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Synthesis of porphyrin dyads with potential use in solar energy conversion

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A convenient procedure for the synthesis of porphyrin derivative dyads is described. The dyads consist of a free base porphyrin covalently linked to a zinc porphyrin or ferrocene by an amide bond. 5-(4-Substituted phenyl)-10,15,20-tris(4-methylphenyl) porphyrins were synthesized from *meso*-(4-methylphenyl) dipyrromethanes **1**, which was obtained with appreciable yield (83%). The reaction of dipyrromethane **1** with a mixture of two appropriate substituted benzaldehydes affords the desired *meso*-substituted porphyrins, which can be easily separated by flash chromatography. These porphyrins bearing either one 4-acetamidophenyl group **2** or 4-carboxymethylphenyl group **3**, and three 4-methylphenyl peripheral functional groups, were prepared with notable yields (15–17%) in a two-step one-flask reaction. Basic hydrolysis of the porphyrins **2** and **3** yielded amino **4** and acid porphyrin **5**, respectively. Treatment of **5** with zinc acetate afforded the corresponding metal complex Zn-acid porphyrin **6**. The dyads **7** and **8** were obtained by the coupling reaction between the acid chloride derivatives of either Zn-acid porphyrin **6** or ferroceneacetic acid and amino porphyrins **4**, respectively. The present strategy may be easily used for preparation of other similar dyad derivatives. These compounds could have interesting applications in electronic materials. Preliminary studies of light energy conversion by SnO_2 electrodes coated with porphyrin dyads **7** and **8** were performed. The results show that dyads **7** and **8** may be suitable for solar energy conversion devices.

Introduction

The porphyrins lie at the focus of several different fields of research.[1] Like the photosynthetic reaction center, many artificial assemblies incorporate porphyrin and metalloporphyrin derivatives as light receptors in energy conversion and in the design of molecular-scale electronic devices.[2,3] Also, porphyrin derivatives have been used in solar energy conversion, which takes place in the spectral sensitization of wide band gap semiconductors.[4–6] The energy difference between the conduction band edge of an n-type semiconductor and the oxidation potential of the excited adsorbed dye, provides a driving force for photo-induced charge injection.[7,8]

Therefore, the synthesis of well-defined asymmetric porphyrin derivatives is of great interest for the development of new molecular structures. In the present work we are interested in the synthesis of porphyrin dyads, in which the porphyrin moiety is attached to either Zn-porphyrin **7** or ferrocene **8** by an amide bond. Porphyrin dimers containing structural moieties with both different singlet state energies and redox properties can undergo singlet–singlet energy transfer or photoinduced electron transfer.[9] Porphyrin–ferrocene dyad **8** has a good chance of showing intramolecular photoinduced electron transfer.[10] Thermodynamically, fluorescence quenching of the porphyrin moiety could occur by photoinduced electron transfer from ferrocene to the cyclic tetrapyrrole first excited singlet state to yield a charge-separated species. It has been demonstrated that several covalently linked systems containing synthetic porphyrin as electron acceptor can undergo photoinitiated electron transfer in high yield.[11]

The proposed dyads require the synthesis of peripherally asymmetric porphyrins, such as *meso*-substituted porphyrins bearing a phenyl group substituted with the functional group to make the link and three identical substituted phenyl groups (AB_3-porphyrin). Such porphyrins, bearing two different types of *meso*-substituents, can be prepared by a binary mixed aldehyde condensation.[12,13] However, this approach is statistical in nature and usually multiple porphyrin products are obtained.[12] The isolation requires slow and long chromatographic separation. Even so, obtaining the pure porphyrin is not always possible and the yield can be very poor.[14] On the other hand, porphyrins bearing four different *meso*-substitutents (ABCD-porphyrin) can be synthesized *via* a stepwise synthetic approach. Rational syntheses of ABCD-porphyrins bearing four different aryl rings were performed from MacDonald's routes.[15–17] The ability to place four different groups around the periphery of the porphyrins should enable synthesis of sophisticated building block porphyrins. The yield in the porphyrin condensation is not high and this condensation is mainly useful for synthesis of regioisomerically pure ABCD-porphyrins. However, for AB_3-porphyrins the stepwise method described above requires many steps (*i.e.* about 8 starting from pyrrole and aldehydes). More direct approaches to *trans*-substituted porphyrins (ABAB-porphyrins) are provided by condensation of dipyrromethane with aldehyde. These porphyrins require access to *meso*-substituted dipyrromethane, which can be synthesized from the reaction of aldehyde with excess of pyrrole catalyzed by acid.[18]

This paper reports a convenient procedure for the synthesis of 5-(4-substituted phenyl)-10,15,20-tris(4-methylphenyl) porphyrins from *meso*-(4-methylphenyl) dipyrromethanes **1**. Therefore, dipyrromethanes **1** were synthesized from 4-methylbenzaldehyde and excess of pyrrole. The reaction of dipyrromethane **1** with a mixture of two appropriate substituted benzaldehydes affords a mixture of three *meso*-substituted porphyrins, which can be easily separated by flash chromatography. Thus, the desired *meso*-substituted porphyrins **2** and **3**, bearing one 4-aminophenyl group or 4-acetoxyphenyl group and three identical peripheral functional groups have been prepared with appreciable yields (15–17%) in a two-step one-flask reaction. Preliminary studies of solar energy conversion by SnO_2 electrodes coated with porphyrin

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dyads **7** and **8** were performed. The results showed that these structures could be used as materials for light energy conversion.[19]

Results and discussion

Synthesis of porphyrins

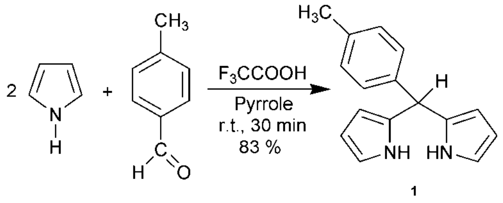
The condensation of 4-methylbenzaldehyde with a large excess of pyrrole (1 : 48 aldehyde : pyrrole molar ratio), catalyzed by trifluoroacetic acid at room temperature, affords *meso*-(4-methylphenyl) dipyrromethane **1**. Flash chromatography on silica gel, using *n*-hexane–ethyl acetate–triethylamine (80 : 20 : 1) as eluent, yields 83% of the dipyrromethane **1**. The use of a mildly basic medium (triethylamine $\cong$1%) prevents the decomposition of the dipyrromethane on the silica column, which is slightly acidic. Thus, dipyrromethane **1** is stable in the purified form upon storage at 0 °C in a nitrogen atmosphere and the absence of light. High purity is essential for its application in the synthesis of asymmetric *meso*-substituted porphyrins.

The 5-(4-substituted phenyl)-10,15,20-tris(4-methylphenyl) porphyrins **2** and **3** were synthesized by the acid-catalyzed condensation of dipyrromethane **1** (Scheme 1) and the corresponding 4-substituted benzaldehydes in chloroform at room temperature (Scheme 2).

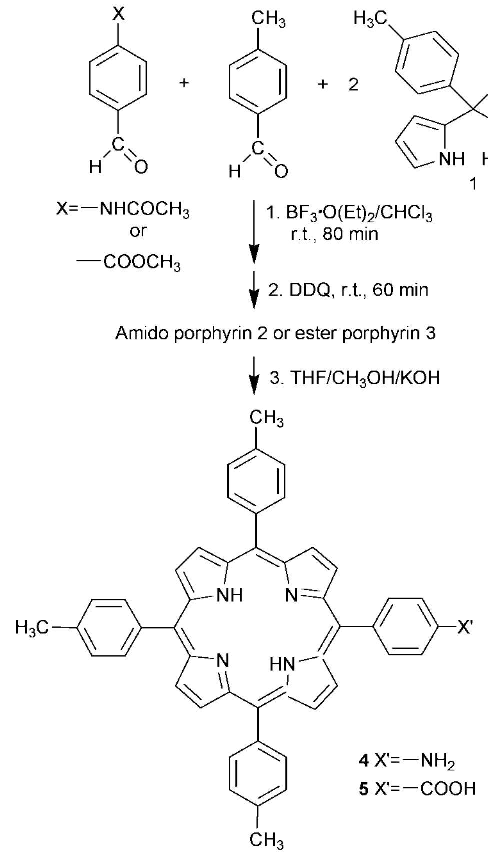
Mixed-benzaldehyde–dipyrromethane condensations were performed using about 2.2 : 1.4 : 1 molar ratio of dipyrromethane **1**, 4-methylbenzaldehyde and 4-substituted benzaldehyde, respectively. This ratio of reactants gives the best yield of the selected porphyrin. The first reaction step was performed using catalytic amounts of $BF_3 \cdot O(Et)_2$, and chloroform as solvent, at room temperature. In the second step, the reaction mixture was subjected to oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). Thus, this mixed condensation affords a mixture of three porphyrins, the 5,10,15,20-tetra(4-methylphenyl) porphyrin, the 5-(4-substituted phenyl)-10,15,20-tris(4-substituted phenyl) porphyrin **2** or **3** and the 5,15-bis(4-substituted phenyl)-10,20-bis(4-substituted phenyl) porphyrin.

The three porphyrins were easily separated by flash chromatography with high purity using dichloromethane–methanol or acetone gradient. In both cases, the first purple band corresponds to *meso*-tetra-substituted porphyrin, the second is the desired mono-amide (or ester) porphyrin **2** or **3** and the third more polar band belongs to bis-amido (or ester) porphyrin. Thus, the desired porphyrins **2** and **3**, bearing one 4-acetamidophenyl or 4-carboxymethylphenyl group, respectively, and three identical peripheral functional groups, were obtained with appreciable yields of 15–17%.

Also, amide porphyrin **2** was previously synthesized by a condensation of a binary mixture of 4-acetamidobenzaldehyde, 4-methylbenzaldehyde and pyrrole in propionic acid. The reaction work up is not simple because of the difficulty of removing propionic acid and the tar present, yielding after a long procedure of purification about 3.6%.[14] Hence, the dipyrromethane method presents two main advantages for the synthesis of AB_3-porphyrins over the modified Alder method:[13] the easier work up and the higher yields obtained. The present method involves only a two-step one-flask reaction, while the stepwise method,[15–17] which gives a pure selected porphyrin, would require many steps. This present strategy may be used for the preparation of other similar porphyrin derivatives bearing only one different peripheral phenyl substituent.



Scheme 1 Synthesis of *meso*-(4-methylphenyl) dipyrromethane **1**.



Scheme 2 Synthesis of porphyrins **4** and **5**.

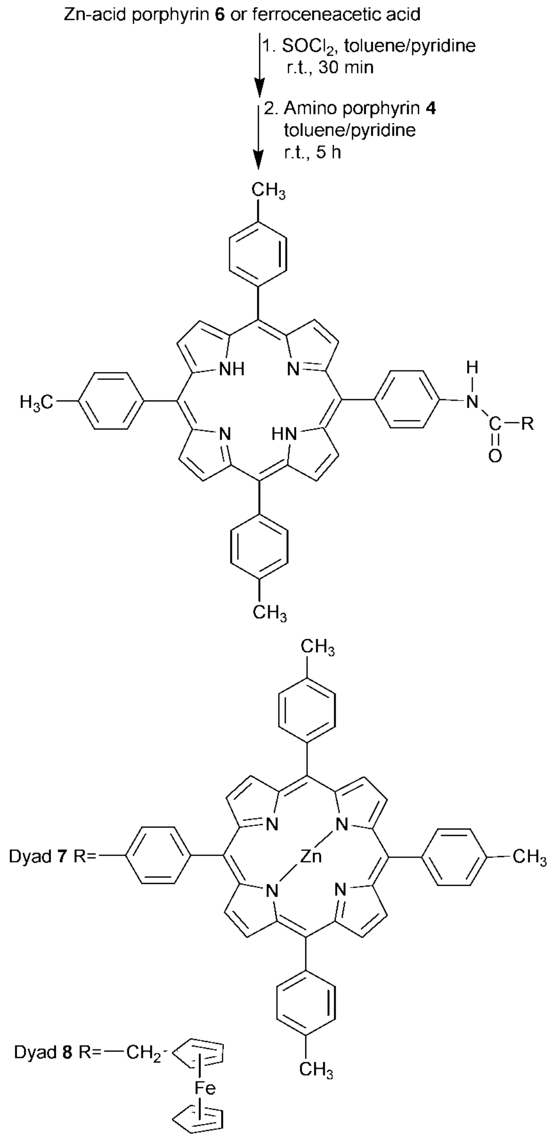
Amide and ester porphyrins **2** and **3** were hydrolyzed to amine **4** and acid **5** porphyrin by heating in tetrahydrofuran–methanol–KOH medium. Acid porphyrin **5** was treated with zinc acetate to afford Zn-acid porphyrin **6** in 100% conversion.

Synthesis of dyads

Scheme 3 shows the synthesis of dyads **7** and **8** by coupling an amide bond. To synthesize the desired porphyrin dyads, the carboxylic acid group of the Zn-acid porphyrin or ferroceneacetic acid was transformed to an acid chloride using thionyl chloride in dry toluene and pyridine. The formation of the acid chloride was evidenced by TLC (dichloromethane–acetone 5%) after mixing a small portion of the reaction mixture with methanol. The acid chloride is not isolated but immediately used for coupling with amino porphyrin **4**. The reaction mixture was allowed to react for 5 h, to yield after work up the desired porphyrin dyads **7** and **8** with 76% and 79% yields, respectively.

Absorption and fluorescence spectra

The absorption spectra of porphyrin monomers and dyads in dichloromethane are shown in Fig. 1. The spectrum of the free base amino porphyrin **4** exhibits a Soret absorption at 420 nm and Q-band maxima at 518, 554, 594 and 650 nm, while Zn-acid porphyrin **6** has maxima at 420 nm (Soret) and two Q-bands at 549 and 588 nm. Fig. 1a shows the spectra in the 490–700 nm region of the monomers **4** and **6**, and the dyad **7**. The spectrum of the dyad **7** has a Soret band at 420 nm and Q-bands at 518, 552, 592 and 650 nm. This spectrum is essentially a linear combination of the spectra of the monomers, with only minor differences in wavelength maxima and band shapes



Scheme 3 Synthesis of porphyrin dyads **7** and **8**.

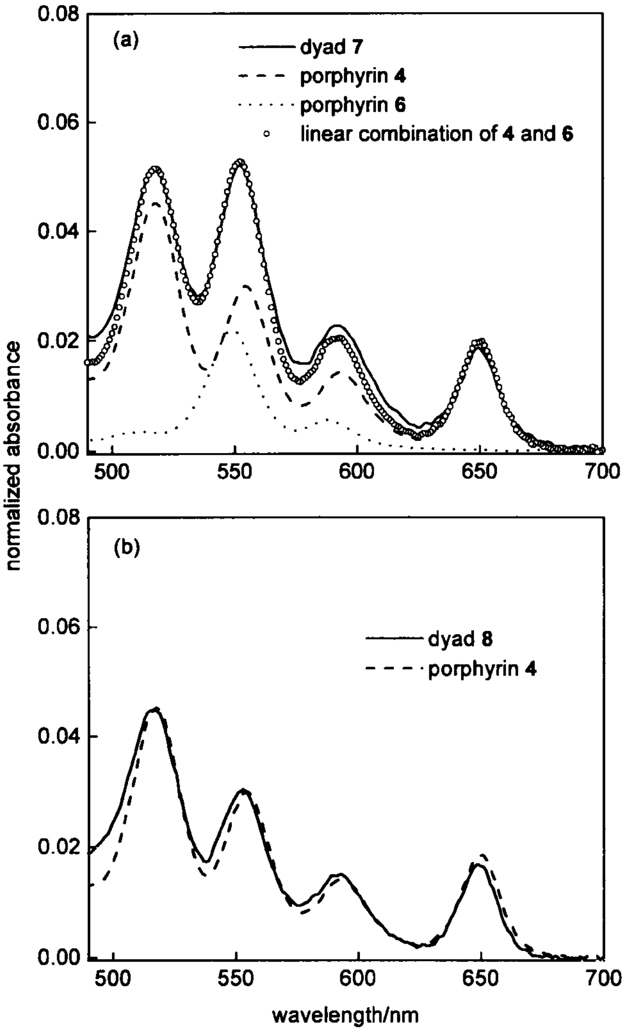


Fig. 1 Normalized absorption spectra in dichloromethane of: (a) amino porphyrin **4** (dashed curve), Zn-acid porphyrin **6** (dotted curve), dyad **7** (solid curve) and of a linear combination of the spectra of porphyrins **4** and **6** (open circles); (b) amino porphyrin **4** (dashed curve) and dyad **8** (solid curve).

(Fig. 1a). The spectra of dyad **8** and the amino porphyrin **4** are compared in Fig. 1b. The Soret band of dyad **8** has a maximum at 420 nm and the Q-bands are at 518, 553, 593 and 650 nm. The ferroceneacetic acids do not absorb in the region shown and moreover the dyad **8** spectrum is not changed with respect to the amino porphyrin **4**. Thus, in both dyads, the absorption spectra are consistent with only a weak interaction between the moieties and the two chromophores retain their individual identities.

The corrected emission spectra were taken in dichloromethane exciting the sample at 550 nm. The free base amino porphyrin **4** features maxima at 652 and 715 nm, while Zn-acid porphyrin **6** has maxima at 598 and 646 nm. The fluorescence spectrum of dyad **7** presents two maxima at 653 and 716 nm. These results show that singlet–singlet energy transfer efficiently occurs in dyad **7**. Porphyrin–ferrocene dyad **8** has an emission spectrum with maxima at 653 and 717 nm, which has a spectral shape similar to porphyrin **4**. However, emission is quenched in the dyad **8** by about 20% relative to monomer **4**.

Photoelectrochemical results

Preliminary results on photoelectrochemical properties of dyads **7** and **8** over SnO_2 nanostructured semiconductor showed good light harvesting. The incident-photon-to-photocurrent efficiency (IPCE) was obtained through measuring the generated photocurrent when the electrodes are illuminated with monochromatic light, by using eqn. (1),

$$\mathrm{IPCE}(\%) = 100(i_{\mathrm{sc}}1240)/(I_{\mathrm{inc}}\lambda) \qquad (1)$$

where i_{sc} is the short circuit photocurrent (A cm^{-2}), I_{inc} is the incident light intensity (W cm^{-2}), and λ is the excitation wavelength (nm). The photo-induced charge separation efficiencies, with IPCE around 10% were found for both dyads (Fig. 2).

There is a close correspondence between the photocurrent action spectrum and the absorption spectrum of the electrodes (Fig. 2). This fact confirms that light absorption by the porphyrin dyads is the initial step in the generation of photo-induced charge transfer mechanism, like in the natural photosynthetic apparatus.[6]

Conclusion

Two basic steps were used sequentially in the synthesis: (1) *meso*-(4-methylphenyl) dipyrromethane **1** was formed from 4-methylbenzaldehyde and excess pyrrole catalyzed by acid; (2) the desired porphyrins **4** and **5**, bearing one 4-acetamidophenyl or 4-carboxymethylphenyl group and three identical peripheral methyl groups, were obtained with appreciable yields of 15–17% by condensation of dipyrromethane **1** with appropriate benzaldehydes. The resultant amido or ester

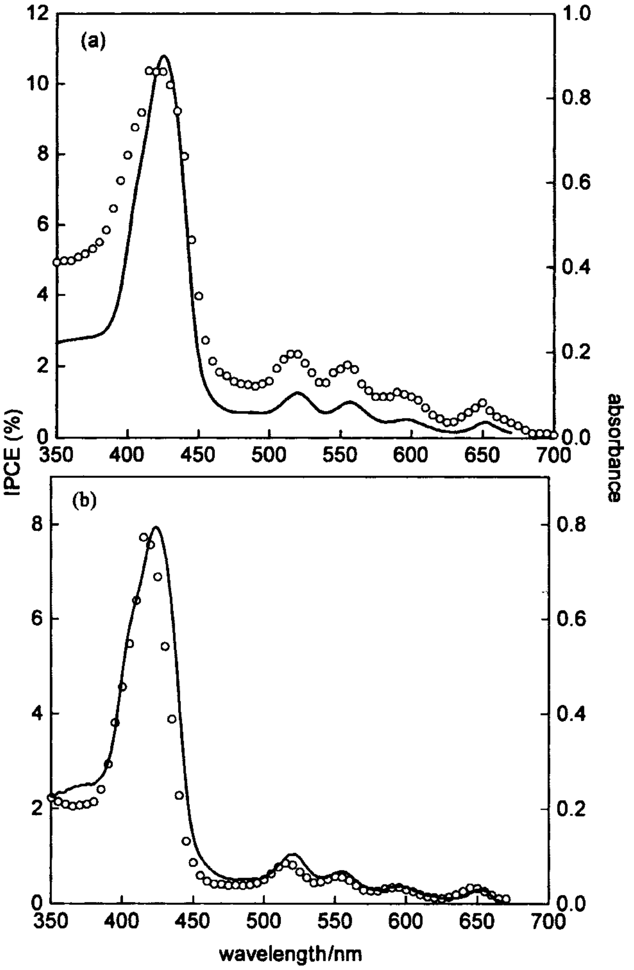


Fig. 2 Absorption spectrum (solid curve) and photocurrent action spectrum (open circles) of electrode ITO/SnO_2/Dyad, for (a) dyad **7** and (b) dyad **8**.

porphyrins **4** and **5** were hydrolyzed to amine and acid porphyrin, respectively, by heat in tetrahydrofuran–methanol–KOH medium. Zn-acid porphyrin **6** was obtained by treatment of **5** with zinc acetic acid. Dyads **7** and **8** were formed by coupling reaction between the corresponding acid chloride and amino porphyrin **4**.

These dyads have two moieties separated by a relatively rigid amide linkage, which provides electronic coupling between the chromophores.[20] Particularly, dyad **7** contains structural moieties with different singlet state energies, undergoing singlet–singlet energy transfer efficiently to the free base after irradiation with visible light.[21] In the porphyrin–ferrocene dyad **8**, the redox properties of both moieties indicate a possible photo-induced electron transfer quenching of porphyrin emission.[10] However, further evidence for electron transfer from ferrocene to the cyclic tetrapyrrole is required. Further studies concerning the mechanism of photocurrent generation are presently in progress in our laboratory.

Experimental

General

Absorption spectra and FT-IR spectra were recorded on a Shimadzu UV-2401PC and on a Nicolet Impact 400, respectively. NMR spectra were taken on a Varian Gemini spectrometer at 300 MHz. Mass spectra were taken with a Varian Matt 312 operating in EI mode at 70 eV and with a Vestec Laser Tec Research Instrument by laser desorption time of flight mass spectroscopy. TLC Uniplate Silica gel GHLF (250 microns) thin layer chromatography plates from Analtech and silica gel (230–400 mesh) for column chromatography from Aldrich were used. Fluorescence spectra were recorded on a Spex FluoroMax fluorimeter.

Starting materials

All the chemicals from Aldrich were used without further purification, except hydroquinone, which was recrystallized from toluene. Toluene, dichloromethane and chloroform (GR grade) from Merck were distilled and stored over 4 Å molecular sieves.

Synthesis of *meso*-(4-methylphenyl)dipyrromethane (1)

A solution of 4-methylbenzaldehyde (1.2 g, 10 mmol) and pyrrole (33.3 mL, 480 mmol) was degassed by bubbling with argon for 15 min, then trifluoroacetic acid (231 μL, 3 mmol) was added. The solution was stirred for 30 min at room temperature, at which point no starting aldehyde was shown by TLC analysis (cyclohexane–ethyl acetate–triethylamine; 80 : 20 : 1). The mixture was diluted with dichloromethane (150 mL), washed with aqueous 0.1 M NaOH and then washed with water. The organic phase was dried with $MgSO_4$, filtered and the solvent was removed under reduced pressure. The unreacted pyrrole was removed by vacuum distillation at 40 °C. The product was purified by flash chromatography (silica gel, cyclohexane–ethyl acetate–triethylamine; 80 : 20 : 1) and yielded 1.96 g (83%) of the pure *meso*-(4-methylphenyl)dipyrromethane **1**. MS *m*/*z* 236.1 (M^+) (236.1315 calculated for $C_{16}H_{16}N_2$). Spectroscopic data of **1** agree with those previously reported.[18]

Synthesis of *meso*-substituted porphyrins

5-(4-Aminophenyl)-10,15,20-tris(4-methylphenyl) porphyrin (4). A solution of 4-methylbenzaldehyde (174 mg, 1.45 mmol), 4-acetamidobenzaldehyde (307 mg, 1.88 mmol) and *meso*-(4-methylphenyl)dipyrromethane **4** (718 mg, 3.04 mmol) in 250 mL of chloroform was purged with argon for 15 min. Then $BF_3{\cdot}O(Et)_2$ (0.44 mmol, 176 μL of 2.5 M stock solution in chloroform) was added. The solution was stirred for 80 min at room temperature. Then, DDQ (340 mg, 1.50 mmol) was added and the mixture was stirred for an additional 1 h at room temperature. The solvent was removed under reduced pressure and flash column chromatography (silica gel, dichloromethane–methanol 1%, gradient from 0.01 to 1% methanol) yielded 155 mg (15%) of the pure selected 5-(4-acetamidophenyl)-10,15,20-tris(4-methylphenyl) porphyrin **2** as the second porphyrin moving band. TLC analysis (dichloromethane–methanol 3%) R_f 0.46. MS *m*/*z* 713.3 (M^+) (713.3158 calculated for $C_{49}H_{39}N_5O_1$).

To a solution of acetamido porphyrin **2** (110 mg, 0.15 mmol) in 50 mL of THF–methanol 2 : 1 was added 10 mL of KOH 50%. The reaction mixture was stirred under an argon atmosphere for 22 h at 60 °C. Then, the mixture was diluted with dichloromethane and washed with aqueous sodium carbonate. The organic solvent was evaporated under reduced pressure. Flash column chromatography (silica gel, dichloromethane–acetone 2%) afforded 298 mg (76%) of the desired 5-(4-aminophenyl)-10,15,20-tris(4-methylphenyl) porphyrin **4**. MS *m*/*z* 671.3 (M^+) (671.3052 calculated for $C_{47}H_{37}N_5$). Spectroscopic data of amine porphyrin **4** coincide with those previously reported.[14,22]

5-(4-Carboxyphenyl)-10,15,20-tris(4-methylphenyl) porphyrin (5). A solution of 4-methylbenzaldehyde (186 mg, 1.55 mmol), 4-carboxymethylbenzaldehyde (328 mg, 2.00 mmol) and *meso*-(4-methylphenyl)dipyrromethane **1** (804 mg, 3.41 mmol) in 250 mL of chloroform was purged with argon for 15 min. Then, $BF_3{\cdot}O(Et)_2$ (0.46 mmol, 184 μL of 2.5 M stock solution in chloroform) was added and the solution was stirred for 80 min at room temperature. After that, DDQ (352 mg, 1.55 mmol) was added and the mixture was stirred for 1 h at room temperature. The solvent was removed under reduced pressure and flash chromatography (silica gel, dichloromethane–methanol 3%, gradient) afforded 188 mg (17%) of 5-(4-carboxymethylphenyl)-10,15,20-tris(4-methylphenyl) porphyrin **3**. MS *m*/*z* 714.3 (M^+) (714.2997 calculated for $C_{49}H_{38}N_4O_2$).

This ester porphyrin **3** (100 mg, 0.140 mmol) was hydrolyzed in 50 mL of THF–CH_3OH (2 : 1) and 6 mL of KOH 40%. The reaction was stirred under argon atmosphere for 16 h at 60 °C. Then, the mixture was neutralized with hydrochloric acid solution and extracted with dichloromethane. The organic solvent was evaporated under reduced pressure and flash column chromatography (silica gel, dichloromethane–methanol 8%) afforded 77 mg (79%) of the desired acid porphyrin **5**. MS *m*/*z* 700.3 (M^+) (700.2841 calculated for $C_{48}H_{36}N_4O_2$). Spectroscopic data of acid porphyrin **5** agree with those previously reported.[22–24]

Zinc 5-(4-carboxyphenyl)-10,15,20-tris(4-methylphenyl) porphyrin (6). To a solution of acid porphyrin **5** (50 mg, 0.071 mmol) in 20 ml of dichloromethane was added 5 mL of a saturated solution of zinc(II) acetate in methanol. The mixture was stirred for 30 min at room temperature. Solvents were evaporated under reduced pressure and flash chromatography (silica gel, dichloromethane–methanol 4%) gave 52 mg (95%) of pure Zn-acid porphyrin **6**. MS *m*/*z* 763.6 (M^+) (763.64 calculated for $C_{48}H_{34}N_4O_2Zn$).

Synthesis of dyads

Dyad 7. Zn-acid porphyrin **6** (40 mg, 0.052 mmol) was dissolved in 20 mL of dry toluene and 8 mL of pyridine. This solution was stirred under argon for 10 min. Then, thionyl chloride (10 μL, 0.14 mmol) was added. The reaction mixture was stirred for 30 min at room temperature. The solvents were removed by distillation at reduced pressure. Excess of pyridine and thionyl chloride was removed under vacuum. The acid chloride was redissolved in 16 mL of toluene and 6 mL of pyridine. A solution of amide porphyrin **4** (40 mg, 0.060 mmol) in 4 mL of toluene and 2 mL of pyridine was added. The reaction was stirred under argon atmosphere for 6 h at room temperature. Then, the mixture was partitioned between dichloromethane and water. The organic layer was extracted with dichloromethane and the solvents were evaporated under reduced pressure. Flash column chromatography (silica gel, dichloromethane–acetone 5%) afforded 54 mg (74%) of pure dyad **7**. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ/ppm −2.78 (br s, 2H, pyrrole N-H), 2.71 (s, 18H, Ar-CH_3), 7.55 (d, 12H, *J* 8.0 Hz, 10,15,20,10′,15′,20′ Ar 3,5-H), 7.89 (d, 2H, 5 Ar 3,5-H), 8.07 (d, 12H, *J* 8.0 Hz, 10,15,20,10′,15′,20′ Ar 2,6-H), 8.15 (s, br s, 1H, NHCO), 8.22 (d, 2H, *J* 8.3 Hz, 5 Ar 2,6-H), 8.26 (d, 2H, *J* 8.2 Hz, 5′ Ar 2,6-H), 8.34 (d, 2H, *J* 8.2 Hz, 5′ Ar 3,5-H), 8.80–9.00 (m, 16 H, pyrrole). FT-IR ν_{max}/cm^{-1} (KBr) 3310, 2928, 2855, 1689, 1419, 1342, 1208, 1177, 998, 801. MS *m*/*z* 1417.0 (M^+) (1416.93 calculated for $C_{95}H_{69}N_9O_1Zn$). Anal. Calcd. C 80.47, H 4.90, N 8.89; found C 80.59, H 4.98, N 8.77%.

Dyad 8. The reaction was performed as described above for dyad **7**, using 13 mg (0.052 mmol) of ferroceneacetic acid. Flash column chromatography (silica gel, dichloromethane–methanol 1.5%) yielded 32 mg (69%) of pure dyad **8**. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ/ppm −2.77 (br s, 2H, pyrrole N-H), 2.72 (s, 9H, 10,15,20 Ar-CH_3), 3.11 (s, 2H), 4.17 (m, 2H), 4.16 (m, 2H), 4.24 (s, 5H), 7.56 (d, 6H, *J* 7.8 Hz, 10,15,20 Ar 3,5-H), 7.85 (d, 2H, *J* 8.4 Hz, 5 Ar 3,5-H), 8.10 (d, 12H, *J* 7.8 Hz, 10,15,20 Ar 2,6-H), 8.17 (s, br s, 1H, NHCO), 8.22 (d, 2H, *J* 8.4 Hz, 5 Ar 2,6-H), 8.85–8.96 (m, 8H, pyrrole). FT-IR ν_{max}/cm^{-1} (KBr) 3311, 3023, 2921, 2855, 1698, 1470, 1284, 1188, 971, 809. MS *m*/*z* 897.2 (M^+) (897.2254 calculated for $C_{59}H_{47}N_5O_1Fe$). Anal. Calcd. C 78.92, H 5.28, N 7.80; found C 78.79, H 5.37, N 7.71%.

Preparation of SnO_2 nanocrystalline films

Optically transparent electrodes were cut from indium tin oxide (ITO) coated glass plates (1.3 mm thickness, 100 Ω/square) obtained from Delta Technologies. A SnO_2 particle diameter of 20–30 Å from Alfa Chemicals was used without further purification. A 1.5% SnO_2 suspension was prepared by dilution of the commercial suspension with water containing a surfactant (0.01% Triton X-100, Aldrich). ITO/SnO_2 electrodes were prepared by coating using Kamat's procedure.[25] An aliquot of 0.1 mL of the diluted suspension was spread onto the clean ITO surface with a 3.5 cm^2 area, followed by drying of the electrodes over a warm plate. Finally, the SnO_2 films were annealed at 450 °C for 1 h. The resulting films, which are transparent in the visible region, have strong absorption in the UV with an onset at around 355 nm. (This onset absorption corresponds to a bulk band gap of 3.5 eV.)

Dyad adsorption onto the semiconductor film was accomplished by soaking the annealed film in a saturated *n*-hexane or petroleum ether solution of the dyad for 2 h. This produces strong coloration of the semiconductor film. A wire was connected to the ITO surface with an indium solder.

Photoelectrochemical measurements

Photoelectrochemical experiments were conducted in an aqueous solution (0.01 M) of hydroquinone, with phosphate buffer (pH = 5.2) prepared from 0.05 M NaH_2PO_4 and NaOH. This solution was thoroughly degassed by bubbling with Ar and an Ar atmosphere was maintained in the top of the cell by passing a continuous stream.

The measurements were carried out in a 10 mm quartz photoelectrochemical cell equipped with Ag/AgCl as reference, and Pt foil as the auxiliary electrodes. A battery operated low noise potentiostat, constructed in our laboratory, was used in all photoelectrochemical measurements, which were recorded on a Radiomiter-Copenaghe X-t recorder. Action spectra for dye-coated SnO_2 electrodes were obtained by sending the output of a 150 W high-pressure Xe lamp (Photon Technology Instrument, PTI) through a PTI high intensity grating monochromator and recording the resulting steady-state photocurrent. The electrodes were located at the focus of the monochromator ouput (illuminated area: 1 cm^2). All the photoelectrochemical measurements were done in front face configuration. The incident light intensities at different wavelengths were measured with a Coherent Laser-Mate Q radiometer.

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