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Meso-substituted Porphyrin Derivatives via Palladium-Catalyzed Amination Showing Wide Range Visible Absorption: Synthesis and Photophysical Studies

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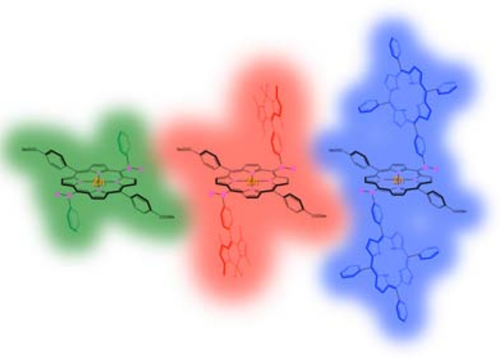
Supporting Information

ABSTRACT: In recent years, there has been a growing interest in the design and synthesis of chromophores, which absorb in a wide region of the visible spectrum, as these constitute promising candidates for use as sensitizers in various solar energy conversion schemes. In this work, a palladium-catalyzed coupling reaction was employed in the synthesis of molecular triads in which two porphyrin or boron dipyrrin (BDP) chromophores are linked to the meso positions of a central Zn porphyrin (**PZn**) ring via an amino group. In the resulting conjugates, which strongly absorb over most of the visible region, the electronic properties of the constituent chromophores are largely retained while detailed emission experiments reveal the energy transfer pathways that occur in each triad.



INTRODUCTION

Porphyrins are one class of organic chromophores that are widely studied due to their key roles in many biological processes.[1] Because of their attractive chemical properties, they are used in electron and oxygen transfer,[2,3] binding or transport of small molecules,[4,5] light harvesting and photosynthesis.[6−9] Moreover, inspired by nature porphyrin molecules are widely used as promising photosensitizers for dye-sensitized solar cells (DSSCs).[10−14] Researchers so far have synthesized various substituted porphyrins and tested them as sensitizers for DSSCs, but the conversion efficiencies remained below 8%. Very recently, Grätzel and co-workers prepared a porphyrin dye with one of the best conversion efficiencies, greater than 12%.[15] This dye was based on a donor-π-acceptor motif. In an effort to prepare more efficient molecules we focused on changing the peripheral substituents of the porphyrin and adding additional chromophores to the main porphyrin core, in order to build panchromatic dyes. Therefore, a central metalated porphyrin is derivatized with (i) two free-base porphyrin molecules and (ii) two boron dipyrrin (BDP) molecules forming trimeric compounds. Free base porphyrins were selected because they absorb light in different energy compared to metalated ones resulting a trimer that will absorb in a wider range of the visible region. On the other hand BDP are highly absorbing antenna chromophores, which act as sensitizers of the porphyrin based excited state. Moreover, BDP molecules combine a high fluorescence quantum yield, a relatively long lifetime, a suitable excited state energy and excellent photostability.[16−18] Attachment of different functional groups to the porphyrin periphery often involves elaborate and multistep synthetic strategies and tedious purification procedures. Furthermore, potential incompatibility between a component in the synthetic strategy and the conditions used for cyclization greatly limits the functional groups that can be present during synthesis. Therefore, the functionalization on the central porphyrin was performed via palladium-catalyzed amination to *meso*-brominated porphyrin. In recent years, palladium catalyzed couplings have been used extensively to prepare many novel mono and oligoporphyrins for a variety of applications. For example, *meso*-linked oligomers of various dimension,[19−21] conjugated multichromophores,[22,23] dendrimeric structures,[24] and self-assembled arrays have been reported.[25] Most of these have involved carbon−carbon couplings, but recently couplings with softer nucleophiles have been achieved, for example, C−N, C−O, and C−S bond formation to the porphyrin periphery.[26−43] The above approach allows the synthesis of a number of derivatives using a single halogenated porphyrin under mild conditions and high yields, and we expected compounds with larger absorption bands in the visible region. All the examples of this kind of compounds presented in the literature are focused mainly on the synthesis and have not been photophysically studied.

With all the above in mind we synthesized C−N linked trimeric molecules **$TPPH_2$-PZn-$TPPH_2$** and **BDP-PZn-BDP**. To the best of our knowledge, this is the first time that trimers have been prepared and coupled with this type of linkage. This

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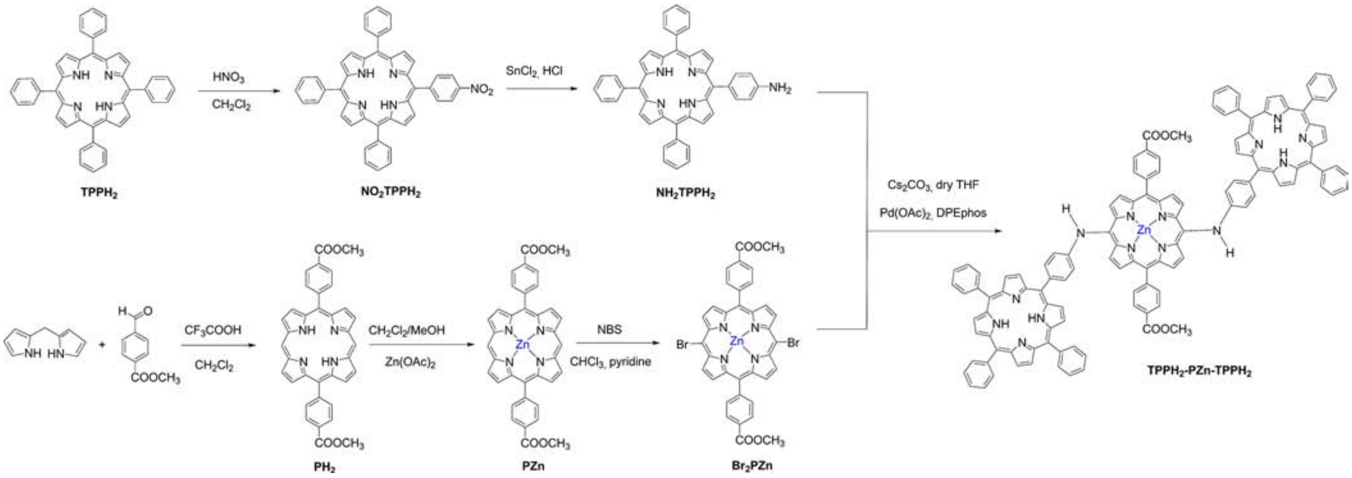
Scheme 1. Synthesis of Trimer $TPPH_2$−PZn−$TPPH_2$

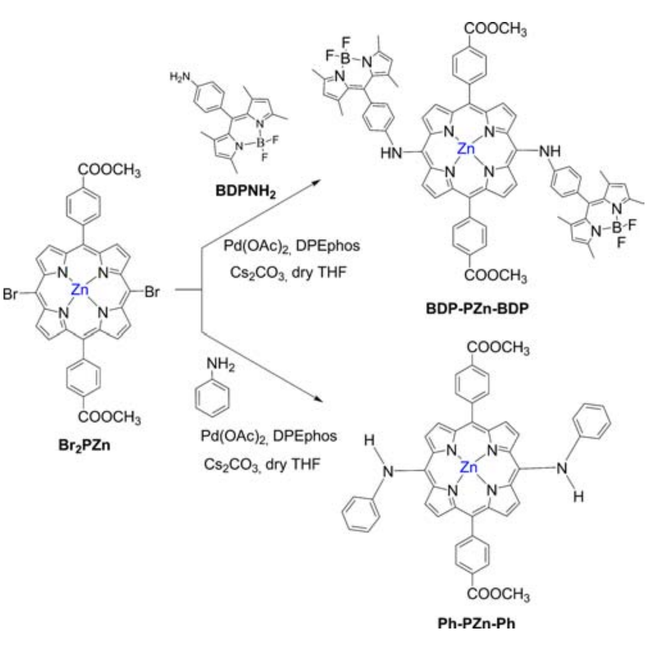


type of bond was chosen to connect other chromophores to the meso position, which have different absorption and emission properties of this type of porphyrins. The triads absorb light over most of the visible region, and bear ester groups that can be hydrolyzed to acid anchoring groups for further DSSC studies. **BDP-PZn-BDP** is the most interesting of the two trimers, where the BDP molecules supplement the porphyrin absorption. Moreover, triad **$TPPH_2$-PZn-$TPPH_2$** seemed interesting because of different dynamic between the central metalated mesosubstituted porphyrin and the two peripheral free base porphyrins. In addition, a novel detailed photophysical study to understand a possible communication between the different chromophores was performed.

■ RESULTS AND DISCUSSION

Synthesis and Characterization. The synthesis of all compounds presented in this paper is shown in Schemes 1 and 2. **NH_2TPPH_2** porphyrin was synthesized in two steps following a literature procedure incorporated with our own modification in a 63% overall yield.[44] Porphyrin **PH_2** was prepared in one step by acid-catalyzed condensation of dipyrromethane with 4-carboxymethylbenzaldehyde, followed in situ oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). Metalation with zinc acetate yielded porphyrin **PZn**, and subsequent bromination with two equivalents of N-bromosuccinimide (NBS) in the presence of pyridine gave dibromo porphyrin **Br_2PZn** in an excellent yield.[45,46] Triad porphyrins were successfully synthesized under palladium-catalyzed double amination conditions with coupling of Zn-*meso*-dibromoporphyrin **Br_2PZn** (1 equiv) and three different amines. The synthesis can be carried out under mild conditions, typically giving high yields. All reactions were carried out in THF at 68 °C under argon atmosphere with excess amine (4.8 equiv), and the use of 0.1 equiv of palladium acetate, 0.15 equiv of bis(2-diphenylphosphinophenyl)ether (DPEphos) in the presence of 2.8 equiv of cesium carbonate as a weak base. The desired products were separated by flash column chromatography and the excess of amines were recovered. First, Zn-*meso*-dibrominated porphyrin (**Br_2PZn**) was coupled with **NH_2TPPH_2** in 63% yield. The progress of the reaction was monitored by TLC and after 4 days porphyrin **Br_2PZn** had been consumed forming the desired compound (**$TPPH_2$-PZn-$TPPH_2$**). In addition a trace amount of monoamination product was present. To the best of our knowledge, this is the first time that a triad porphyrin has been synthesized linked with a NH group. Then **$BDPNH_2$** (Scheme 2) was used as an amine and triad porphyrin **BDP-PZn-BDP** was prepared in high yield, 93%, the reaction was again monitored by TLC and after 20 h all starting material had been consumed. Compound **$BDPNH_2$** was synthesized according to the literature.[47] Finally, under the same conditions aniline was coupled with porphyrin **Br_2PZn** to obtain compound **Ph-PZn-Ph** in 91% yield. A trace amount of monoamination byproduct was also present after the flash column chromatography and was removed by washing the product with CH_2Cl_2, since triad **Ph-PZn-Ph** is not soluble in this solvent. Single crystals of this compound were obtained suitable for diffraction analysis. All new compounds were characterized on the basis of their ^1H and ^{13}C NMR spectra, MALDI-TOF mass spectra and elemental analyses. Further details on their synthesis and characterization can be found in the Experimental Section.

Scheme 2. Synthesis of Trimers BDP-PZn-BDP and Ph-BDP-Ph



As already mentioned all compounds were fully characterized by NMR experiments including ^1H, ^{13}C, COSY, HMQC, and

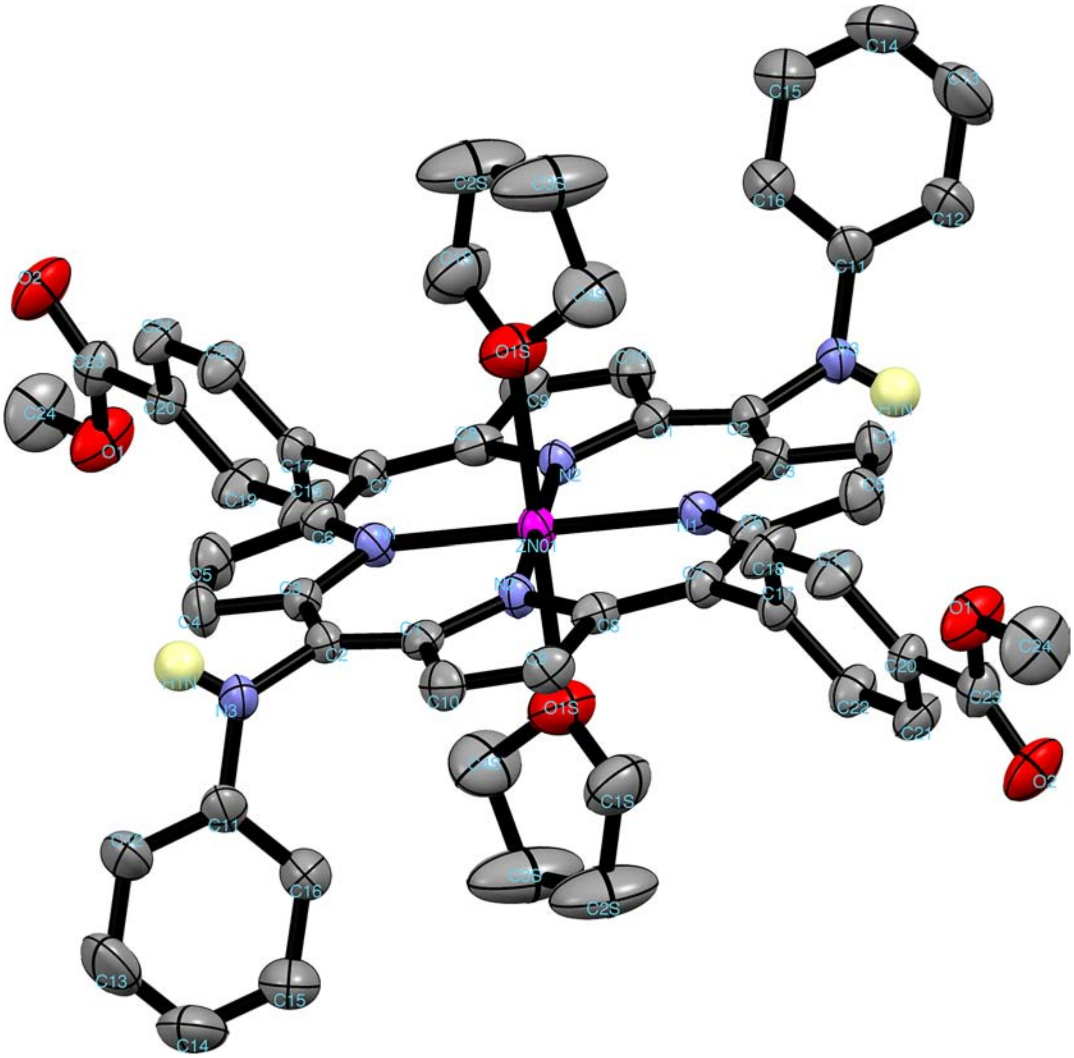


Figure 1. ORTEP view of molecular structure **Ph-PZn-Ph**·3THF. Thermal ellipsoids are drawn at 50% occupancy. Hydrogen atoms have been omitted for clarity except amine hydrogen (labeled H1N) and one of the THF molecules found in the asymmetric unit. Atoms having the same label are generated from each other by symmetry.

HMBC. In the ^{1}H NMR (d_8-THF) spectra of all trimeric compounds the protons of the NH bridge are considerably shifted downfield at 9.04, 9.54, and 9.19 ppm, respectively compared to the free amino components. All synthesized products can exist in a mixture of two atropisomers ($\alpha\alpha$- and $\alpha\beta$-isomers), but in both ^{1}H and ^{13}C spectra only one set of resonances were observed indicating that there is a free rotation around the C−N bond at ambient temperature, as has been reported in the literature.[29] In the case of trimer **TPPH$_2$-PZn-TPPH$_2$** we observed a split of the peak corresponding to the NH bridge whereas for compounds **BDP-PZn-BDP** and **Ph-PZn-Ph** only a singlet peak was present (Supporting Information). Possibly, in the case of **TPPH$_2$-PZn-TPPH$_2$**, where three porphyrins are linked, the rotation around the bond between the amino nitrogen atom and the porphyrin *meso*-carbon atom has a higher rotation barrier compared to the other two trimers.

Single-Crystal X-ray Diffraction Structures. An ORTEP of **Ph-PZn-Ph** is depicted in Figure 1 and selected bonds and angles in Supporting Information Table S1. The porphyrin plane displays a slight ruffling from planarity (0.0336) and the distances and angles of **Ph-PZn-Ph** are similar to Zn-tetraphenyl pophyrin.[48] Due to the coordination of Zn with two THF molecules, Zn is in the plane of the four N atoms[49] contrary to four or five coordinated Zn-porphyrins. The average bond distance of Zn−N is 2.0645 Å. Two THF molecules are weakly bound axially to Zn (Zn−O distance 2.403 Å). The dihedral angle formed by the plane P_1 (of the phenyl ring of the aniline) to the P2 (plane of the porphyrin ring) is 81.51° (0.14) and is slightly bigger than the other phenyl ring forms (73.99° (0.12)). The torsion angle of aniline (C_{11}−N_3−C_{meso}−C_a) is 88.77°.

Close intermolecular packing arrangement is observed, mainly the short contact of 2.239 Å formed by the H of the secondary amine with the carbonyl group of the ester of a neighboring porphyrin ring. The hydrogen of the THF (H_3) form short contacts (2.366 Å) with the β-H_9 and with aniline group [H_{1s} with C_{14}(2.886 Å)] (Figure 2).

Electrochemistry. Cyclic voltammetry was used in order to study the electrochemical properties of the trimers. For trimer **TPPH$_2$-PZn-TPPH$_2$** it was not possible to obtain any voltammograms in either CH_2Cl_2, THF, or acetonitrile because of stability and/or solubility difficulties. Trimer **BDP-PZn-BDP** was studied in CH_2Cl_2 and **Ph-PZn-Ph** in THF, all data are

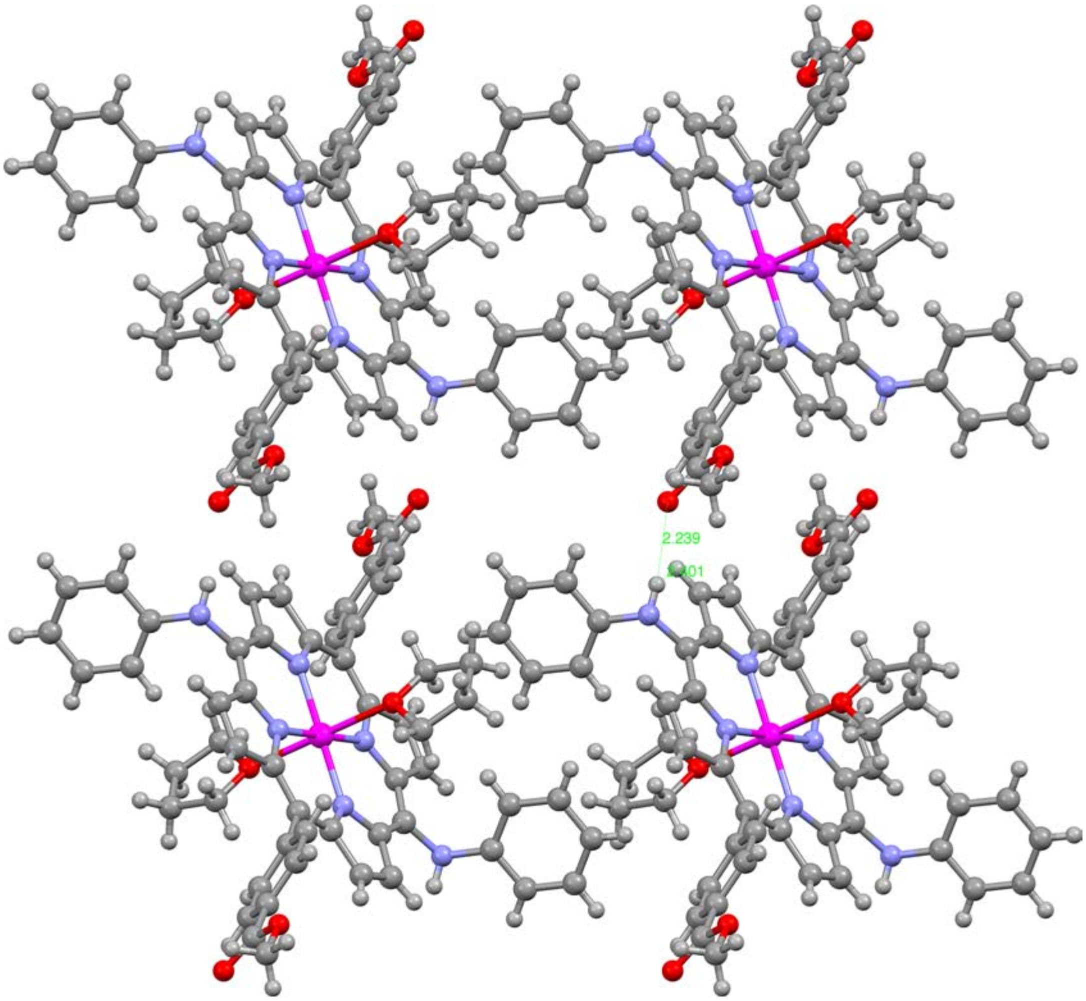


Figure 2. Packing arrangement of trimeric compound **Ph-PZn-Ph**. The packing was viewed along *a* axis.

reported vs the ferrocene/ferrocenium couple (Fc/Fc$^+$). Cyclic voltammograms are shown in Figure 3. **BDPNH$_2$** in CH_2Cl_2 showed a reversible oxidation at 0.76 V due to formation of the BDP cationic radical (Figure 3c).[50,51] Reference triad **Ph-PZn-Ph** in THF showed one reversible oxidation at −0.01 V, attributed to the oxidation of the porphyrin ring[1] (Figure 3b).

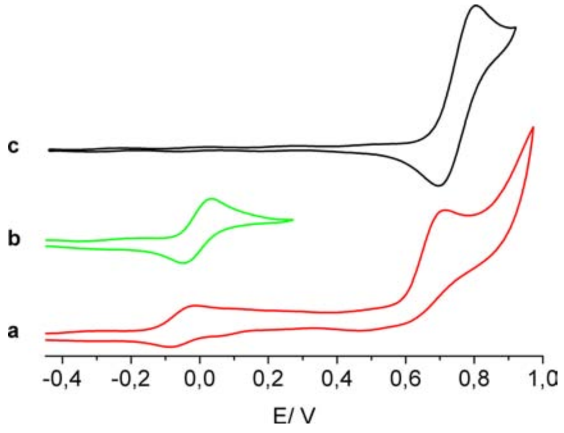


Figure 3. Cyclic voltammograms of (a) **BDP-PZn-BDP** in CH_2Cl_2, (b) **Ph-PZn-Ph** in THF and (c) **BDPNH$_2$** in CH_2Cl_2 containing 0.1 M (TBA)PF_6 as supporting electrolyte. The voltages are vs Fc/Fc$^+$.

The cyclic voltammetry of **BDP-PZn-BDP** shows one reversible process at 0.04 V and one irreversible at 0.76 V. The first one is attributed to the first porphyrin oxidation and the second to the oxidation of the BDP, respectively (Figure 3a). This feature is also corroborated by DFT studies. The HOMO localized on Zn-porphyrin corresponds to the first oxidation of **BDP-PZn-BDP**, while HOMO-1 localized on the BDP unit, and corresponds to the second oxidation. In addition triad **BDP-PZn-BDP** shows one reversible process at −1.74 V, attributed to BDP reduction (Supporting Information Figure S9 and Table S2). Porphyrin reductions in the case of **BDP-PZn-BDP** and **Ph-PZn-Ph** could not be observed.

Photophysical Properties. *Electronic Absorption Spectra.* The electronic absorption spectra of compounds **NH$_2$TPPH$_2$**, **TPPH$_2$-PZn-TPPH$_2$**, and **Ph-PZn-Ph** are presented in Figure 4, and those of compounds **BDPNH$_2$**, **BDP-PZn-BDP**, and **Ph-PZn-Ph** in Figure 5. All absorption spectra were measured in toluene. The absorption maxima and molar absorption coefficients (ε) of the Soret and Q bands are listed in Table 1. Compound **NH$_2$TPPH$_2$** exhibits typical free-base porphyrin absorption features[1] with an intense Soret band at 422 nm and moderate Q bands at 516, 552, 594, and 650 nm. **Ph-PZn-Ph** shows the characteristic bands of Zn-meso-arylamino substituted porphyrins with a Soret at 444 nm and two Q bands at 561 and 614 nm.[29] The spectrum of triad **TPPH$_2$-PZn-TPPH$_2$** shows the characteristic absorptions of

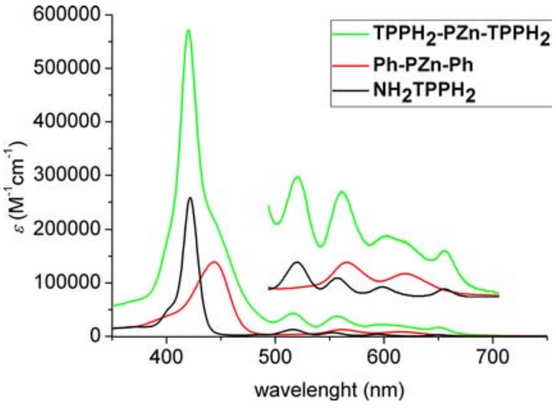


Figure 4. UV−vis absorption spectra of **NH_2TPPH_2**, **$TPPH_2$-PZn-$TPPH_2$**, and **Ph-PZn-Ph** in toluene and expansion of the Q bands.

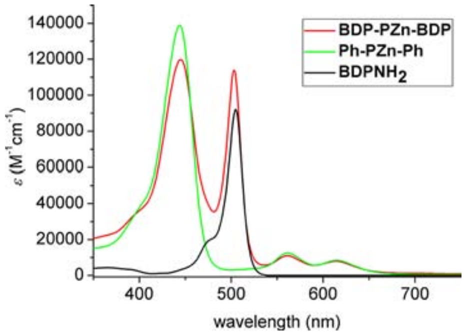


Figure 5. UV−vis absorption spectra of **$BDPNH_2$**, **BDP-PZn-BDP**, and **Ph-PZn-Ph** in toluene.

Table 1. Spectroscopic Data of Trimeric Compounds and NH_2TPPH_2 and $BDPNH_2$

	absorption	emission		
compound	λ_{max}/nm (ε/mM^{-1}cm^{-1})	λ_{max}/nm	Φ	τ/ns
$TPPH_2$-PZn-$TPPH_2$	420 (571.6), 445 sh (213.6) 516 (17.2), 556 (15.0), 595 (8.7), 650 (6.6)	661, 719	0.12	2.9, 9.8
BDP-PZn-BDP	445 (119.8), 503 (113.9), 561 (11.0), 614 (8.1)	518, 684	0.073	3.8
Ph-PZn-Ph	444 (138.9), 561 (12.5), 614 (8.5)	698	0.11	3.5
NH_2TPPH_2	422 (258.2), 516 (12.5), 552 (6.8), 594 (3.6), 650 (2.8)	661, 722	0.11	8.8
$BDPNH_2$	505 (92.1)	519	0.38[a]	3.1[a]

[a] Values were taken from ref 51.

the individual macrocyclic components, namely strong absorptions assigned to the Zn-meso-arylamino substituted porphyrin and the **NH_2TPPH_2** chromophores (Figure 4). Triad **$TPPH_2$-PZn-$TPPH_2$** displays a broad Soret band centered at ~420 nm with a shoulder on its low energy side (~445 nm) attributable to the central porphyrin of the triad. Thus the absorption spectrum of **$TPPH_2$-PZn-$TPPH_2$** is largely the sum of those of its components indicating that there is little electronic interaction between the central and the peripheral porphyrin chromophores in the ground state. Similarly, the absorption spectrum of triad **BDP-PZn-BDP** (Figure 5) clearly shows features attributed to both of its components namely an intense absorption at 503 nm because of the BDP chromophores and the characteristic porphyrin based peaks (Soret at 445 nm and Q bands at 561, 614 nm).[50] Therefore, in triad **BDP-PZn-BDP**, as in **$TPPH_2$-PZn-$TPPH_2$**, there is weak electronic interaction between the two side BDP molecules and the central Zn-porphyrin in the ground state.

Emission Spectra. Steady state and time-resolved emission spectroscopy in toluene at ambient temperature was used in order to study all trimeric compounds. A summary of measured spectroscopic data is presented in Table 1. **$BDPNH_2$** shows the intense fluorescence of a BDP dye at 519 nm in toluene. **NH_2TPPH_2** displays two emission bands at 661 and 722 nm (Supporting Information Figure S10). The reference porphyrin **Ph-PZn-Ph** exhibits a broad fluorescence band with maximum at 698 nm and with a lifetime of τ_1 = 3.5 ns. Triad **$TPPH_2$-PZn-$TPPH_2$** when irradiated at 517 nm, corresponding to selective excitation of **NH_2TPPH_2**, shows emission which closely resembles that of the free base porphyrin chromophore at 661 and 719 nm (Figure 6a). Also, when excited at 467 nm corresponding mainly to the central Zn porphyrin, an almost identical spectrum was observed (Figure 6a). The excitation spectrum of **$TPPH_2$-PZn-$TPPH_2$** monitoring at the emission of the free base side porphyrins at 661 nm shows absorption features from both chromophores constituting **$TPPH_2$-PZn-$TPPH_2$** (Figure 6b). In addition, time-resolved emission measurements with pulsed excitation of mainly the peripheral porphyrins at 400 nm, show that **$TPPH_2$-PZn-$TPPH_2$** exhibits a dual exponential decay with lifetimes of 2.9 and 9.8 ns respectively. By comparison with the fluorescence lifetimes of reference compound **Ph-PZn-Ph** and **NH_2TPPH_2** we attribute the short lifetime of **$TPPH_2$-PZn-$TPPH_2$** to the central Zn-porphyrin and the longer one to the peripheral freebase porphyrins. Combination of the results from the excitation spectrum and the time-resolved fluorescence measurements of

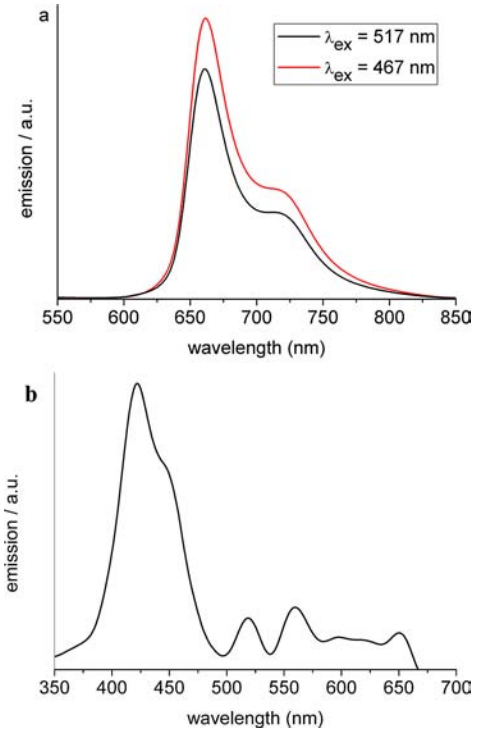


Figure 6. (a) Emission spectra of **$TPPH_2$-PZn-$TPPH_2$** exciting at 517 nm (peripheral porphyrin) and 467 nm (central porphyrin) and (b) excitation spectrum of **$TPPH_2$-PZn-$TPPH_2$** monitoring at 661 nm at room temperature in toluene.

$TPPH_2$-PZn-$TPPH_2$ show that excitation of either of the chromophores of **$TPPH_2$-PZn-$TPPH_2$** into its first singlet excited state results in partial energy transfer to the first singlet excited state of the other chromophore. This is expected because, as shown by the emission spectra of **$TPPH_2$-PZn-$TPPH_2$** and **Ph-PZn-Ph** in toluene glass at 77 K (Supporting Information Figure S11), the first singlet excited states of the freebase (1.88 eV) and Zn-porphyrin chromophores (1.82 eV) of **$TPPH_2$-PZn-$TPPH_2$**, are almost isoenergetic (energy deference of ca. 500 cm^{-1}). In the case of triad **BDP-PZn-BDP**, irradiation at 491 nm, corresponding to selective excitation of the two BDP units, results in emission from the Zn-porphyrin chromophore at 684 nm, as well as residual fluorescence from the two BDP groups at 518 nm (Figure 7a). The BDP based emission in **BDP-PZn-BDP** is strongly quenched when compared to the emission measured for **$BDPNH_2$**. Moreover, the excitation spectrum of **BDP-PZn-BDP** monitoring at the fluorescence of the porphyrin moiety at 685 nm shows an intense BDP absorption feature at 499 nm (Figure 7b). This is a clear indication of BDP to porphyrin singlet energy transfer following excitation of the BDP unit.

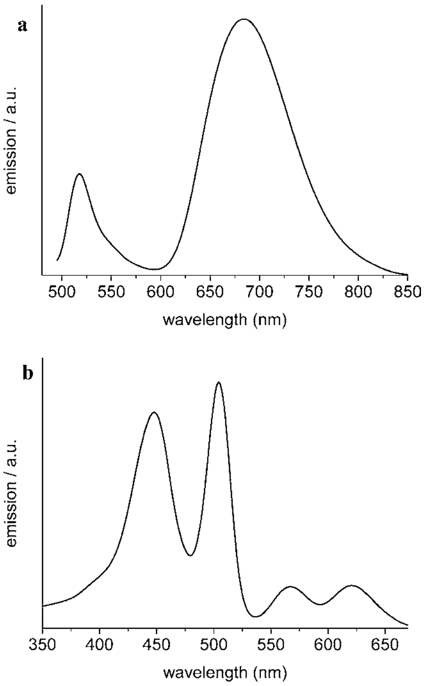


Figure 7. (a) Emission spectrum of **BDP-PZn-BDP** exciting at 491 nm (BDP chromophore) and (b) excitation spectrum of **BDP-PZn-BDP** monitoring at 685 nm at room temperature in toluene.

DFT Results. To obtain further insight about the electronic and orbital properties, density functional theory (DFT) calculations were carried out on **$TPPH_2$-PZn-$TPPH_2$**, **BDP-PZn-BDP**, and the reference compound **Ph-PZn-Ph**. The geometry optimized structures of compounds **$TPPH_2$-PZn-$TPPH_2$**, **BDP-PZn-BDP**, and **Ph-PZn-Ph** are shown in Figures 8 and 9 and Supporting Information Figure S12, respectively. A comparison of bond lengths in optimized **$TPPH_2$-PZn-$TPPH_2$** and **BDP-PZn-BDP** with X-ray data is presented in Table S3 (Supporting Information). Coordinates of the optimized

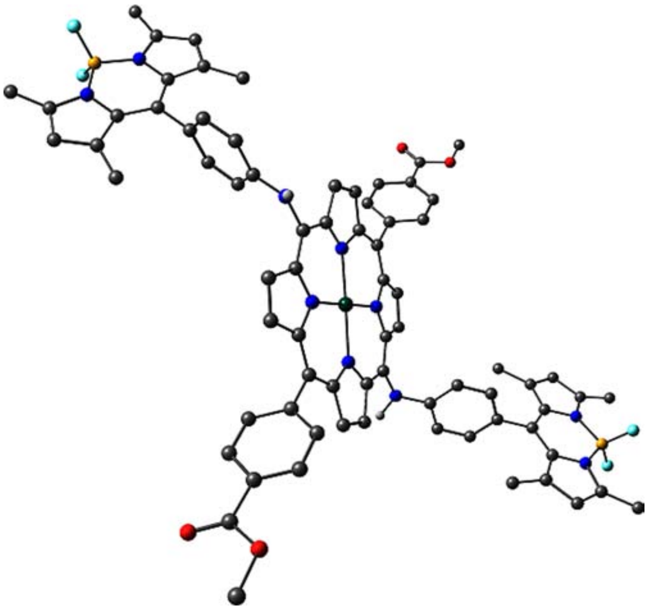


Figure 9. Gas phase geometry optimized (B3LYP/6-31G*) structure of **BDP-PZn-BDP**. Hydrogen atoms on the carbon have been omitted for clarity.

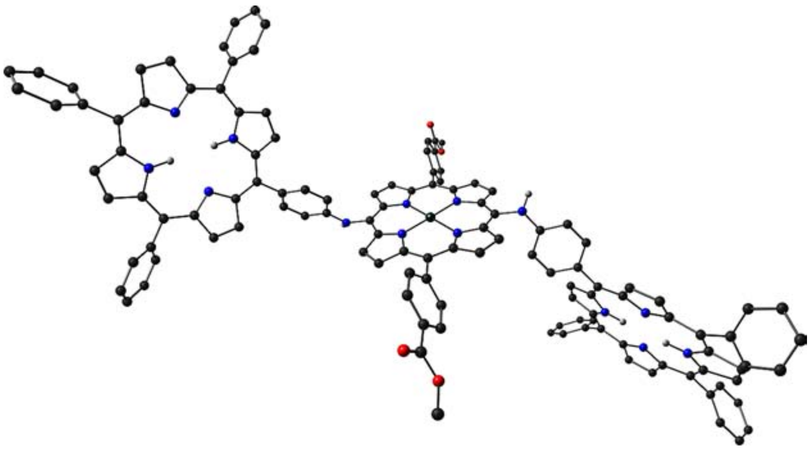


Figure 8. Gas phase geometry optimized (B3LYP/6-31G*) structure of **$TPPH_2$-PZn-$TPPH_2$**. Hydrogen atoms on the carbon have been omitted for clarity.

structures and their energies are given in Supporting Information Tables S4–S6. The electron density maps and the energies of the frontier molecular orbitals (FMOs) are shown in Supporting Information Figures S13 and S14. The geometry optimized structure of **$TPPH_2$-PZn-$TPPH_2$** revealed two trans oriented terminal porphyrins in the two sides of the central Zn-porphyrin ring (Figure 8). As observed from the Supporting Information Figure S13, the HOMO and HOMO-1 of the triad **$TPPH_2$-PZn-$TPPH_2$** are located on the terminal free base porphyrin moieties, with a partial delocalization through central Zn-porphyrin, while LUMO and LUMO + 1 orbitals are localized on the central Zn-porphyrin. This suggests that, very weak electronic communication exists between the chromophores in **$TPPH_2$-PZn-$TPPH_2$**.

In the case of **BDP-PZn-BDP**, HOMO is localized mainly on the central Zn-porphyrin with a little delocalization into the phenyl ring of the BDP units, while both HOMO − 1 and HOMO-2 are localized on two BDP units. In order to gain better insight into the electronic transitions we have carried out TDDFT calculation adopting coordinates from geometry optimized structures. The TDDFT calculation of **BDP-PZn-BDP** exhibited peaks at 597 and 592 nm (oscillator strengths 0.108 and 0.192 respectively), which corresponds to the Q bands of the porphyrin and assigned to a $\pi-\pi^*$ transition of the ring having major contribution from HOMO → LUMO + 1, HOMO → LUMO (Figure S15, Supporting Information). BDP $\pi-\pi^*$ transitions were observed much more blue-shifted at 474 nm (oscillator strength 0.430). Notably, the TDDFT calculated blue shift of BDP transitions was also reported earlier.[52,53] The calculated porphyrin soret band of the **BDP-PZn-BDP** appeared at 422 nm (oscillator strength 0.789) involving major contribution from HOMO − 3 → LUMO + 1. In the case of **$TPPH_2$-PZn-$TPPH_2$**, our approach to simulate vertical transitions in gas phase did not produce satisfactory results, while the solvent phase calculation was unsuccessful even after several attempts.

CONCLUSIONS

Novel triads were synthesized successfully via a palladium-catalyzed amination reaction in high yields. To the best of our knowledge, this is the first time that triads with an NH linkage on the porphyrin meso position have been prepared and photophysically studied. We believe that due to the facile preparation and the mild conditions involved this synthetic method can be applied to the synthesis of multichromophoric compounds. X-ray crystallography of compound **Ph-PZn-Ph** revealed the structure of this type of triads. Photophysical studies of triad **BDP-PZn-BDP** showed that selective excitation of the BDP chromophores into their first singlet excited state is followed by energy transfer to the first singlet excited state of the central Zn-porphyrin. Finally, the architecture of triads **$TPPH_2$-PZn-$TPPH_2$** and **BDP-PZn-BDP** makes them promising sensitizers for future studies of their photovoltaic properties into DSSCs.

EXPERIMENTAL SECTION

Materials. $BDPNH_2$ and porphyrins **PH_2**, **PZn**, and **Br_2PZn** were prepared according to the literature.[46,47] All dry solvents used were dried by the appropriate techniques.[54]

NMR Spectra. ^1H NMR spectra were recorded on Bruker AMX-500 MHz and Bruker DPX-300 MHz spectrometers as solutions in deuterated solvents by using the solvent peak as the internal standard.

Mass Spectra. High-resolution mass spectra were performed on a Bruker ultrafleXtreme MALDI-TOF/TOF spectrometer.

X-ray Crystallography. Single crystals for **Ph-PZn-Ph** were obtained by slow evaporation of a THF/pentane mixture (1:1 v/v). The crystals were protected with paratone-N and were mounted for data collection. Intensity data were collected at STOE IPDSII diffractometer using graphite monochromated Mo–Kα radiation (λ = 0.71070 Å). The data were collected at 300 K using two ω scans with an increment of 1°, an exposure time of 2 min for each oscillation and distance of 100 mm. Data reduction including absorption correction and cell dimension post refinement were performed using X-Area software package. The structure was solved using SIR 92[55] program and refined by full matrix least-squares on F^2 values for all reflections using (SHELX-S97). All nonhydrogen atoms were refined with anisotropic displacement parameters using SHELXL-97.[56] All the hydrogen atoms were introduced at calculated positions as riding on bonded atoms. The deposited CIF remains in the Supplementary Data Archive and is made freely available for bona fide research purposes via http://www.ccdc.cam.ac.uk/data_request/cif.

Electrochemistry. Cyclic and square wave voltammetry experiments were carried out at room temperature using an AutoLab PGSTAT20 potentiostat and appropriate routines available in the operating software (GPES, version 4.9). All measurements were carried out in freshly distilled and deoxygenated dichloromethane and THF with a solute concentration of ~1.0 mM in the presence of tetrabutylammonium hexafluorophosphate (0.1 M) as supporting electrolyte. A three-electrode cell setup was used with a platinum working electrode, a saturated calomel (SCE) reference electrode, and a platinum wire as counter electrode. All potentials are reported versus the ferrocene/ferrocenium couple (0.44 V versus SCE under the above conditions).

Photophysical Measurements. UV–vis absorption spectra were measured on a Shimadzu UV-1700 spectrophotometer using 10 mm path-length cuvettes. The emission spectra were measured on a JASCO FP-6500 fluorescence spectrophotometer equipped with a red-sensitive WRE-343 photomultiplier tube (wavelength range 200–850 nm). Quantum yields were determined from corrected emission spectra following the standard methods[57] using meso-tetraphenylporphyrin (TPP) (Φ = 0.11 in toluene[58]) or zinc meso-tetraphenylporphyrin (ZnTPP) (Φ = 0.03 in toluene[58]) as standards. Emission lifetimes were determined by the time-correlated single-photon counting technique using an Edinburgh Instruments mini-tau lifetime spectrophotometer equipped with an EPL 405 pulsed diode laser at 406.0 nm with a pulse width of 71.52 ps and pulse periods of 200 and 100 ns and a high-speed red sensitive photomultiplier tube (H5773–04) as detector.

Computational Methods. Theoretical calculations of the trimeric compounds were performed using density functional theory (DFT)[59] on GAUSSIAN 03[60] program. Gas phase geometry optimization of the compounds was carried out employing Becke three parameter exchange functional in conjunction with Lee–Yang–Parr correlation functional (B3LYP).[61,62] 6-31G(d) basis sets was used for lighter atoms and LANL2DZ basis set was used for Zn atom. The geometry optimization of reference compound **Ph-PZn-Ph** was carried out adopting the coordinates from the X-ray structure, while input structure of the **$TPPH_2$-PZn-$TPPH_2$** and **BDP-PZn-BDP** was modeled on the optimized structure of the **Ph-PZn-Ph** using *ChemCraft* software (version 1.6). The global minimum of the optimized structure was confirmed by observation of no negative frequencies in frequency calculation. Single point calculations of all the compounds were carried out employing the geometry optimized coordinates. TDDFT calculations were performed in THF solvent using polarizable continuum model (PCM) implemented on Gaussian 03.[63] All the computed structures and the orbitals were visualized by *ChemCraft* software (version 1.6).

5-(4-Aminophenyl)-10,15,20-triphenylporphyrin (NH_2TPPH_2). Tetraphenyl porphyrin (2 g, 3.25 mmol) was dissolved in dichloromethane (300 mL). Nitric acid 65% (4.2 mL, 61.75 mmol) was added with a dropping funnel at 0 °C over a 2 h period. The reaction was monitored by TLC and when it was converted to the desired product the solution was washed 3 × 150 mL with saturated solution of $NaHCO_3$ and then 3 × 150 mL with H_2O and dried using sodium sulfate. The solvent was removed under reduced pressure and the crude product was dissolved in HCl (65 mL), tin chloride (2 g, 10.5 mmol) was added and the solution was refluxed overnight. The mixture was neutralized by addition of aqueous ammonia, and washed with ethyl acetate (5 × 150 mL) dried and solvent was removed. The product was isolated by silica column chromatography CH_2Cl_2 to obtain the desired product as a purple solid (1.3 g, 63%). ^1H NMR (500 MHz, $CDCl_3$): δ 8.96 (d, J = 4.5 Hz, 2 H), 8.86 (s, 6 H), 8.24 (m, 6 H), 8.00 (d, J = 8.5, 2 H), 7.77 (m, 9H), 7.05 (d, J = 8.5, 2 H), 3.99 (s, 2H), −2.71 (s, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 146.2, 142.4, 135.8, 134.7, 132.5,131.2, 127.8, 126.8, 121.0, 120.1, 119.9, 113.6. UV/vis (toluene) λ_{max}, nm (ε, mM^{-1} cm^{-1}) 422 (258.2), 516 (12.5), 552 (6.8), 594 (3.6), 650 (2.8). HRMS (MALDI-TOF) calcd for $C_{44}H_{32}N_5$ $[M + H]^+$ 630.2658, found 630.2662. Anal. Calcd for $C_{44}H_{31}N_5$: C, 83.92; H, 4.96; N, 11.12. Found: C, 83.85; H, 4.89; N, 11.26.

Synthesis of Trimer Porphyrin TPPH$_2$-PZn-TPPH$_2$. Zn-*meso*-dibromoporphyrin **Br$_2$PZn** (48 mg, 0.06 mmol), palladium acetate (1.3 mg, 0.006 mmol), bis(2-diphenylphosphinophenyl)ether (DPEphos) (4.8 mg, 0.009 mmol), and cesium carbonate (55 mg, 0.17 mmol) were added in a dry Schlenk tube. Then monoaminophenyl porphyrin (**NH$_2$TPPH$_2$**) (181 mg, 0.29 mmol) and dry THF (6 mL) were added. The mixture was refluxed at 68 °C under argon for 4 days. The reaction was monitored by TLC. The desired compound was isolated by silica column chromatography THF:Hex (3/7) to obtain **TPPH$_2$-PZn-TPPH$_2$** as a purple solid (71 mg, 63%). ^1H NMR (300 MHz, d_8-THF): δ 9.77 (d, J = 4.5 Hz, 4H), 9.04 (d, 2H), 8.89 (d, J = 4.8 Hz, 4H), 8.79 (m, 16H), 8.48 (d, J = 8.1 Hz, 4H), 8.40 (d, J = 8.1 Hz, 4H), 8.19 (m, 12H), 7.97 (d, J = 8.4 Hz, 4H), 7.75 (m, 18H), 7.30 (d, J = 8.4 Hz, 4H), 4.10 (s, 6H), −2.67 (s, 4H). ^{13}C NMR (75 MHz, d_8-THF): δ 167.5, 155.0, 152.6, 150.5, 149.3, 146.5, 143.6, 143.5, 136.7, 136.4, 135.5, 133.1, 132.6, 131.8, 130.9, 130.5, 129.6, 128.7, 127.7, 126.1, 122.5, 121.2, 120.9, 120.3, 113.6, 52.5. UV/vis (toluene) λ_{max}: nm (ε, mM^{-1} cm^{-1}) 420 (571.6), 445 sh (213.6), 516 (17.2), 556 (15.0), 595 (8.7), 650 (6.6). HRMS (MALDI-TOF) calcd for $C_{124}H_{83}N_{14}O_4Zn$ $[M + H]^+$: 1895.6013, found 1895.6009. Anal. Calcd for $C_{124}H_{82}N_{14}O_4Zn$: C, 78.49; H, 4.36; N, 10.33. Found: C, 78.55; H, 4.32; N, 10.26.

Synthesis of Porphyrin BDP-PZn-BDP. Zn-*meso*-dibromoporphyrin **Br$_2$PZn** (32 mg, 0.04 mmol), palladium acetate (0.9 mg, 0.004 mmol), bis(2-diphenylphosphinophenyl)ether (DPEphos) (3.2 mg, 0.006 mmol) and cesium carbonate (36 mg, 0.11 mmol) were added in a dry Schlenk tube. Then **BDPNH$_2$** (65 mg, 0.19 mmol) and dry THF (5 mL) were added. The mixture was refluxed at 68 °C under argon for 20 h. The reaction was monitored by TLC. The desired compound was isolated by column chromatography THF/Hex (3/7) to obtain **BDP-PZn-BDP** as a purple solid (49 mg, 93%). ^1H NMR (500 MHz, d_8-THF): δ 9.54 (s, 2H), 9.40 (d, J = 4.5 Hz, 4H), 8.71 (d, J = 4.5 Hz, 4H), 8.41 (d, J = 8.0 Hz, 4H), 8.28 (d, J = 8.0 Hz, 4H), 7.01 (m, 8H), 6.00 (s, 4H), 4.06 (s, 6H), 2.45 (s, 12H), 1.69 (s, 12H). ^{13}C NMR (75 MHz, d_8-THF): δ 167.4, 155.9, 155.5, 152.1, 150.3, 148.9, 144.2, 143.6, 135.4, 133.0, 132.3, 130.5, 130.0, 129.8, 128.4, 124.7, 121.5, 120.3, 119.7, 115.6, 52.4, 15.0, 14.6. UV/vis (toluene) λ_{max}, nm (ε, mM^{-1} cm^{-1}): 445 (119.8), 503 (113.9), 561 (11.0), 614 (8.1). HRMS (MALDI-TOF) calcd for $C_{74}H_{60}B_2F_4N_{10}O_4Zn$ $[M]^+$: 1314.4213, found 1314.4217. Anal. Calcd for $C_{74}H_{60}B_2F_4N_{10}O_4Zn$: C, 67.52; H, 4.59; N, 10.64. Found: C, 67.63; H, 4.46; N, 10.52.

Synthesis of Porphyrin Ph-PZn-Ph. Zn-*meso*-dibromoporphyrin **Br$_2$PZn** (32 mg, 0.04 mmol), palladium acetate (0.9 mg, 0.004 mmol), bis(2-diphenylphosphinophenyl)ether (DPEphos) (3.2 mg, 0.006 mmol), and cesium carbonate (36 mg, 0.11 mmol) were added in a dry Schlenk tube. Then aniline (18 μL, 0.19 mmol) and dry THF (5 mL) were added. The mixture was refluxed at 68 °C under argon for 15 h. The reaction was monitored by TLC. The desired compound was isolated by column chromatography THF:Hex (2/8) to obtain **Ph-PZn-Ph** as a purple solid (30 mg, 91%). ^1H NMR (500 MHz, d_8-THF): δ 9.39 (d, J = 4.5 Hz, 4 H), 9.19 (s, 2 H), 8.67 (d, J = 4.5 Hz, 4H), 8.39 (d, J = 7.5 Hz, 4H), 8.27 (d, J = 7.5 Hz, 4 H), 7.04 (m, 4 H), 6.84 (d, J = 7.5, 4 H), 6.65 (m, 2 H), 4.04 (s, 6 H). ^{13}C NMR (75 MHz, d_8-THF): δ 167.5, 155.2, 152.4, 150.2, 149.3, 135.6, 132.1, 130.5, 130.3, 129.8, 128.5, 120.5, 120.2, 118.6, 115.3, 52.5. UV/vis (toluene) λ_{max}, nm (ε, mM^{-1} cm^{-1}): 444 (138.9), 561 (12.5), 614 (8.5). HRMS (MALDI-TOF) calcd for $C_{48}H_{34}N_6O_4Zn$ $[M]^+$: 822.1933, found 822.1929. Anal. Calcd for $C_{48}H_{34}N_6O_4Zn$: C, 69.95; H, 4.16; N, 10.20. Found: C, 69.87; H, 4.22; N, 10.12.

ASSOCIATED CONTENT

Supporting Information

X-ray crystallographic data for **Ph-PZn-Ph** in CIF format; ^1H NMR and ^{13}C NMR of **NH$_2$TPPNH$_2$**, **TPPH$_2$-PZn-TPPH$_2$**, **BDP-PZn-BDP**, **Ph-PZn-Ph**; selected bond lengths and angles; redox data of compounds **BDP-PZn-BDP**, **Ph-PZn-Ph** and **BDPNH$_2$**; cyclic voltammograms of **BDP-PZn-BDP** and **BDPNH$_2$**; normalized room temperature emission spectra of **BDPNH$_2$**, **Ph-PZn-Ph**, **NH$_2$TPPH$_2$**; normalized emission spectra of **Ph-PZn-Ph** and **TPPH$_2$-PZn-TPPH$_2$** at 77 K; gas phase B3LYP/6-31G* optimized structure of **Ph-PZn-Ph**; frontier orbital energy levels for compounds **TPPH$_2$-PZn-TPPH$_2$**, **BDP-PZn-BDP**; TDDFT computed vertical transitions for **BDP-PZn-BDP**; Bond lengths obtained from of theoretical calculation and X-ray structure for compound **TPPH$_2$-PZn-TPPH$_2$** and **BDP-PZn-BDP**; and Cartesian coordinates of the B3LYP/6-31G* optimized structure of **TPPH$_2$-PZn-TPPH$_2$**, **BDP-PZn-BDP** and **Ph-PZn-Ph** This material is available free of charge via the Internet at http://pubs.acs.org. CCDC staff scan major chemistry and crystallography journals; printed deposition numbers CCDC 894217 are noted and the deposited data are processed to the Cambridge Structural Database in conjunction with the printed publication.

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Notes

The authors declare no competing financial interest.

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DEDICATION

The authors would like to dedicate this manuscript in memoriam of Ivano Bertini, who was an excellent friend, advisor, and co-worker throughout all these years.

REFERENCES

(1) Kadish, K. M.; Smith, K. M.; Guilard, R. *The Porphyrin Handbook*; Academic Press: San Diego, CA, 2000.

(2) Takai, A.; Chkounda, M.; Eggenspiller, A.; Gros, C. P.; Lachkar, M.; Barbe, J.-M.; Fukuzumi, S. *J. Am. Chem. Soc.* **2010**, *132*, 4477−4489.

(3) Jurow, M.; Schuckman, A. E.; Batteas, J. D.; Drain, C. M. *Coord. Chem. Rev.* **2010**, *254*, 2297−2310.

(4) Collman, J. P.; Brauman, J. I.; Doxsee, K. M.; Halbert, T. R.; Hayes, S. E.; Suslick, K. S. *J. Am. Chem. Soc.* **1978**, *100*, 2761−2766.

(5) Ladomenou, K.; Bonar-Law, R. P. *Chem. Commun.* **2002**, 2108.

(6) Wasielewski, M. R. *Chem. Rev.* **1992**, *92*, 435−461.

(7) Garg, V.; Kodis, G.; Chachisvilis, M.; Hambourger, M.; Moore, A. L.; Moore, T. A.; Gust, D. *J. Am. Chem. Soc.* **2011**, *133*, 2944−2954.

(8) Gust, D.; Moore, T. A.; Moore, A. L. *Acc. Chem. Res.* **2009**, *42*, 1890−1898.
(9) D'Souza, F.; Amin, A. N.; El-Khouly, M. E.; Subbaiyan, N. K.; Zandler, M. E.; Fukuzumi, S. *J. Am. Chem. Soc.* **2011**, *134*, 654−664.
(10) Ooyama, Y.; Harima, Y. *Eur. J. Org. Chem.* **2009**, *2009*, 2903−2934.
(11) Imahori, H.; Umeyama, T.; Ito, S. *Acc. Chem. Res.* **2009**, *42*, 1809−1818.
(12) Wang, X.-F.; Tamiaki, H. *Energy Environ. Sci.* **2010**, *3*, 94−106.
(13) Hagfeldt, A.; Boschloo, G.; Sun, L.; Kloo, L.; Pettersson, H. *Chem. Rev.* **2010**, *110*, 6595−6663.
(14) Martinez-Diaz, M. V.; de la Torre, G.; Torres, T. *Chem. Commun.* **2010**, *46*, 7090−7108.
(15) 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.
(16) Maligaspe, E.; Kumpulainen, T.; Subbaiyan, N. K.; Zandler, M. E.; Lemmetyinen, H.; Tkachenko, N. V.; D'Souza, F. *Phys. Chem. Chem. Phys.* **2010**, *12*, 7434−7444.
(17) Rio, Y.; Seitz, W.; Gouloumis, A.; Vázquez, P.; Sessler, J. L.; Guldi, D. M.; Torres, T. *Chem.—Eur. J.* **2010**, *16*, 1929−1940.
(18) Lazarides, T.; Charalambidis, G.; Vuillamy, A.; Réglier, M.; Klontzas, E.; Froudakis, G.; Kuhri, S.; Guldi, D. M.; Coutsolelos, A. G. *Inorg. Chem.* **2011**, *50*, 8926−8936.
(19) Aratani, N.; Osuka, A.; Kim, Y. H.; Jeong, D. H.; Kim, D. *Angew. Chem., Int. Ed.* **2000**, *39*, 1458−1462.
(20) Aratani, N.; Kim, D.; Osuka, A. *Acc. Chem. Res.* **2009**, *42*, 1922−1934.
(21) Holten, D.; Bocian, D. F.; Lindsey, J. S. *Acc. Chem. Res.* **2001**, *35*, 57−69.
(22) Lin, V.; DiMagno, S.; Therien, M. *Science* **1994**, *264*, 1105−1111.
(23) Susumu, K.; Therien, M. J. *J. Am. Chem. Soc.* **2002**, *124*, 8550−8552.
(24) Fukuzumi, S.; Saito, K.; Ohkubo, K.; Khoury, T.; Kashiwagi, Y.; Absalom, M. A.; Gadde, S.; D'Souza, F.; Araki, Y.; Ito, O.; Crossley, M. J. *Chem. Commun.* **2011**, *47*, 7980−7982.
(25) Milic, T.; Garno, J. C.; Batteas, J. D.; Smeureanu, G.; Drain, C. M. *Langmuir* **2004**, *20*, 3974−3983.
(26) Esdaile, L. J.; Senge, M. O.; Arnold, D. P. *Chem. Commun.* **2006**, 4192−4194.
(27) Matano, Y.; Matsumoto, K.; Terasaka, Y.; Hotta, H.; Araki, Y.; Ito, O.; Shiro, M.; Sasamori, T.; Tokitoh, N.; Imahori, H. *Chem.—Eur. J.* **2007**, *13*, 891−901.
(28) Atefi, F.; McMurtrie, J. C.; Turner, P.; Duriska, M.; Arnold, D. P. *Inorg. Chem.* **2006**, *45*, 6479−6489.
(29) Chen, Y.; Zhang, X. P. *J. Org. Chem.* **2003**, *68*, 4432−4438.
(30) Gao, G. Y. Y.; Chen, Y.; Zhang, X. P. *J. Org. Chem.* **2003**, *68*, 6215−6221.
(31) Gao, G.-Y.; Colvin, A. J.; Chen, Y.; Zhang, X. P. *J. Org. Chem.* **2004**, *69*, 8886−8892.
(32) Peters, M. V.; Goddard, R.; Hecht, S. *J. Org. Chem.* **2006**, *71*, 7846−7849.
(33) Gao, G. Y.; Ruppel, J. V.; Allen, D. B.; Chen, Y.; Zhang, X. P. *J. Org. Chem.* **2007**, *72*, 9060−9066.
(34) Liu, C.; Shen, D.-M.; Chen, Q.-Y. *J. Org. Chem.* **2007**, *72*, 2732−2736.
(35) Chen, Y.; Fields, K. B.; Zhang, X. P. *J. Am. Chem. Soc.* **2004**, *126*, 14718−14719.
(36) Gao, G.-Y.; Colvin, A. J.; Chen, Y.; Zhang, X. P. *Org. Lett.* **2003**, *5*, 3261−3264.
(37) Gao, G. Y.; Chen, Y.; Zhang, X. P. *Org. Lett.* **2004**, *6*, 1837−1840.
(38) Soares, A. R. M.; Martínez-Díaz, M. V.; Bruckner, A.; Pereira, A. M. V. M; Tomé, J. P. C.; Alonso, C. M. A.; Faustino, M. A. F.; Neves, M. G. P. M. S.; Tomé, A. C.; Silva, A. M. S.; Cavaleiro, J. A. S.; Torres, T.; Guldi, D. M. *Org. Lett.* **2007**, *9*, 1557−1560.
(39) Pereira, A. M. V. M; Neves, M. G. P. M. S.; Cavaleiro, J. A. S.; Jeandon, C.; Gisselbrecht, J.-P.; Choua, S.; Ruppert, R. *Org. Lett.* **2011**, *13*, 4742−4745.
(40) Khan, M. M.; Ali, H.; van Lier, J. E. *Tetrahedron Lett.* **2001**, *42*, 1615−1617.
(41) Takanami, T.; Hayashi, M.; Hino, F.; Suda, K. *Tetrahedron Lett.* **2003**, *44*, 7353−7357.
(42) Chen, Y.; Gao, G.-Y.; Peter Zhang, X. *Tetrahedron Lett.* **2005**, *46*, 4965−4969.
(43) Esdaile, L. J.; McMurtrie, J. C.; Turner, P.; Arnold, D. P. *Tetrahedron Lett.* **2005**, *46*, 6931−6935.
(44) Kruper, W. J.; Chamberlin, T. A.; Kochanny, M. *J. Org. Chem.* **1989**, *54*, 2753−2756.
(45) DiMagno, S. G.; Lin, V. S. Y.; Therien, M. J. *J. Org. Chem.* **1993**, *58*, 5983−5993.
(46) Mikroyannidis, J. A.; Charalambidis, G.; Coutsolelos, A. G.; Balraju, P.; Sharma, G. D. *J. Power Sources* **2011**, *196*, 6622−6628.
(47) Imahori, H.; Norieda, H.; Yamada, H.; Nishimura, Y.; Yamazaki, I.; Sakata, Y.; Fukuzumi, S. *J. Am. Chem. Soc.* **2000**, *123*, 100−110.
(48) Golder, A. J.; Povey, D. C.; Silver, J.; Jassim, Q. A. A. *Acta Crystallogr., Sect. C* **1990**, *46*, 1210−1212.
(49) Schauer, C. K.; Anderson, O. P.; Eaton, S. S.; Eaton, G. R. *Inorg. Chem.* **1985**, *24*, 4082−4086.
(50) Mula, S.; Elliott, K.; Harriman, A.; Ziessel, R. *J. Phys. Chem. A* **2010**, *114*, 10515−10522.
(51) Matsuzaki, Y.; Nogami, A.; Tsuda, A.; Osuka, A.; Tanaka, K. *J. Phys. Chem. A* **2006**, *110*, 4888−4899.
(52) Sabatini, R. P.; McCormick, T. M.; Lazarides, T.; Wilson, K. C.; Eisenberg, R.; McCamant, D. W. *J. Phys. Chem. Lett.* **2011**, *2*, 223−227.
(53) Lazarides, T.; Kuhri, S.; Charalambidis, G.; Panda, M. K.; Guldi, D. M.; Coutsolelos, A. G. *Inorg. Chem.* **2012**, *51*, 4193−4204.
(54) Armarego, W. L. F.; Chai, C. *Purification of Laboratory Chemicals*, 6th ed.; Elsevier Inc.: Oxford, 2009.
(55) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A. *J. Appl. Crystallogr.* **1993**, *26*, 343−350.
(56) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2008**, *64*, 112−122.
(57) Crosby, G. A.; Demas, J. N. *J. Phys. Chem.* **1971**, *75*, 991−1024.
(58) Seybold, P. G.; Gouterman, M. *J. Mol. Spectrosc.* **1969**, *31*, 1−13.
(59) Kohn, W.; Sham, L. J. *Phys. Rev.* **1965**, *140*, A1133−A1138.
(60) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Lyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A.; Inc., G. *Gaussian 03*; Gaussian, Inc.: Wallingford CT, 2004.
(61) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098−3100.
(62) Lee, C. T.; Yang, W. T.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785−789.
(63) Cossi, M.; Barone, V.; Cammi, R.; Tomasi. *J. Chem. Phys. Lett.* **1996**, *255*, 327−335.