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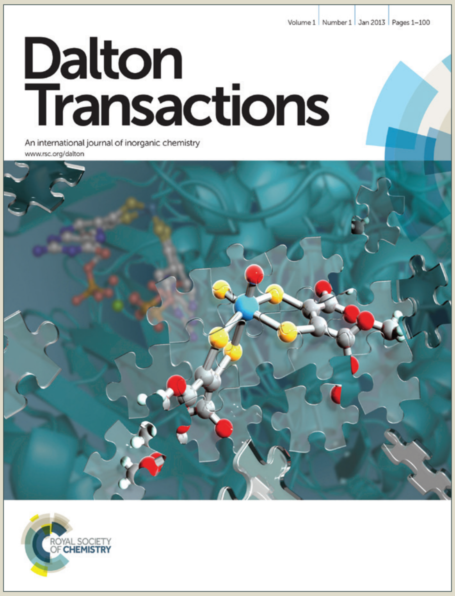

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Click made porphyrin-corrole dyad: a system for photo-induced charge separation

Vasilis Nikolaou,[a] Kostas Karikis,[a] Yoann Farre,[b] Georgios Charalambidis,[a] F. Odobel,*[b] and Athanassios G. Coutsolelos.*[a]

[a]*Department of Chemistry, University of Crete, Laboratory of BioInorg. Chem., Voutes Campus, P.O. Box 2208, 71003, Heraklion, Crete, Greece*

[b]*Université LUNAM, Université de Nantes, CNRS, Chimie et Interdisciplinarité: Synthèse, Analyse, Modélisation (CEISAM), UMR 6230,2 rue de la Houssinière, 44322 Nantes cedex 3, France.*

The preparation of the first porphyrin-corrole dyad through click chemistry is described. The absorption, the emission and the electrochemical properties were investigated and suggest efficient excited state interaction between the porphyrin and the corrole unit. Theoretical calculations were performed and proven that the dyad can potentially act as molecular system for solar energy conversion scheme.

To mimic natural processes such as photosynthesis, scientists choose using entities that have great similarity to natural systems.[1] Porphyrins and their Corroles analogues proven to be effective candidates for this purpose, because of their similarities to natural systems both in terms of structure and properties.[2] Photo-induced energy and electron transfer processes govern artificial photosynthesis,[3] therefore preparation of chemical devices that stimulate the above mentioned processes is fundamental.[4] One of the long term goals of the scientific community is composition of systems that imitate photo-induced electron transfer reactions and convert solar energy into chemical potential. There is an increasing interest for new multi chromophore compounds over the last decade, that exhibit light-initiated processes and replicate characteristics of natural dyes.[5] More importantly, components with donor and acceptor orientation provide insights about electron and energy transfer mechanisms[4b], thus composition of dyads consisted of different chromophores with relevant orientation could be proven crucial. Porphyrin derivatives appear to be very promising sensitizers for this purpose, due to their unique properties such as light harvesting, low cost, environmentally friendly and simple synthetic procedures.[6] Furthermore, their optical and physical properties, as well as their electronic, can be tuned through functionalization or substitution at their *β* and *meso* positions.[7] Corroles are analogues of porphyrins with on direct pyrrole-pyrrole linkage and three *meso* carbons.[8] In addition, corroles can stabilize metals with high oxidation states because of the three interior *N*-pyrrolic protons. So far, only a few porphyrin-corrole dyads have been prepared and studied,[9] mainly by virtue of the challenging corrole synthesis and the instability of the composed dimers.[10] The last decade such conjugates have been synthesized through various synthetic approaches, namely functionalization of the *meso* position,[9c,f,11] through phenolic[9g] or amide bond.[9e] Porphyrins and corroles have been used in great number of scientific fields, for instance photodynamic therapy (PDT),[12] dye sensitized solar cells (*n*-DSSCs,[13] *p*-DSSCs,[14]) self-assembly,[15] biochemistry[16] and materials chemistry.[17] Consequently, novel porphyrin-corrole derivatives are promising species with potential to act as agents in all those prior mentioned applications. Additionally, derivatives that contain a functional anchoring group, similar to the dyad reported in this work, could potential be used in photovoltaic and/or catalytic applications on TiO_2 if comprising suitable properties. Such properties that permit the photoexcitation of the chromophore followed by the hole injection in the valence band of a *p*-type semi-conductor as NiO. The main obstacle for the construction of a porphyrin-corrole dyad is the proper selection of the synthetic approach, mainly due to the instability of corroles and corrole dimers to harsh reaction conditions. However, there are approaches as "click chemistry" that provide mild reaction conditions and enable stitching moieties together in high yield.[18] Click reaction can be consider as a powerful tool that provides simple purification methods and high selectivity (minimal or no byproducts), attributes essential in porphyrin chemistry.

Herein, the preparation and characterizations of a zinc porphyrin-copper corrole dyad (**3**), based on click reaction between the alkyne-corrole (**1**) and the azide-porphyrin (**2**) is described. In order to gain insight into the photophysical properties, absorption and emission measurements have been performed. The redox properties of the dyad and the starting compounds were studied through electrochemistry. In addition, Density Functional Theory (DFT) calculations were carried out and revealed that HOMO and LUMO orbitals are located in suitable positions to favor the intramolecular electron transfer from the porphyrin moiety to the corrole. To the best of our knowledge, no porphyrin-corrole dyad has been synthesized by click reaction and this is the first compound with suitable properties to potential act as a new dye in *p*-DSSCs.

As shown in Scheme 1, the dyad consists of one copper corrole and one zinc porphyrin, which are covalently linked at their peripheries by 1,2,3-triazole. The porphyrin is functionalized with a benzoic acid at the *meso* position that can function as anchoring group for efficient attachment on NiO surface. The azide-carboxy-porphyrin (**2**) was derived from the azide-methoxy-porphyrin[19] through hydrolysis of the ester group, while the alkyne-corrole (**1**) was prepared according to previously published procedure.[20] The composition of the final compound **3** was verified by NMR, and IR spectroscopies and by mass spectrometry. The ^1H NMR spectrum of **3** is depicted in Figure S3 and the most noticeable feature is the appearance of the characteristic signal of the triazole ring at 9.33 ppm. In the ^{13}C NMR spectrum we observe the characteristic peak of the triazole ring and the carboxylate group at 135.5 ppm and 167.6 ppm respectively (Figure S4 and S5). Concerning the ^{19}F NMR spectrum of **3** typical signals for a *bis*-pentafluoro corrole are observed[20] and presented in Figure S6. Moreover, MALDI-TOF MS shows a peak at 1668.66 m/z (Figure S7), corresponding to the molecular ion of **3**, with the appropriate isotopic distribution. In Figure S13 the AT-FTIR spectra of **1**, **2** and **3** are depicted. We observe that the C-H stretching at 3289 cm^{-1} that corresponds to the terminal alkyne of **1**, as well as the N=N=N stretching at 2082 cm^{-1} and 2119 cm^{-1} due to the terminal azide in porphyrin **2** have disappeared in the final spectrum of the dyad (**3**). Moreover, in the IR spectra of **3**, we can detect peaks that can be assigned to the newly formed triazole ring. Those characteristic peaks are the C-N stretching at 1336 cm^{-1}, the N=N stretching at 1491 cm^{-1} and the C=C stretching at 1603 cm^{-1}.

The photophysical properties of the dyad (**3**) as well the starting chromophores porphyrin (**2**) and corrole (**1**) were examined through absorption and steady state fluorescence spectroscopy. The UV-vis absorption spectra of the dyad (**3**), the porphyrin (**2**) and the corrole (**1**) are depicted in Figure 1. In the case of **2** the spectral features that we observed are the Soret band at 424 nm and two Q-bands at the 556 and 597 nm (Table 1), which are attributed to π–π* electronic transitions within the porphyrin framework. The UV-Vis spectra of **1** showed typical Cu-Corrole features, namely two bands at the 400-435 nm range and two bands at 553 and 613 nm (Figure S10). The absorption spectra of **3** can be described as superimposition of the UV-Vis spectra of **1** and **2**. In table 1, a collection of emission data and quantum yield is given, along with absorption peaks of **3** and the starting compounds (**1** and **2**). The normalized absorption spectra (Figure S10) and UV-vis spectra (Figure 1) of **1** and **2** indicate that the lowest singlet absorption for **1** appears at 615 nm whereas **2** shows a peak at the 597 nm. These facts suggest that **2** can act as the energy donor group while **1** as the energy acceptor in our dyad (**3**), similarly to the corrole-porphyrin dyad that was studied by Harvey, Guilard and coworkers.[11] Insights into the fluorescence properties of **1**, **2** and **3** came from emission measurements at room temperature and at 77 K. Upon photoexcitation, the fluorescence spectra of the azide porphyrin **2** showed strong emission signals with peaks at 607 nm and 658 nm. On the contrary, no emission signals was detected in the case of **1**, at room temperature and at 77 K. The emission spectra of **3** and **2** in isoabsorbing solutions (0.1 at 550 nm) are presented in Figure 2, taking into account the residual absorbance of **1** in order to determine the quenching percentage. Comparing the fluorescence spectrum of **2** and **3**, we calculated that the porphyrin unit shows 95 % quenching in the final dyad. The fluorescence quantum yields concerning the porphyrin chromophore are given in Table 2 and the exact values are: $\Phi=0.044$ in case of **2** and $\Phi=0.0021$ in the dyad (**3**). In order to further investigate the fluorescence properties of **3**, a solution of alkyne corrole **1** - azide porphyrin **2** with equal concentration to the dyad (**3**) has been prepared. As showed from the emission measurements (Figure S8), no significant quenching is observed. In summary, there is efficient interaction between the porphyrin and the corrole unit in the excited state. Further studies at 77 K performed and revealed that compound **2** shows a peak at 792 nm which can be attributed to the phosphorescence of the porphyrin. In the case of **3** though, there is no such characteristic signal supporting that the singlet excited state of the porphyrin has been efficiently quenched by the nearby corrole.

The electrochemical properties of final dyad (**3**) and the starting compounds (**1** and **2**) were investigated by both cyclic and square wave voltammetry. The electrochemical redox data are summarized in Table 2 and the voltammograms for **3**, **1** and **2** are displayed in Figures 3, S11 and S12 respectively. Compound **1** exhibits one reversible oxidation process at 1.04 V and two reversible reduction, the first at 0.16 V due to copper reduction (Cu^{III}/Cu^{II})[21] and the second at -1.6 V. In the case of **2**, typical data for *meso* tetra-aryl substituted zinc porphyrins are observed,[22] specifically two reversible oxidations and two reversible reductions at 1.03 V, 1.38 V and -1.16 V, -1.52 V respectively. Careful comparison with the redox potential of **1** and **2** has been made, for the successful assignment of the signals in the voltammograms of **3**. The dyad undergoes two reversible oxidations $E_{1/2}^{Ox1}$ = 1.03 V and $E_{1/2}^{Ox2}$ = 1.34 V and three reversible reductions $E_{1/2}^{Red1}$ = 0.14 V, $E_{1/2}^{Red2}$ = -1.39 V and $E_{1/2}^{Red3}$ = -1.61 V. The first reduction ($E_{1/2}^{Red1}$) as well as the third ($E_{1/2}^{Red3}$) are attributed to the redox properties of copper corrole, while the second oxidation ($E_{1/2}^{Ox2}$) and the second reduction ($E_{1/2}^{Red2}$) to zinc porphyrin. The reversible oxidation at 1.03 V corresponds to the overlapping oxidations of both zinc porphyrin and copper corrole. The difference between the $E_{1/2}$ values of the first oxidation and first reduction (HOMO-LUMO gap) is 0.89 V, (Table 2).

In order to gain insight into the molecular structure and the electron density distribution of the frontier molecular orbitals of **3**, theoretical calculations (DFT[23]) at the

B3LYP/6-31G(d)[24] level of theory were performed. The gas-phase geometry optimized structure of **3** is presented in Figure S14 and S15, while the corresponding coordinates are provided in Table S1. In the gas-phase geometry optimized structure of **3** (Figure S14, and S15) indicates that the porphyrin and the corrole are almost perpendicular with the triazole group and the bridging phenyl groups. Furthermore, the above mentioned groups adopt a perpendicular orientation with respect to the terminal porphyrin unit (phenyl group that bears the carboxylic acid). The electron density maps and the corresponding energies of the Frontier Molecular Orbitals (FMOs) of **3** are depicted in Figure 4. In the highest energy molecular orbital (HOMO) electron density is mainly spread over the central zinc-porphyrin unit and with some additional contributions on the respective the carboxylic acid group and bridging phenyl group. The corresponding electron densities of the two lowest energy unoccupied molecular orbitals (LUMO and LUMO+1) are predominantly located on the copper-corrole, and partially on the bridging phenyl group. Consequently, the dyad (**3**) can be described as a D-A system, with the zinc-porphyrin unit bearing the carboxylic acid group as donor (D) group, the copper-corrole unit as acceptor (A) group. Therefore, we conclude that the intramolecular electron transfer is favorable observing the electron density distributions on HOMO, LUMO and LUMO+1. More precisely, upon photo-excitation, intramolecular electron transfer from the zinc-porphyrin to the copper-corrole possibly occurs. This is also supported by the calculations of the charge separation driving force (ΔG_{cs}= -1.21 eV) according to the simplified Rehm-Weller equation (1)

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

in which $E_{00}(ZnP^*)$ stands for the energy of the singlet excited state of the zinc porphyrin (taken as 2.1 eV). Alternatively, energy transfer from the zinc porphyrin to copper corrole could be a possible quenching process, since corrole exhibits a little red-shifted absorbance (Figure 2). However, referring to the zero-zero energy of singlet excited state of similar free base corrole[25] and free base porphyrin,[26] we can observe that they are very close (1.9 eV in both cases) indicating that those of the dyad **3** are certainly also very close too. Energy transfer is, however, a possible deactivation process for the zinc porphyrin fluorescence but which is less likely than electron transfer first because its driving force is most certainly weaker and second because the overlapping between the emission spectrum of ZnP and absorption spectrum of corrole is also weak.

Experimental

Synthesis of **2**. To a solution of [5-(4-methoxycarbonylphenyl)-15-(4-azidophenyl)-10,20-bis(2,4,6 trimethylphenyl) porphyrinato][19] zinc (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. The solvents were evaporated under reduced pressure and distilled H_2O (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 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 $C_{58}H_{41}N_5O_2Zn$ [M – 2N + 2H]+ 819.26, found 819.28. Anal. Calc for $C_{58}H_{39}N_7O_2Zn$: C, 72.29; H, 4.64; N, 11.57. Found: C 74.26; H 4.68; N 11.60.

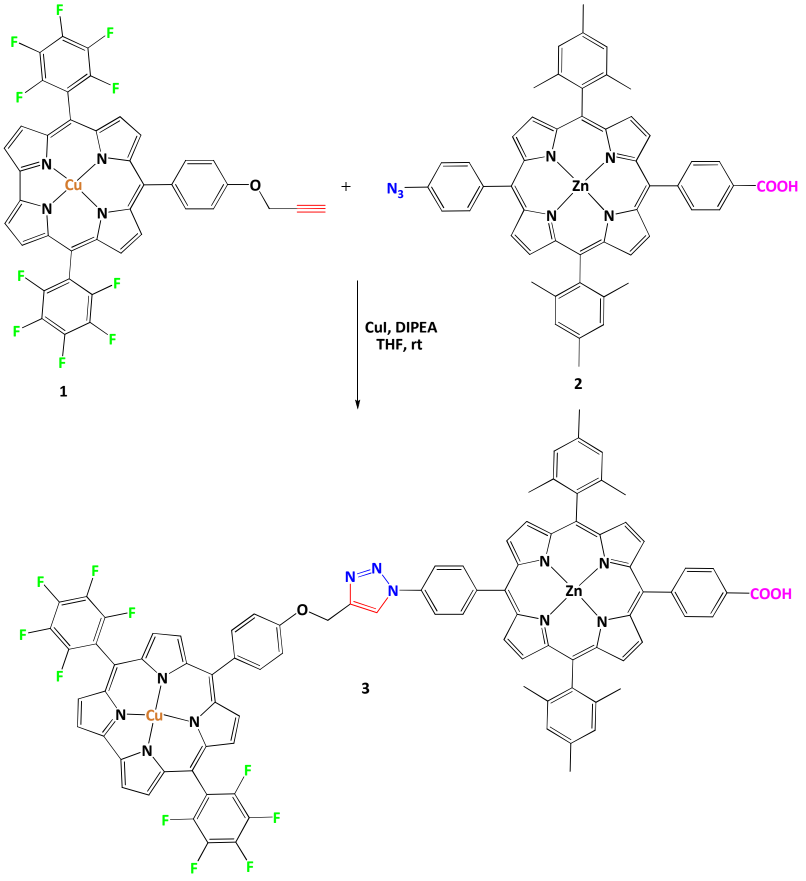
Synthesis of **3.** Equimolar amounts of **1** (48 mg, 0.059 mmol) and **2** (50 mg, 0.059 mmol) were dissolved in THF (3 mL) under a nitrogen atmosphere. Next, CuI (9 mg, 0.047 mmol) and DIPEA (10 µlt, 0.059) were added and the reaction mixture was stirred at room temperature for 16 hours. Upon reaction completion, the volatiles were removed under reduced pressure and the crude solid, after diluting in CH_2Cl_2, was purified by column chromatography (silica gel, CH_2Cl_2/MeOH, 98:2) yielding 41 mg of **3** (yield: 42%). ^{1}H NMR (500 MHz, DMSO-d^6): δ 9.00 (s, 4H), 9.95 (m, 4H), 8.82 (m, 6H), 8.76 (d, J = 4.6 Hz, 2H), 8.40 (d, J = 8 Hz, 2H), 8.34 (d, J = 7.9 Hz, 2H), 8.27 (m, 6H), 8.21 (d, J = 8.0 Hz, 2H), 8.06 (d, J = 7.9 Hz, 2H), 7.74 (m, 6H), 7.67 (m, 3H), 7.41 (s, 1H), 7.39 (m, 2H), 7.30 (s, 4H), 6.82 (d, J = 7.6 Hz, 2H), 4.05 (s, 3H), 2.96 (s, 2H), 2.64 (s, 6H), 1.85 (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. Anal. Calc. for $C_{91}H_{54}CuF_{10}N_{11}O_3Zn$: C 65.51; H, 3.26; N, 9.23. Found: C 65.54; H, 3.22; N, 9.26.

Conclusions

In summary, this is the first reported corrole-porphyrin dimer that was composed through click reaction, containing suitable FMOs to act as molecular system for solar energy conversion. The photophysical investigation revealed that the fluorescence of zinc-porphyrin is strongly quenched due to the copper-corrole in the dyad **3**. Consequently upon photoexcitation, an efficient excited state interaction between the copper-corrole (**1**) and the zinc-porphyrin (**2**) exists. The theoretical calculations confirmed the above hypothesis, suggesting that the porphyrin moiety acts as donor while the corrole unit as acceptor in dimer **3**. Finally, the electrochemical properties of **3** were also examined by cyclic voltammetry and square wave measurements.

Acknowledgments

Financial support from the European Commission (FP7-REGPOT-2008-1, Project BIOSOLENUTI No. 229927) is greatly acknowledged. This research has also been co-financed the Special Research Account of the University of Crete. ANR is gratefully acknowledged for the financial support of these researches through the program POSITIF (ANR-12-PRGE-0016-01).



Scheme 1: Synthetic route for the synthesis of the corrole-porphyrin dyad (**3**).

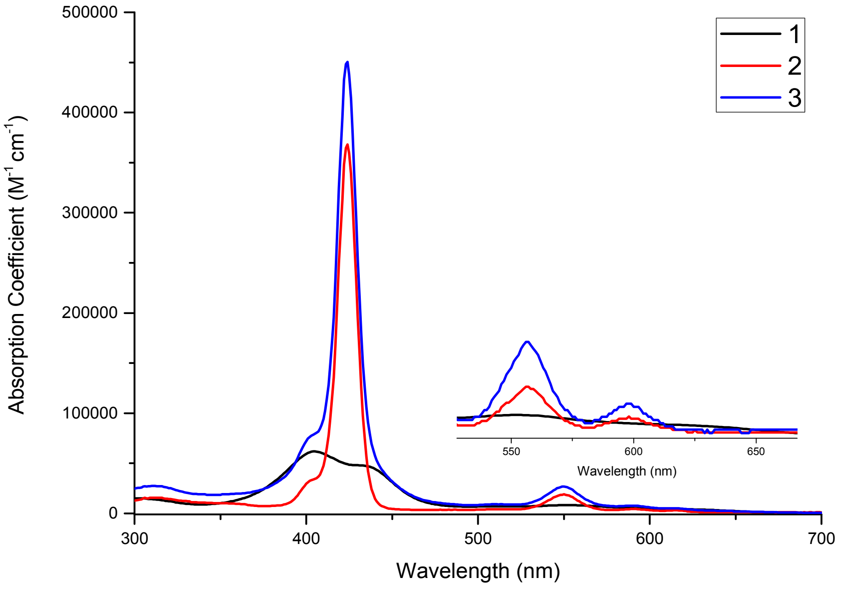


Figure 1: Absorption spectra of alkyne-corrole (**1**) (black), azide-porphyrin (**2**) (red) and dyad (**3**) (blue) in THF.

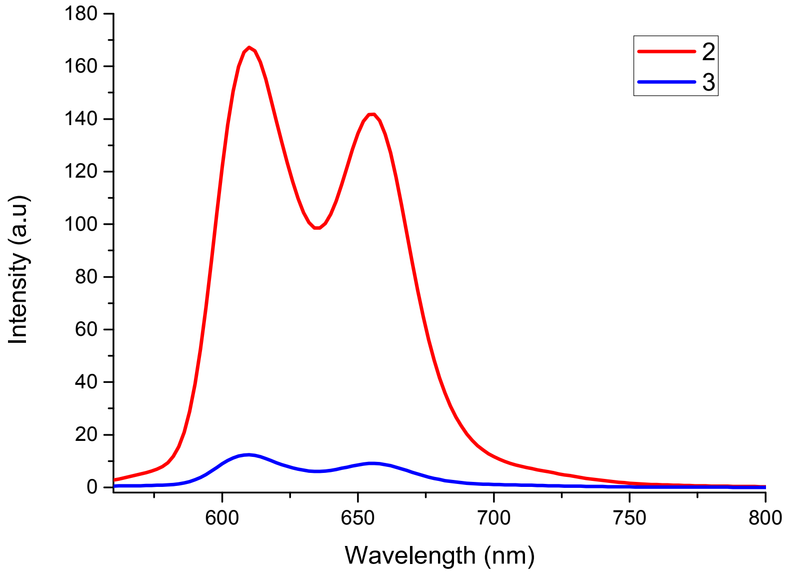


Figure 2: Room temperature emission spectra of isoabsorbing solutions (A = 0.1, at 550 nm) of **2** (red) and **3** (blue) when excited the porphyrin chromophore (550 nm).

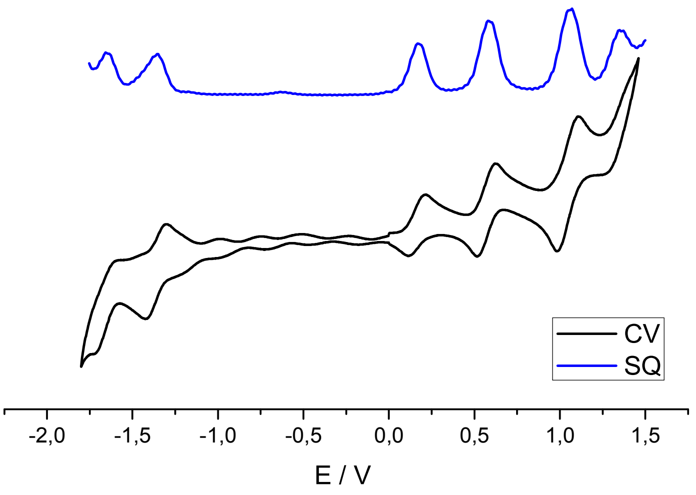


Figure 3: Cyclic (black) and square wave (blue) voltammograms of **3** in THF. All potentials are reported vs. SCE and FcH/FcH$^+$ was used as internal standard ($E_{1/2}$Ox = 0.55 V).

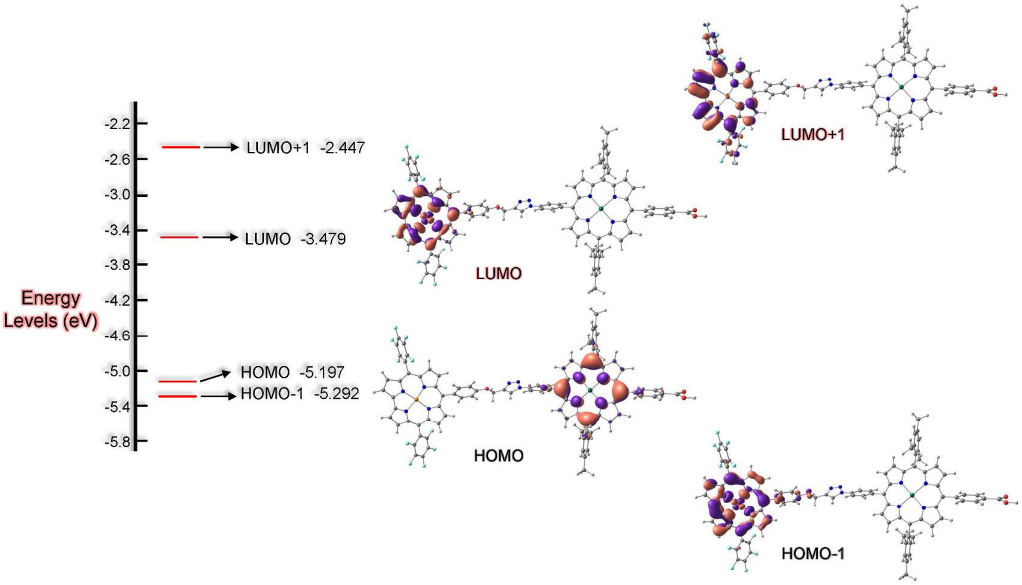


Figure 4: Frontier molecular orbitals of the dyad (**3**) with the corresponding energy levels.

Table 1: Absorption and Fluorescence data of **1**, **2** and **3** in THF solution at room temperature and in Toluene glass at 77 K.

	Absorption	**Fluorescence**		
Compound	**λmax/ nm**	**Emission λmax/ nm rt**	**Emission λmax/ nm 77K**	**Φ(λ_{ex}=550)**
1	405; 433; 553; 615	-	-	-
2	424; 556; 597	607; 657	607; 657; 793	0.044
3	424; 556; 596	608; 656	604; 654	0.0021

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

Table 2: Summary of the electrochemical redox data of **1**, **2** and **3** 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	**$E_{1/2}$ Red^1 (V)**	**$E_{1/2}$ Red^2 (V)**	**$E_{1/2}$ Red^3 (V)**	**$E_{1/2}$ Ox^1 (V)**	**$E_{1/2}$ Ox^2 (V)**	**HOMO-LUMO gap Electrochemical (V)**

1	0.16	-1.6	-	1.04	-	0.88
2	-1.16	-1.52	-	1.03	1.38	2.19
3	0.14	-1.39	-1.61	1.03	1.34	0.89

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