom on the aromatic region of ¹H NMR spectrum of **Zn-3DoH-click-COOH** (500 MHz, CDCl₃).



Figure 8.66: ¹³C NMR spectrum of Zn-3DoH-click-COOH (75 MHz, CDCl₃).



Figure 8.67: ¹H NMR spectrum of 9 (500 MHz, CDCl₃).



Figure 8.68: ¹H NMR spectrum of Zn-3DoH-click-CNCOOH (500 MHz, CDCl₃).



Figure 8.69: Zoom on the aromatic region of ¹H NMR spectrum of **Zn-3DoH-click-CNCOOH** (500 MHz, CDCl₃).



Figure 8.70: ¹³C NMR spectrum of Zn-3DoH-click-CNCOOH (75 MHz, CDCl₃).



Figure 8.71: ¹H NMR spectrum of 12 (500 MHz, CDCl₃).



Figure 8.72: Zoom on the aromatic region of ¹H NMR spectrum of 12 (500 MHz, CDCl₃).



Figure 8.74: ¹H NMR spectrum of Zn-3DoH-COOH (500 MHz, CDCl₃).



Figure 8.75: ¹H NMR spectrum of 15 (500 MHz, CDCl₃).



Figure 8.76: ¹H NMR spectrum of 16 (500 MHz, CDCl₃).



Figure 8.77: ¹H NMR spectrum of Zn-3DoH-CNCOOH (500 MHz, CDCl₃).

Table 8.10: Coordinates of gas phase geometry optimized structure of **Zn-3DoH-click COOH** calculated by DFT at the B3LYP/LANL2DG/6-31G* level with energy E = -4902.2770170 Hartree/particle.

	-		
	X	У	Z
С	-2.440430000	-2.940098000	-7.360897000
С	-1.373987000	-3.526266000	-6.748459000
С	-0.952037000	-4.625955000	-7.590266000
Ν	-1.766340000	-4.690338000	-8.691898000
С	-2.685716000	-3.672205000	-8.583376000
С	-4.937471000	-4.672226000	-12.649697000
С	-5.016288000	-3.763691000	-11.637195000
С	-3.965533000	-4.084243000	-10.696137000
Ν	-3.268956000	-5.177071000	-11.149496000
С	-3.838267000	-5.560086000	-12.340038000
С	-3.707540000	-3.378245000	-9.503959000
С	-0.906145000	-9.234563000	-13.063604000
С	-1.960638000	-8.633771000	-13.682813000
С	-2.365114000	-7.521210000	-12.851099000
Ν	-1.551940000	-7.464988000	-11.744863000
С	-0.651707000	-8.496541000	-11.845800000
С	-3.427198000	-6.643263000	-13.140580000
С	1.633779000	-7.480465000	-7.801678000
С	1.696362000	-8.398204000	-8.806393000
С	0.631853000	-8.088180000	-9.734698000
Ν	-0.062142000	-6.991770000	-9.276584000
С	0.524024000	-6.599561000	-8.100131000
С	0.116574000	-5.502970000	-7.313345000
С	0.367013000	-8.797809000	-10.919482000
С	-4.182052000	-6.881342000	-14.415224000

С	0.898095000	-5.239642000	-6.066864000
С	-3.776411000	-6.262766000	-15.612958000
С	-4.472062000	-6.487449000	-16.810372000
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С	-6.005632000	-7.962797000	-15.631767000
С	-5.303673000	-7.731384000	-14.439240000
С	1.774137000	-4.153429000	-5.968707000
С	2.510313000	-3.905780000	-4.815331000
С	2.390788000	-4.737253000	-3.696890000
С	1.509495000	-5.821805000	-3.770610000
С	0.790206000	-6.060875000	-4.939981000
F	1.936431000	-3.322519000	-7.006285000
F	-0.042533000	-7.108940000	-4.954245000
F	3.345801000	-2.854321000	-4.779007000
F	1.328120000	-6.623635000	-2.719499000
N	3 149160000	-4 489770000	-2.531023000
Zn	-1 664297000	-6.082325000	-10 217729000
C	3 377594000	-3 307291000	-1 896561000
C	4 204038000	-3 630819000	-0.839489000
N	4 436099000	-4 985649000	-0.893030000
N	3 816225000	-5 507401000	-1 898605000
C	4 787122000	2 786725000	0.206420000
C	4.787122000	3 370986000	1 227180000
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C	0.121119000 5.035477000	-2.381918000	2.222874000
C	5.955477000	-1.191164000	2.229134000
C	3.149972000	-0.010317000	1.223039000
C	4.392103000	-1.394218000	0.222093000
C	0.304381000	-0.284/85000	3.270524000
0	7.550951000	-0.705522000	4.003042000
C	-5.05515/000	-8.290824000	-13.24124/000
C	-9.479022000	-12.521263000	-8.386920000
C	-9.338259000	-12.065820000	-9.843125000
C	-8.180659000	-11.082335000	-10.0595/3000
C	-8.036305000	-10.618984000	-11.515410000
C	-6.8/3566000	-9.6398/9000	-11./225/3000
C	-6./4/0/6000	-9.1/946/000	-13.169185000
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C	2.69/811000	-0.736224000	-17.741696000
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C	-0.361497000	-3.190644000	-17.418945000
С	-0.990253000	-3.957064000	-16.248137000
С	-2.196564000	-4.786143000	-16.669954000
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Η	-3.015225000	-2.091127000	-7.018775000
Η	-0.924560000	-3.244396000	-5.806198000
Η	-5.562889000	-4.742749000	-13.528449000
Η	-5.717611000	-2.948298000	-11.529869000
Η	-0.346391000	-10.097756000	-13.395200000
Н	-2.427406000	-8.912959000	-14.616917000
Н	2.285866000	-7.405334000	-6.942514000
Н	2.399809000	-9.211122000	-8.917131000
Н	-4.161816000	-6.014139000	-17.733845000
Η	-6.118675000	-7.512900000	-17.726102000
Н	-6.868479000	-8.616921000	-15.653962000

Η	2.948674000	-2.380741000	-2.240622000
Η	5.693418000	-4.446566000	1.229629000
Η	6.676375000	-3.075067000	3.018186000
Η	4.993140000	0.462892000	1.244712000
Η	3.999887000	-0.919404000	-0.555263000
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Η	-8.568972000	-13.026244000	-8.039205000
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Н	-9.656637000	-11.668178000	-7.719980000
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Н	-10.277119000	-11.598204000	-10.172548000
Н	-8.323592000	-10.204567000	-9.411916000
Η	-7.240213000	-11.550084000	-9.732253000
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Н	2.415550000	0.007968000	-16.986328000
Н	1.797372000	-2.291707000	-18.945273000
Н	0.735423000	-0.928710000	-18.630244000
Н	0.545965000	-1.634764000	-16.221211000
Н	1.605281000	-2.999732000	-16.538780000
Н	-0.056050000	-3.900534000	-18.201962000
Н	-1.116348000	-2.535666000	-17.879047000
Н	-1.304948000	-3.257943000	-15.462900000
H	-0.249481000	-4.626617000	-15.792639000
Н	-1.915145000	-5.522656000	-17.437285000
Н	-2.983229000	-4.143706000	-17.092717000
Н	-6.537715000	-14.100252000	-6.747821000
Н	-5.612891000	-13.856591000	-5.259366000
С	-5.764596000	-14.539357000	-6.104446000
Н	-6.159107000	-15.480907000	-5.705649000
С	-4.460703000	-14.761025000	-6.878139000
Η	-4.635795000	-15.477300000	-7.693680000
Н	-3.718196000	-15.229580000	-6.216561000
С	-3.874910000	-13.467007000	-7.458041000
Н	-4.615153000	-12.999537000	-8.124525000
Н	-3.704517000	-12.748267000	-6.643078000
С	-2.564009000	-13.679699000	-8.226658000
Н	-2.734410000	-14.401189000	-9.039737000
Н	-1.824608000	-14.143867000	-7.557221000
Н	-2.712212000	-11.917423000	-9.488529000
Н	-1.807548000	-11.655424000	-8.001670000
С	-1.988813000	-12.380497000	-8.805286000
C	-0.684294000	-12.603565000	-9.559318000
Η	-0.831488000	-13.302267000	-10.396371000
Н	0.081487000	-13.030716000	-8.894993000
0	-0.250692000	-11.338329000	-10.052745000
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Н	1.457189000	-13.359769000	-10.717014000

С	2.876012000	-12.174369000	-11.814502000
Η	3.509242000	-13.028028000	-12.041748000
Η	4.149494000	-10.792530000	-12.859144000
С	3.242769000	-10.912808000	-12.279013000
С	2.422432000	-9.813904000	-11.982331000
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Н	4.749686000	-8.589782000	-12.613150000
Н	3.812805000	-8.863424000	-14.099129000
С	3.885995000	-6.787689000	-13.463088000
Н	2.954033000	-6.510266000	-13.972041000
Н	3.898128000	-6.241922000	-12.511068000
C	5.095881000	-6.388145000	-14.317711000
H	6.022599000	-6.691610000	-13.808275000
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C	5 154170000	-4 883353000	-14 612682000
н	5 178800000	-4 328504000	-13 663387000
н	4 227142000	-4 575975000	-15 119469000
C	6 359730000	-4 475805000	-15 469829000
н	7 28/793000	-4 788877000	-1/ 96/98/000
н	6 331092000	-5.0270/2000	-14.904904000 -16.420619000
C	6/17981000	-2 970925000	-15.752470000
с ц	7 288604000	2 711/04/000	16 365464000
и П	5 521603000	2 632004000	16 287864000
и П	5.521005000 6.481042000	-2.032994000	-10.287804000
н Ц	2 202101000	-2.334333000	-14.821093000
п	2.203191000	2.070046000	-13.1101/9000
п	2 244086000	2.070940000	-13.024333000
	2.344980000	2.300033000	-14.201770000
п	2.724047000	3.439014000	-14.049133000
	1.05/920000	2.098478000	-13.463436000
п	0.288518000	3.100934000	-14.1391/3000
П	1.203989000	5.404485000	-12.059282000
	0.4/0838000	1.388237000	-12.923490000
H	0.305/89000	0.6/99/3000	-13./49189000
Н	1.219418000	0.919890000	-12.26/76/000
C H	-0.8389/9000	1.5/3213000	-12.145919000
H	-1.588180000	2.036990000	-12.804855000
H	-0.6/3190000	2.285799000	-11.324238000
H	-1.5699/5000	-0.458341000	-12.392020000
H	-0.661880000	-0.202088000	-10.906360000
C	-1.394360000	0.2595/4000	-11.580622000
C	-2.698550000	0.45/3/2000	-10.818964000
Н	-3.471850000	0.883086000	-11.475572000
H	-2.556632000	1.148222000	-9.974550000
0	-3.115337000	-0.818393000	-10.338814000
С	-4.270800000	-0.916674000	-9.622784000
С	-5.098696000	0.175125000	-9.320639000
Η	-4.847979000	1.174806000	-9.653490000
С	-6.258675000	-0.041194000	-8.579501000
Η	-6.902032000	0.802356000	-8.343096000
Η	-7.521416000	-1.451034000	-7.559618000
С	-6.613707000	-1.312980000	-8.134251000
С	-5.779678000	-2.398573000	-8.441593000
С	-4.599457000	-2.214303000	-9.186704000

-6.030921000	-3.681804000	-8.057098000
-7.201154000	-3.964945000	-7.294146000
-8.097303000	-3.652757000	-7.850562000
-7.178531000	-3.401730000	-6.349335000
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-8.439274000	-5.892269000	-6.191493000
-8.429280000	-5.357266000	-5.230283000
-9.365407000	-5.586648000	-6.700886000
-8.484678000	-7.403063000	-5.926390000
-7.556271000	-7.711447000	-5.423719000
-8.502115000	-7.939743000	-6.886706000
-9.688014000	-7.838658000	-5.080009000
-9.668216000	-7.302398000	-4.120561000
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-10.597589000	-9.628444000	-4.215421000
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-8.828956000	-9.681858000	-4.285570000
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<u>**Table 8.11:**</u> Coordinates of gas phase geometry optimized structure of **Zn-3DoH-click-CNCOOH** calculated by DFT at the B3LYP/LANL2DG/6-31G* level with energy E = -5071.9229698

Hartree/particle.

	Х	У	Z
С	-2.441213000	-3.084715000	-7.299443000
С	-1.373817000	-3.670694000	-6.688424000
С	-0.951329000	-4.768917000	-7.531841000
Ν	-1.766486000	-4.832832000	-8.632810000
С	-2.686678000	-3.815556000	-8.522573000
С	-4.940398000	-4.812614000	-12.588548000
С	-5.018945000	-3.905004000	-11.575181000
С	-3.967694000	-4.226197000	-10.634919000
Ν	-3.271134000	-5.318494000	-11.089531000
С	-3.840940000	-5.700554000	-12.280153000
С	-3.709168000	-3.521200000	-9.442243000
С	-0.909186000	-9.374432000	-13.007934000
С	-1.964047000	-8.773283000	-13.626126000
С	-2.367898000	-7.661112000	-12.793561000
Ν	-1.553946000	-7.605444000	-11.687865000
С	-0.653829000	-8.636927000	-11.790006000
С	-3.430131000	-6.782994000	-13.081852000
С	1.637035000	-7.621137000	-7.748956000
С	1.698425000	-8.538500000	-8.754005000
С	0.632067000	-8.228922000	-9.680318000
Ν	-0.061939000	-7.133115000	-9.220610000
С	0.525870000	-6.741069000	-8.044954000
С	0.118515000	-5.645244000	-7.256878000
С	0.365905000	-8.938414000	-10.864834000
С	-4.185205000	-7.019842000	-14.356585000
С	0.901871000	-5.381984000	-6.011724000
С	-3.778469000	-6.401534000	-15.554090000

С	-4.473909000	-6.625347000	-16.751771000
С	-5.580206000	-7.472581000	-16.742172000
С	-6.009516000	-8.099145000	-15.573857000
С	-5.307721000	-7.868687000	-14.381045000
С	1.770514000	-4.289863000	-5.911262000
С	2.509365000	-4.042921000	-4.759556000
С	2.400901000	-4.881604000	-3.645387000
С	1.526899000	-5.971885000	-3.720902000
C	0.804088000	-6.209537000	-4.888417000
F	1.922995000	-3.452282000	-6.944931000
F	-0.021686000	-7.262850000	-4.904309000
F	3.337268000	-2.985308000	-4.720579000
F	1.355919000	-6.780180000	-2.673250000
N	3.164419000	-4.636586000	-2.482255000
Zn	-1 665495000	-6 224050000	-10 159647000
C	3 392299000	-3 457542000	-1 843656000
C	4 229747000	-3 782628000	-0 794434000
N	4 467959000	-5 136555000	-0.857640000
N	3 842809000	-5 655249000	-1 860073000
C	4 817340000	-2 941804000	0.247975000
C	5 63237/000	-3 5182/3000	1 2/0680000
C	6 2017/0000	-2 7/2925000	2 239609000
C	5 977655000	-1 3/8238000	2.237007000
C	5 158104000	0.770555000	2.288070000
C	1 580870000	1 555161000	0.288012000
C	4.389870000	-1.555101000	3 282770000
C	7 327481000	-0.440085000	1 363388000
	5 640112000	-0.047400000	4.303388000
C	-3.040112000	-0.428017000	-13.183277000 8.224075000
C	-9.463026000	-12.003141000	-0.334073000
C	-9.344009000	-12.200000000	-9.789851000
C	-0.100002000	-11.222430000	-10.004701000
C	-8.041301000	-10.736002000	-11.4001/2000
C	-0.8/9030000	-9.778556000	-11.003948000
	-0.732011000	-9.5108/5000	-15.112108000
C	-2.083304000	-3.394010000	-13.449884000
C	2.707009000	-0.888025000	-17.082237000
C	1.499948000	-1./3041/000	-18.10/225000
C	0.856722000	-2.495010000	-16.942850000
C	-0.356222000	-3.337428000	-17.359754000
C	-0.98/926000	-4.100909000	-16.188612000
C	-2.195383000	-4.928158000	-16.610/56000
C	7.747682000	0.4///61000	5.242974000
0	8.462898000	0.3566/2000	6.214469000
0	7.246622000	1.678323000	4.850546000
C	7.843606000	-1.920641000	4.760484000
N	8.25859/000	-2.961273000	5.075335000
Н	-3.016664000	-2.236/4/000	-6.955911000
Н	-0.924279000	-3.389768000	-5.745927000
Н	-5.566184000	-4.882489000	-13.467086000
H	-5.720419000	-3.089874000	-11.466833000
H	-0.349669000	-10.237485000	-13.340267000
Η	-2.431486000	-9.052009000	-14.560026000
Η	2.291055000	-7.545924000	-6.891291000
Η	2.402304000	-9.350818000	-8.866261000
Η	-4.162811000	-6.152313000	-17.675097000

Η	-6.121299000	-7.648937000	-17.668178000
Η	-6.873040000	-8.752355000	-15.596461000
Η	2.957780000	-2.530995000	-2.180627000
Η	5.810964000	-4.587556000	1.212754000
Η	6.822891000	-3.223924000	2.984560000
Η	4.971406000	0.291308000	1.302353000
Η	3.967642000	-1.080362000	-0.464372000
Η	6.228319000	0.596987000	3.140711000
Η	-8.575635000	-13.168001000	-7.986058000
Η	-10.321091000	-13.361862000	-8.212120000
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Η	-9.198088000	-13.083908000	-10.436048000
Η	-10.282835000	-11.739172000	-10.119644000
Η	-8.330441000	-10.345204000	-9.356568000
Η	-7.246263000	-11.690032000	-9.677144000
Η	-8.981840000	-10.287556000	-11.784263000
Н	-7.901286000	-11.636490000	-12.107397000
Η	-5.932544000	-10.244849000	-11.364493000
Н	-7.010311000	-8.894939000	-11.028133000
Н	-6.591275000	-10.174021000	-13.782926000
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Н	3.494448000	-1.515752000	-17.244481000
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Н	1.806694000	-2.445046000	-18.884234000
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Н	0.551958000	-1.780837000	-16.163479000
Η	1.609500000	-3.148167000	-16.476828000
Н	-0.050801000	-4.049112000	-18.141135000
Н	-1.109338000	-2.681991000	-17.822044000
Η	-1.302160000	-3.400020000	-15.404757000
Η	-0.249057000	-4.771303000	-15.731273000
Н	-1.914608000	-5.665999000	-17.377032000
Н	-2.980396000	-4.284654000	-17.034965000
Н	7.588503000	2.324326000	5.495931000
Н	-6.541816000	-14.239799000	-6.697069000
Н	-5.617294000	-13.996662000	-5.208308000
С	-5.768982000	-14.679226000	-6.053554000
Η	-6.163851000	-15.620726000	-5.655010000
С	-4.464949000	-14.901155000	-6.826935000
Н	-4.640028000	-15.617269000	-7.642618000
Η	-3.722761000	-15.369990000	-6.165224000
С	-3.878660000	-13.607214000	-7.406507000
Н	-4.618644000	-13.139410000	-8.073065000
Н	-3.708197000	-12.888676000	-6.591377000
С	-2.567675000	-13.820160000	-8.174913000
Н	-2.738133000	-14.541459000	-8.988145000
Н	-1.828528000	-14.284622000	-7.505429000
Η	-2.715295000	-12.057557000	-9.436389000
Н	-1.810567000	-11.796198000	-7.949411000
Ċ	-1.992043000	-12.521003000	-8.753225000
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H	-0.834967000	-13.442728000	-10.344498000
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Η	1.453505000	-13.500959000	-10.665559000
С	2.873247000	-12.315542000	-11.761806000
Н	3.506125000	-13.169360000	-11.989374000
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С	2.421101000	-9.954707000	-11.928062000
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Н	4.749562000	-8.732149000	-12.554182000
Н	3.815057000	-9.002084000	-14.042331000
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H	2.958514000	-6.648165000	-13.912302000
Н	3.900634000	-6.383611000	-12.449325000
C	5 101047000	-6 527850000	-14 254351000
H	6.026595000	-6.833485000	-13.744114000
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C	5 161641000	-5 022537000	-14 546163000
н	5 185472000	-4 469673000	-13 595680000
н	4 235784000	-4 712976000	-15.053785000
C	6 369064000	-4 614697000	-15 400545000
н	7 292925000	-4 929953000	-14 894883000
н	6 341267000	-5 163892000	-16 352530000
$\hat{\mathbf{C}}$	6 429595000	-3 109300000	-15 679929000
н	7 301689000	-2 8/9622000	-16 2908/15000
н	5 53/55/000	-2 769166000	-16 216180000
и Ц	6 402622000	2 535420000	1/ 7/7213000
H	2 191339000	1 686957000	-15.065984000
н	2.171557000	1.000/37000	-13 575977000
C	2 33/115000	2 361880000	14 212504000
с ц	2.334113000	2.301889000	14.601452000
C	1 02800000	2 554045000	13 /3//00000
н	0.277374000	2.004040000	-14 087631000
и Ц	1 10510000	3 261028000	12 600327000
C	0.462327000	1 244220000	12.870310000
с ц	0.402327000	0.535030000	13 605010000
и Ц	1 212083000	0.555050000	12 215272000
C	0.846371000	1 429475000	12.213272000
с u	1 506830000	1.429475000	12 740241000
и П	-1.590850000	2 1/3178000	-12.749241000
и П	1 576600000	2.143178000	12 222254000
и П	-1.570099000	-0.002737000	-12.333334000
Γ	-0.000332000	-0.344230000	-10.849319000
C	-1.4001/3000	0.110252000	-11.323139000
с u	-2.703247000	0.314130000	-10.739383000
п u	-3.478080000	1.006606000	-11.413331000
	-2.300469000	0.061150000	-7.7103/3000
C	-3.11/949000	-0.901130000	-10.2/0393000
C	-4.273040000 5 101101000	-1.039/91000	-7.337783000
U U	-3.101101000	1.021502000	-7.23/431000 0 500592000
п	-4.030943000	1.031302000	-7.370380000 8 515754000
	-0.2000/8000	-0.184942000	-0.313/34000
п	-0.904310000	0.038303000	-0.2/9184000
п	-1.322342000	-1.393238000	-7.473418000

С	-6.615057000	-1.456840000	-8.070326000
С	-5.780868000	-2.542219000	-8.378135000
С	-4.601041000	-2.357544000	-9.123789000
0	-6.031638000	-3.825496000	-7.993704000
С	-7.202639000	-4.109420000	-7.232139000
Η	-8.098212000	-3.796673000	-7.789144000
Η	-7.180918000	-3.547081000	-6.286771000
С	-7.228473000	-5.609356000	-6.967963000
Η	-6.298828000	-5.890311000	-6.456899000
Η	-7.227580000	-6.134079000	-7.931894000
С	-8.441759000	-6.037690000	-6.132306000
Η	-8.432417000	-5.503686000	-5.170522000
Η	-9.367443000	-5.731388000	-6.642100000
С	-8.487603000	-7.548752000	-5.868809000
Η	-7.559548000	-7.857841000	-5.365927000
Η	-8.504590000	-8.084419000	-6.829690000
С	-9.691525000	-7.984995000	-5.023592000
Η	-9.672189000	-7.449745000	-4.063564000
Η	-10.618862000	-7.674451000	-5.526013000
С	-9.731086000	-9.494785000	-4.764762000
Η	-10.601962000	-9.775512000	-4.161480000
Η	-9.782753000	-10.056841000	-5.705898000
Н	-8.833307000	-9.829188000	-4.230536000



Figure 8.78: Frontier molecular orbitals of **Zn-3DoH-COOH** with the corresponding energy levels.



Figure 8.79: Frontier molecular orbitals of **Zn-3DoH-CNCOOH** with the corresponding energy levels.



Figure 8.80: Cyclic voltammogram (green) and Square Wave (cyan) of **Zn-3DoH-click-COOH** in dry degassed THF.



Figure 8.81: Cyclic voltammogram (purple) and Square Wave (magenta) of **Zn-3DoH-click-CNCOOH** in dry degassed THF.



Figure 8.82: Cyclic voltammogram (black) and Square Wave (blue) of **Zn-3DoH-COOH** in dry degassed THF.



Figure 8.83: Cyclic voltammogram (brown) and Square Wave (blue) of **Zn-3DoH-CNCOOH** in dry degassed THF.