

A Novel Electron Donor-Acceptor Carbazole-Zn(II)Phthalocyanine – Perfluorinated Subphthalocyanine Conjugate: Synthesis, Characterization, and Photoinduced Electron-Transfer

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Porphyrinoids are considered perfect candidates for the preparation of model electron donor-acceptor (D-A) systems as they enable fast and efficient photoinduced electron transfer. Herein, we report on the synthesis and photophysical characterization of a ZnPc–SubPc conjugate covalently connected through a short-range alkyne spacer. We designed and prepared the conjugate, which comprise, on the one hand, a perfluorinated SubPc with strong electron acceptor character and, on the

other, a Pc peripherally functionalized with carbazoles with strong electron donor character. Photoinduced electron transfer events are in-depth analyzed by several techniques, including steady-state absorption, time-resolved emission and transient absorption measurements on different time scales. Our studies confirm a full charge separation occurring from a photoexcited charge transfer state.

Introduction

Due to their key role in molecular photovoltaics and artificial photosynthesis, electron donor-acceptor (D-A) systems capable

of mimicking natural photosynthetic reaction centers have gained increased attention.^[1a–i] In this regard, porphyrinoids have been widely employed as antennas because they exhibit strong absorption, trigger fast and efficient electron/energy transfer processes, and generate long-lived charge separated states in combination with electron acceptors such as fullerenes. With this focus, a plethora of D-A systems employing porphyrins (Pors),^[2a–d] phthalocyanines (Pcs)^[3a–c] or even dipyrromethenes (BODIPYs)^[4a–b] have been prepared to unravel how the driving force, reorganization energy, and electronic coupling govern the rate of charge separation and recombination.

One step further, significant efforts have been made in developing multi-chromophore systems able to efficiently harvest light across the entire visible range.^[5a–c] To this end, electron accepting fullerenes are replaced by porphyrinoids. Among them, subphthalocyanines (SubPcs),^[6] contracted analogues of Pcs, are perfect candidates by virtue of their excellent photophysical and electronic features.^[7a–i] As a result of their non-planar 14 π -aromatic structure, SubPcs exhibit high excited state energies and low reorganization energies, as well as strong electron acceptor properties when decorated with electron-withdrawing groups. Such high electronic excitation energies, which typically exceed 2.0 eV, efficiently promote exergonic electron-transfer processes.^[8a–b] In addition, their optoelectronic and photophysical properties are easily modulated by varying their axial peripheral position by means of chemical modifications.^[9] These features, together with their high molar absorption coefficients and a small Stokes shift, render them unique chromophores for the preparation of D-A systems with long-lived charge-separated states.^[10]

Electron transfer processes are further promoted by increasing the HOMO energy of the electron donor. To this end, some of us have recently reported that the introduction of electron-

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donating carbazoles on the Pc periphery significantly increases its electron donating features, as well as red-shifts their visible absorption above 700 nm.^[11a–c] Taking these results into account, we envisaged that an electron donor-acceptor conjugate comprising an electron accepting SubPc and a carbazole-based Pc could be a suitable model platform to evaluate the photoinduced electron in all-porphyrinic D-A systems.

As such, we prepared a new electron donor-acceptor conjugate employing a fully fluorinated SubPc as an electron-acceptor, which is linked to a carbazole-Pc through an axial alkyne spacer. Then, the photoinduced electron-transfer events are systematically investigated using steady-state absorption, time-resolved emission and transient absorption techniques at different time scales. Our studies document that photoinduced electron transfer from the Pc to the SubPc efficiently occurs.

Results and Discussion

Synthesis

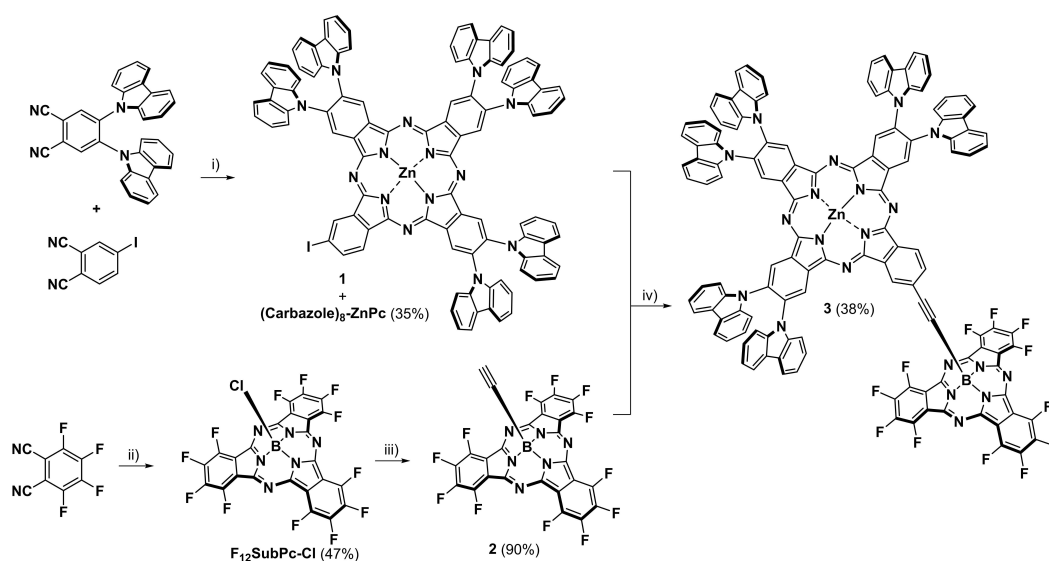
For the preparation of ZnPc-SubPc conjugate **3**, we designed the synthetic pathway depicted in Scheme 1. The non-symmetrical mono-iodo hexacarbazole ZnPc **1** was prepared by a statistical cross-condensation between 4,5-di(9H-carbazol-9-yl)phthalonitrile and 4-iodophthalonitrile in the presence of ZnCl₂ under reflux in 2-dimethylaminoethanol (DMAE) for 8 h. It should be noted that the use of ZnCl₂ led to better yields as compared to the results obtained when Zn(OAc)₂ was used. Unfortunately, the chromatographic separation of the ZnPc **1** from the symmetrically substituted octacarbazole ZnPc [(Carbazole)₈-ZnPc] formed as a minor component in the same reaction failed. Responsible is the similarity between their RF values, as confirmed by different spectroscopic tools (Fig-

ure S5.1). Mixtures of the ZnPc **1** and symmetrical [(Carbazole)₈-ZnPc] (ca. 1:2 ratio) were isolated after column chromatography on silica and size exclusion (Bio-Beads SX1) gels with chloroform as eluent, and recrystallized using THF/MeOH solvent system to yield a pure mixture (1:2) of both compounds in 35% yield.

Among the different SubPcs showing low-lying LUMO energies, the perfluorinated SubPc (F₁₂SubPc) has been selected to complement the electron-rich characteristics of the ZnPc **1**. Thus, the axially chlorinated F₁₂SubPc-Cl (Scheme 1) was prepared using standard cyclotrimerization conditions of the corresponding phthalonitrile in the presence of BCl₃.^[12] Next, employing a mild and versatile methodology developed by Nielsen and co-workers^[13a] for the preparation of axially ethynyl-substituted SubPc derivatives, F₁₂SubPc-Cl was treated with ethynyltrimethylsilane in the presence of AlCl₃ to afford SubPc **2**^[13b] in 90% yields (Scheme 1). Finally, ZnPc-SubPc **3** was prepared using a Pd(0)-catalyzed Sonogashira cross-coupling reaction between SubPc **2** and a 1:2 mixture of ZnPc **1** and (Carbazole)₈-ZnPc

Electrochemistry and spectroelectrochemistry

Cyclic (CV) and differential pulse voltammetry (DPV) were performed with SubPc **2** and ZnPc **1** in dichloromethane using a Au working electrode (WE), a Pt counter electrode (CE), and a Ag-wire as pseudo-reference electrode (RE) with ferrocene as internal standard (Figures S6.1 and S6.2).^[14a–b] ZnPc **1** features a nearly irreversible oxidation and a reversible reduction at +0.60 and −1.35 V vs. Ag-wire, respectively, which correlate with +0.20 and −1.75 V vs. Fc/Fc⁺. SubPc **2** is reversibly oxidized at +1.38 and reduced at −0.66 V vs. Ag-wire or at +0.98 and −1.04 V vs. Fc/Fc⁺. From the aforementioned we conclude that ZnPc is the stronger electron donor and SubPc is



Scheme 1. Synthetic route for the preparation of ZnPc-SubPc **3**. i) ZnCl₂, DMAE, reflux, 8 h. ii) BCl₃ (1.0 M in *p*-xylene), 145 °C, 2 h. iii) Ethynyltrimethylsilane, AlCl₃, *o*-DCB, RT, 5 min. iv) ^tBuXPhosPd G3, CuI, THF, Et₃N, RT, 16 h.

the stronger electron acceptor in ZnPc-SubPc **3**. For monomers of ZnPc-SubPc **3**, nearly irreversible oxidations and reductions occur at +0.62 and −0.74 V vs. Ag-wire, respectively, which resemble closely the first ZnPc oxidation and the first SubPc reduction (Figure S6.3).

To shed light onto the absorption characteristics of the one-electron oxidized form of ZnPc **1** and the one-electron reduced form of SubPc **2**, absorption spectra were taken upon applying different bias potentials using a Pt-mesh WE, a Pt-wire CE, and a Ag-wire RE. To this end, the differential absorption spectra upon ZnPc **1** oxidation give rise to 420, 540, and 865 nm maxima as well as 373 and 700 nm minima (Figure 1). Upon SubPc **2** reduction, maxima developed at 460 and 650 nm, which are accompanied by a minimum at 570 nm.

Steady-state absorption and fluorescence spectroscopy

Absorption spectra were taken for the two references, that is, SubPc **2** and ZnPc **1**, on the one hand, and ZnPc-SubPc **3**, on the other (Figure 2). The two references reveal absorption maxima in terms of their Q-band absorptions at 577 and

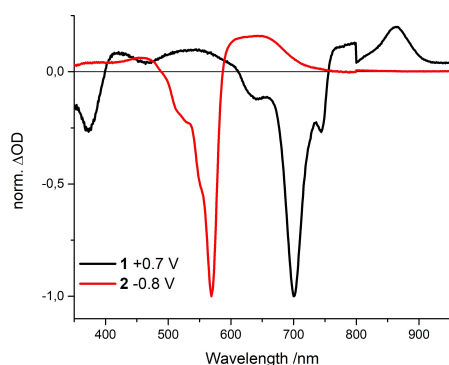


Figure 1. Differential absorption spectra recorded upon oxidation of ZnPc **1** (4×10^{-6} M) and reduction of SubPc **2** (7×10^{-6} M) obtained in deaerated *ortho*-dichlorobenzene (*o*-DCB; 0.1 M TBAClO₄ as electrolyte) and dichloromethane (0.1 M TBAPF₆ as electrolyte), respectively.

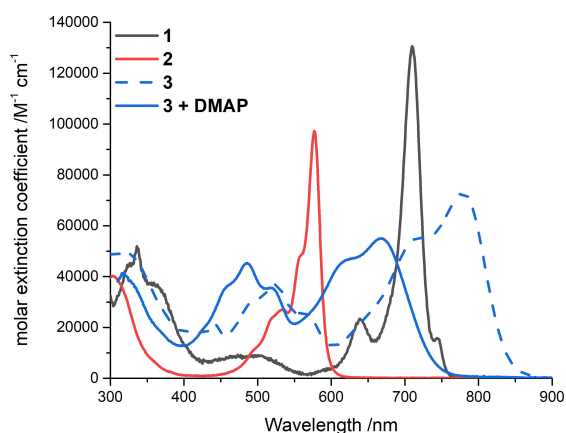


Figure 2. Absorption spectra of **1** (black, 2×10^{-6} M) and **2** (red, 2×10^{-6} M) as well as aggregates of **3** in toluene (dashed blue, 2×10^{-6} M) and monomers of **3** in benzonitrile (blue, 4×10^{-6} M) using an excess amount of DMAP.

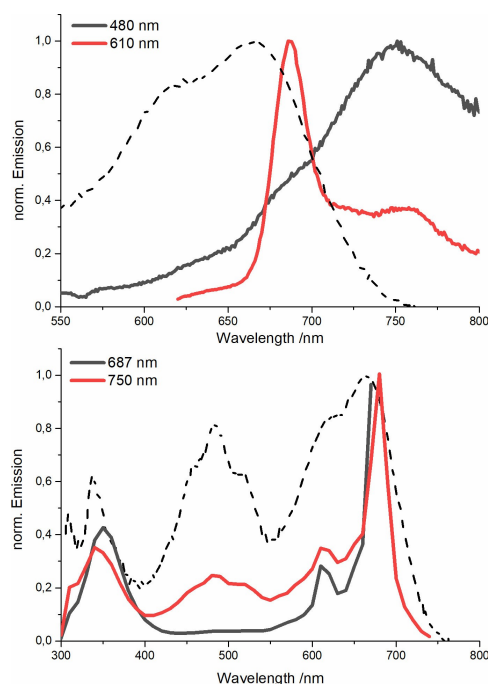


Figure 3. Fluorescence (top) and excitation (bottom) spectra of **3** in pyridine (2×10^{-6} M) following either 480 or 610 nm excitation as well as either 687 or 750 nm fluorescence, respectively. The dashed spectra reflects in each case the absorption spectrum.

710 nm, respectively, and Soret-band absorptions at 300 and 335 nm, respectively. In short, the absorptions of SubPc **2** and ZnPc **1** complement each other. In toluene, **3** gives rise to maxima in the 300 to 350 nm, the 450 to 600 nm, and the 650 to 850 nm ranges, which we ascribe to ZnPc / SubPc Soret-band absorptions, SubPc Q-band absorptions, and ZnPc Q-band absorptions, respectively. Going from toluene to anisole and benzonitrile leads to subsequent blue-shifts of all absorptions (Figure S7.1).

At ZnPc **1** concentrations as low as 2×10^{-7} M, aggregation is seen to evolve. Most notable for aggregation is the broadening of the Q-band absorption. In stark contrast, evidence for quantitative aggregation of ZnPc-SubPc **3** already sets in at concentrations of $\leq 5 \times 10^{-9}$ M. In toluene, quantitative deaggregation was impossible even when employing saturated solutions of 4-methylaminopyridine (DMAP) (Figure S7.2). More successful was the use of benzonitrile albeit in the presence of a DMAP excess. Under these conditions, maxima at 460, 485, and 515 nm as well as 620 and 668 nm stem from SubPc and ZnPc, respectively. Moreover, monomeric **3** was realized in the less polar pyridine, for which a maximum evolved at 664 nm. Importantly, monomers of **3** are characterized by panchromatic absorptions starting at 300 nm all the way up to 750 nm.

Fluorescence spectra of SubPc **2** and ZnPc **1** were taken in toluene (Figure S7.3). The corresponding fluorescence quantum yields were calculated versus ZnTtBuPc and F₁₂SubPc–OPh (also in toluene) as references.^[15–16] Both of them feature fluorescence spectra that are essential mirror images of their absorption spectra with maxima at 720 and 581 nm, respectively. The corresponding fluorescence quantum yields are

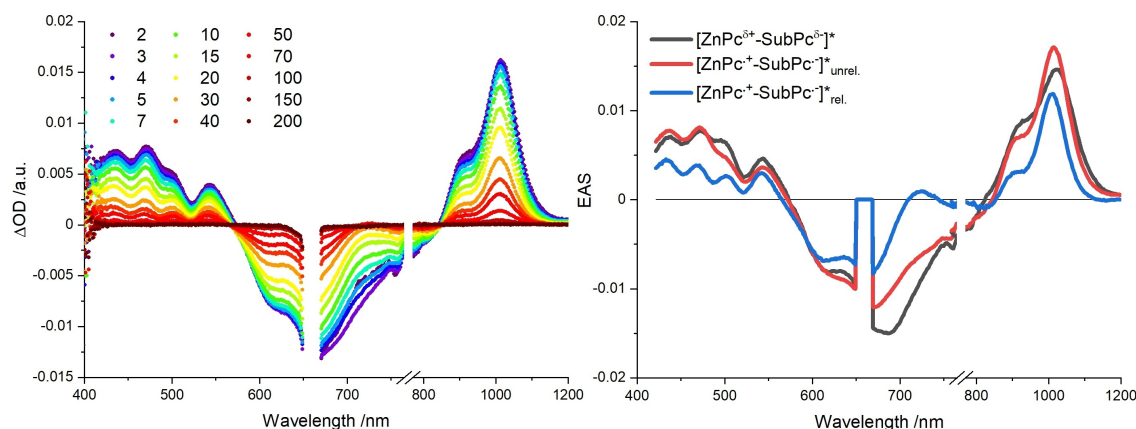


Figure 4. Differential absorption spectra recorded upon femtosecond flash-photolysis of ZnPc-SubPc **3** in PhCN with excess amounts of DMAP and photoexcitation at 660 nm with time delays between 2 and 200 ps (left) and corresponding evolution associated spectra (right).

0.259 for ZnPc **1** and 0.175 for SubPc **2**. Interestingly, a closer look at the 3D fluorescence heat map recorded for monomers of **3** in pyridine reveals two fluorescence maxima: 687 and 750 nm. From Figures 3 and S7.4 we conclude that the 687 nm maximum originates from excitation solely into the ZnPc. When turning to the 750 nm maximum in the 3D fluorescence heat map, which most likely stems from a ZnPc-centered species, its excitation spectrum corroborates that it matches the absorption spectrum reasonably well. In other words, panchromatic excitation, namely SubPc and ZnPc populates the same low energy state. In the case of SubPc excitation an energy transfer to the energetically lower-lying ZnPc is the *modus operandi*.

Femtosecond transient absorption spectroscopy

Photoexcitation into the SubPc Q-band absorption of **2** results into transient absorption changes that are dominated by ground state bleaching between 500 and 600 nm following by stimulated fluorescence at 625 nm. Besides these minima, 430 and 900 nm maxima are detected (Figure S8.1). A Glotaran fit based on a three species model includes a vibrationally hot singlet excited state, which solvent and vibration relaxes to the relaxed singlet excited state, before forming the triplet excited state via intersystem crossing. Notable is a substantial blue-shift of the broad 900 nm maximum to a sharp 600 nm maximum. The corresponding lifetimes of the two singlet excited state species are 14 ps and 1.6 ns, respectively, while the triplet excited state persists beyond the maximum time-delay of 5.5 ns.

Finally, transient absorption spectra of monomers of **3** were recorded using benzonitrile as solvent and an excess of DMAP (Figure 4). The corresponding raw data, upon photoexcitation into the ZnPc Q-band absorption, were fit by a kinetic model based on three consecutively formed species. Their respective lifetimes are 1, 12 and 26 ps. Common to all species are characteristics in the range of SubPc absorption, that is, from 400 to 575 nm and ZnPc absorption, that is, from 575 and 825 nm. For example, minima at 452, 488, and 521 nm correlate

with the ground state absorption of SubPc, while those at 615 and around 660 nm stem from ZnPc. In addition, maxima around 435, 470, 500, and 542 nm complement the SubPc characteristics. At last, the 905 nm shoulder and the 1020 nm maximum should be mentioned, which are likely to be associated with ZnPc.

The fact that ZnPc Q-band photoexcitation leads to SubPc- and ZnPc-centered features corroborates the strong coupling, which we already concluded from the steady-state measurements in the form of a charge transfer. Important is in this context that the 1020 nm maximum, which resembles the fingerprint absorption seen upon spectroelectrochemical oxidation of ZnPc **1**, is subject to subtle changes in the three different species: 1021 nm for the first species, 1014 nm for the second species, 1010 nm for the third species. Along with the latter is the 700 nm minimum, which is stimulated fluorescence rather than ground state bleaching, and, which is only seen in the first species. Accordingly, we ascribe the first species to a weakly emissive charge transfer, which undergoes a rapid charge separation and eventually vibrational relaxation before reinstating the ground state. Notable is also that the vibrationally relaxed charge separated state reveals a 725 nm maximum, which is in agreement with the spectroelectrochemical reduction of SubPc. In essence, identification of the fingerprints due to the one-electron oxidized form of ZnPc and the one-electron reduced form of SubPc assists in confirming full charge separation occurring from a photoexcited charge transfer state.

Conclusion

A novel conjugate based on an electron donating carbazole-based Pc and an electron accepting perfluorinated SubPc has been successfully prepared. The synthetic route comprises a key Sonogashira cross-coupling reaction over the SubPc axial position, which was previously functionalized with a free alkyne moiety. This conjugate displays a panchromatic absorption that ranges from 400 to 700 nm and arises from the combination absorption of both porphyrinic components. Electrochemical

measurements of the corresponding precursors revealed that the SubPc is the electron acceptor, while the Pc is the electron donor. Thus, as demonstrated by time-resolved emission and transient absorption at different time scales, an electron transfer process followed by the formation of a charge separated state $\text{Pc}^+ - \text{SubPc}^-$ is enabled upon photoexcitation. From these results, it was concluded that carbazole-Pc and perfluorinated SubPc are excellent components for the preparation of D-A systems. Our study demonstrates that a careful functionalization of porphyrinoids enable the formation of long-lived CS photoexcited states, which ensembles a model photosynthetic reaction center and, therefore, can be exploited in molecular photovoltaics.

Experimental Section

Synthetic procedures

4,5-di(9H-carbazol-9-yl)phthalonitrile^[11a] and $\text{F}_{12}\text{SubPc-Cl}$ ^[12] were prepared as described in the literature.

2-Iodo-9,10,16,17,23,24-hexa(9H-carbazol-yl)-29H,31H-phthalocyanato zinc (II) (1) (mixture with (Carbazole)₈-Pc)

A mixture of 4,5-di(9H-carbazol-9-yl)phthalonitrile (1.36 g, 0.80 mmol), 4-iodophthalonitrile (0.05 g, 0.20 mmol), and ZnCl_2 (0.03 mg, 0.20 mmol) was refluxed in DMAE (2 mL) under argon for 8 h. After cooling, the solvent was concentrated under reduced pressure to offer a dark green solid residue composed of a statistical mixture of (Carbazole)₈-Pc (A4) and the iodo-containing phthalocyanines (A3B, A2B2 and AB3). The resulting green precipitate was filtered off, washed several times with methanol, distilled water and dried under vacuum, followed by recrystallization with THF: MeOH to get rid of AB3. The crude product was purified by column chromatography on silica gel using CHCl_3 /methanol 95:5 (v/v) as eluent, and the residue was further purified by size exclusion chromatography in CHCl_3 . Both, (Carbazole)₆-ZnPc 1 and symmetrical [(Carbazole)₈-ZnPc] were isolated as a 1:2 mixture in good purity as a dark green solid in 35% Yield. $^1\text{H-NMR}$ (600 MHz, DMSO-d_6 , 95°): δ (ppm) = 10.01–9.83 (m, 27H), 9.27 (d, $^3J_{\text{H-H}} = 9$ Hz, 1H), 8.50 (d, $^3J_{\text{H-H}} = 9$ Hz, 1H), 7.62 (bs, 50H), 7.41 (d, $^3J_{\text{H-H}} = 7.8$ Hz, 50H), 6.97 (bs, 50H), 6.87 (bs, 50H). $^{13}\text{C-NMR}$ (150 MHz, DMSO-d_6 , 95°): δ (ppm) = 109.95, 119.97, 122.76, 125.26, 135.67, 138.41, 140.27, 153.04. HR-MS (MALDI-TOF, DCTB): m/z Calcd for $[\text{C}_{104}\text{H}_{57}\text{IN}_4\text{Zn}]$: 1694.9436; Found: (1899.1511 + 1694.9950). UV-Vis (CDCl_3): λ_{max} (nm) ($\log \epsilon$ ($\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$)) = 707 (5.52), 677 (4.71), 636 (4.74), 359 (4.91), 338 (4.95), 326 (4.90), 293 (4.71). FT-IR (KBr): ν (cm^{-1}) = 2955, 2922, 2853, 1715, 1597, 1493, 1453, 1378, 1275, 1205, 1110, 1097 (C–I), 1052, 887, 856, 742, 726.

Ethynyl-

1,2,3,4,8,9,10,11,15,16,17,18-dodecafluorosubphthalocyanateboron (2)^[13b]

To a 10 mL Schlenk flask equipped with a magnetic stirrer, dry *o*-dichlorobenzene (3 mL) deoxygenated via three Freeze-Pump-Thaw cycles was added to a mixture of the corresponding $\text{F}_{12}\text{SubPc-Cl}$ (0.40 mmol) and AlCl_3 (1.60 mmol). The solution was stirred at 25 °C for 10 minutes under argon atmosphere. Ethynyltrimethylsilane (2.00 mmol) was added and the solution was stirred at 25 °C for 5 minutes. Pyridine (0.1 mL) was added and solvent was removed by vacuum distillation. The resulting solid was dissolved in CH_2Cl_2 ,

passed through a short silica plug, and subjected to column chromatography on silica gel using toluene/heptane 1:1 as eluent. SubPc 2 was isolated as a bright magenta solid in 90% yield. $^1\text{H-NMR}$ (300 MHz, CDCl_3): δ (ppm) = 1.11 (s, 1H). $^{11}\text{B-NMR}$ (96 MHz, CDCl_3): δ (ppm) = −21.44. $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): δ (ppm) = 147.8, 144.5 (m), 141.2 (m), 115.0 (m), 84.7, 77.4. $^{19}\text{F-NMR}$ (282 MHz, CDCl_3): δ (ppm) = −137.0 (m, 6F), −147.7 (m, 6F). MS (APCI+): m/z = 637.03 $[\text{M} + \text{H}]^+$. HPLSI-MS (APCI+): m/z Calcd for $[(\text{C}_{26}\text{H}_5\text{B}_1\text{F}_{12}\text{N}_6)\text{H}]$: 637.0241; Found: 637.0258. UV-Vis (CHCl_3): λ_{max} (nm) ($\log \epsilon$ ($\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$)) = 574 (5.0), 556 (sh), 532 (4.6), 494 (sh), 308 (4.4). FT-IR: ν (cm^{-1}) = 3318 (C≡C–H), 2952, 2648, 2084 (C≡C–), 1652, 1606, 1530, 1480, 1426, 1392, 1338, 1286, 1262, 1214, 1160, 1102, 1080, 1054, 962, 880, 838, 772, 738, 714, 684, 670, 592, 568, 466.

Subphthalocyanine-Phthalocyanine dyad (3):

In a 10 mL Schlenk, SubPc 2 (50.4 mg, 0.079 mmol), Pc 1 (43.2 mg, 0.025 mmol), $^t\text{BuXPhosPd G3}$ (2.0 mg, 0.003 mmol) and CuI (1.0 mg, 0.005 mmol) were added. Dry THF (3 mL) and dry Et_3N (0.75 mL), both deoxygenated via three Freeze-Pump-Thaw cycles were added, and the solution was stirred at 25 °C under argon atmosphere for 16 hours. The reaction slurry was dissolved in CH_2Cl_2 and passed through a short silica plug. The solvent was removed by vacuum distillation and the crude was subjected to column chromatography on silica gel using CH_2Cl_2 as eluent. The desired compound was further purified by size exclusion chromatography in CHCl_3 . ZnPc-SubPc 3 was isolated as a dark purple solid in 38% yield. $^1\text{H-NMR}$ (600 MHz, DMSO-d_6 , 95 °C): δ (ppm) = 10.01–9.96 (m, 6H), 9.67 (s, 1H), 9.23 (d, $^3J_{\text{H-H}} = 9$ Hz, 1H), 8.47 (d, $^3J_{\text{H-H}} = 9$ Hz, 1H), 7.51 (bs, 12H), 7.30 (d, $^3J_{\text{H-H}} = 7.8$ Hz, 12H), 6.86 (bs, 12H), 6.77 (bs, 12H). $^{11}\text{B-NMR}$ (96 MHz, DMSO-d_6): δ (ppm) = −20.07. $^{19}\text{F-NMR}$ (282 MHz, DMSO-d_6): δ (ppm) = −136.0 (m, 6F), −146.7 (m, 6F). The low solubility of this product prevented the detection of any signal in both $^{13}\text{C-NMR}$ and mass spectrometry. UV-Vis (Toluene): λ_{max} (nm) ($\log \epsilon$ ($\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$)) = 778 (4.86), 716 (4.74), 536 (4.51), 521 (4.57), 497 (4.49), 441 (4.33), 322 (4.70). FT-IR (KBr): ν (cm^{-1}) = 2952, 2642, 2083 (C≡C–), 1609, 1482, 1426, 1392, 1338, 1286, 1262, 1112, 1080, 1054, 962, 883, 840, 769, 684, 676, 596, 468.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: phthalocyanines • subphthalocyanines • near infrared • electron transfer • organic photovoltaics

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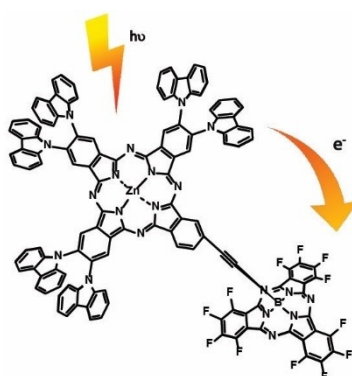
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RESEARCH ARTICLES

Molecular photovoltaics: A novel photoactive dyad based on an electron-donating phthalocyanine (Pc) and an electron-accepting subphthalocyanine (SubPc) has been prepared. The conjugate displays a panchromatic absorption, resulting in an electron transfer process followed by the formation of a charge separated state ($\text{Pc}^+ - \text{SubPc}^-$) upon photoexcitation.



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1 – 7

A Novel Electron Donor-Acceptor Carbazole-Zn(II)Phthalocyanine – Perfluorinated Subphthalocyanine Conjugate: Synthesis, Characterization, and Photoinduced Electron-Transfer

