Synthesis of dithiaporphyrin-based singlet–singlet energy transfer systems

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The synthesis of the first alkynyl core-modified porphyrin building block, 5,10,15,20-tetrakis(4-ethynylphenyl)-21,23-dithiaporphyrin (N_2S_2 core), is reported. The building block was used to construct donor-appended dithiaporphyrin systems under mild palladium-coupling conditions. The porphyrin building block appended to four boron–dipyrrin units, $(BDPY)_4S_2TPP$, did not show any energy transfer from the BDPY unit to the central dithiaporphyrin core. However, the pentaporphyrin containing a central dithiaporphyrin sub-unit and four peripheral normal porphyrin sub-units (N_4 core) showed efficient energy transfer from the peripheral N_4 porphyrins to the central N_2S_2 porphyrin.

Porphyrin arrays are ideal models for the study of photosynthetic processes. Several symmetrical porphyrin arrays have been synthesized as model compounds for natural photosynthetic processes to study photo-induced processes.[1] Since the porphyrin units in symmetrical arrays are identical, it is difficult to achieve selective excitation of the porphyrin unit upon irradiation to study electron transfer or energy transfer. Selective excitation of the porphyrin unit can be achieved easily if the porphyrin units in the array are not identical (unsymmetrical). Unsymmetrical porphyrin arrays that consist of two different porphyrin sub-units are potential models for studying photosynthetic processes. In the recent past attention has been directed towards synthesizing covalently linked unsymmetrical arrays such as porphyrin–corrole or porphyrin–chlorin in order to obtain fast initial charge transfer and a slow back reaction, so giving a long lived charge transfer state.[2] However, the study of unsymmetrical porphyrin arrays is in its infancy and more studies will be required to probe photo-induced processes. Interestingly, there has been only one report[3] on unsymmetrical arrays containing core-modified porphyrins. One of the most interesting modifications of the porphyrin molecule would be a change of the immediate environment around the central metal atom through replacement of the nitrogens by other heteroatoms such as sulfur, oxygen, selenium, tellurium, *etc*.[4] This constitutes an attractive core modification and the insertion of such atoms into the porphyrin core is expected to change the electronic environment of the porphyrin π-system. The substitution of nitrogen by hetero-atoms reduces the porphyrin ring core size. Thus, a series of hetero-atom substituted porphyrins form a group of core-modified porphyrins that exhibit interesting properties in terms of both aromatic character and their ability to stabilize metals in unusual oxidation states.[5–9] Herein we report the first synthesis of a dithiaporphyrin building block (N_2S_2 core) bearing ethyne groups and its application in the synthesis of dithiaporphyrin systems appended to energy donors.[10] We have chosen *N*,*N*′-difluoroboryl-1,9-dimethyl-5-phenyldipyrrin (BDPY) and normal porphyrin (N_4) to act as energy donors. Thus, we report the synthesis of dithiaporphyrin appended to four BDPY units and of a pentaporphyrin containing one central N_2S_2 porphyrin sub-unit and four peripheral N_4 porphyrin sub-units. Steady state fluorescence spectra confirmed the energy transfer from the N_4 sub-units to the N_2S_2 sub-unit in the pentaporphyrin. However, we did not observe any energy transfer from BDPY to the N_2S_2 unit in BDPY-appended dithia array, which is in contrast to the boron–dipyrrin-appended N_4 porphyrin array in which an efficient energy transfer occurred from BDPY to the N_4 porphyrin unit.

Results and discussion

The synthetic method followed here to prepare the desired dithiaporphyrin building block, **2**, is outlined in Scheme 1. The unknown diol **1** was prepared by following the method of Ulman and Manassen.[11] One equivalent of 2,5-dilithiothiophene was condensed with two equivalents of 4-(2-trimethylsilylethynyl)benzaldehyde[12] in ice-cold dry tetrahydrofuran, which was followed by recrystallization from toluene to yield 69% of diol **1** as a white solid. One equivalent of **1** was condensed with one equivalent of pyrrole in $CHCl_3$ in the presence of a catalytic amount of $BF_3{\cdot}OEt_2$. TLC analysis showed a single yellow spot of the desired compound, **2**. Column chromatography with silica using CH_2Cl_2 gave the dithiaporphyrin building block, **2** in 17% yield. The porphyrin building block was characterized by ^{1}H NMR, absorption and fluorescence spectroscopies and by MALDI mass spectrometry. The trimethylsilyl group was removed by stirring **2** with K_2CO_3 in THF–methanol at room temperature for 4 h to afford deprotected porphyrin, **3**, in 80% yield. The deprotection reaction was confirmed by ^{1}H NMR, which clearly showed the disappearance of the peak at 0.39 ppm due to the methyl groups and the appearance of a peak at 3.9 ppm due to the alkyne proton. The building block **3** was used initially to couple with four equivalents of *N*,*N*′-difluoroboryl-1,9-dimethyl-5-(4-iodophenyl)dipyrrin (BDPY-I) in toluene–triethylamine at 35 °C in the presence of a catalytic amount of $Pd_2(dba)_3$ and $AsPh_3$.[13] After work-up and column chromatography, the dithiaporphyrin appended to four BDPY units, $S_2TPP(BDPY)_4$, **4**, was obtained in 58% yield and it was characterized by ^{1}H NMR, absorption and fluorescence spectroscopies and by MALDI mass spectrometry. The symmetric nature of **4** is clearly evident from its ^{1}H NMR spectrum [Fig. 1(a)]. Both the thiophene and the pyrrole protons of the porphyrin unit appeared as singlets at lower field and the pyrrole protons of the BDPY units appeared as a doublet at higher field. MALDI mass spectrometry showed a characteristic molecular ion peak at 1921.3. The absorption spectrum of **4** along with those of **3** and BDPY, presented in Fig. 2, showed bands corresponding to both BDPY and **3** sub-units. However, the Soret band of **4** experienced a slight red shift compared to **3**, indicating a weak interaction between the sub-units. For the purposes of comparison, we also synthesized a normal N_4 porphyrin appended

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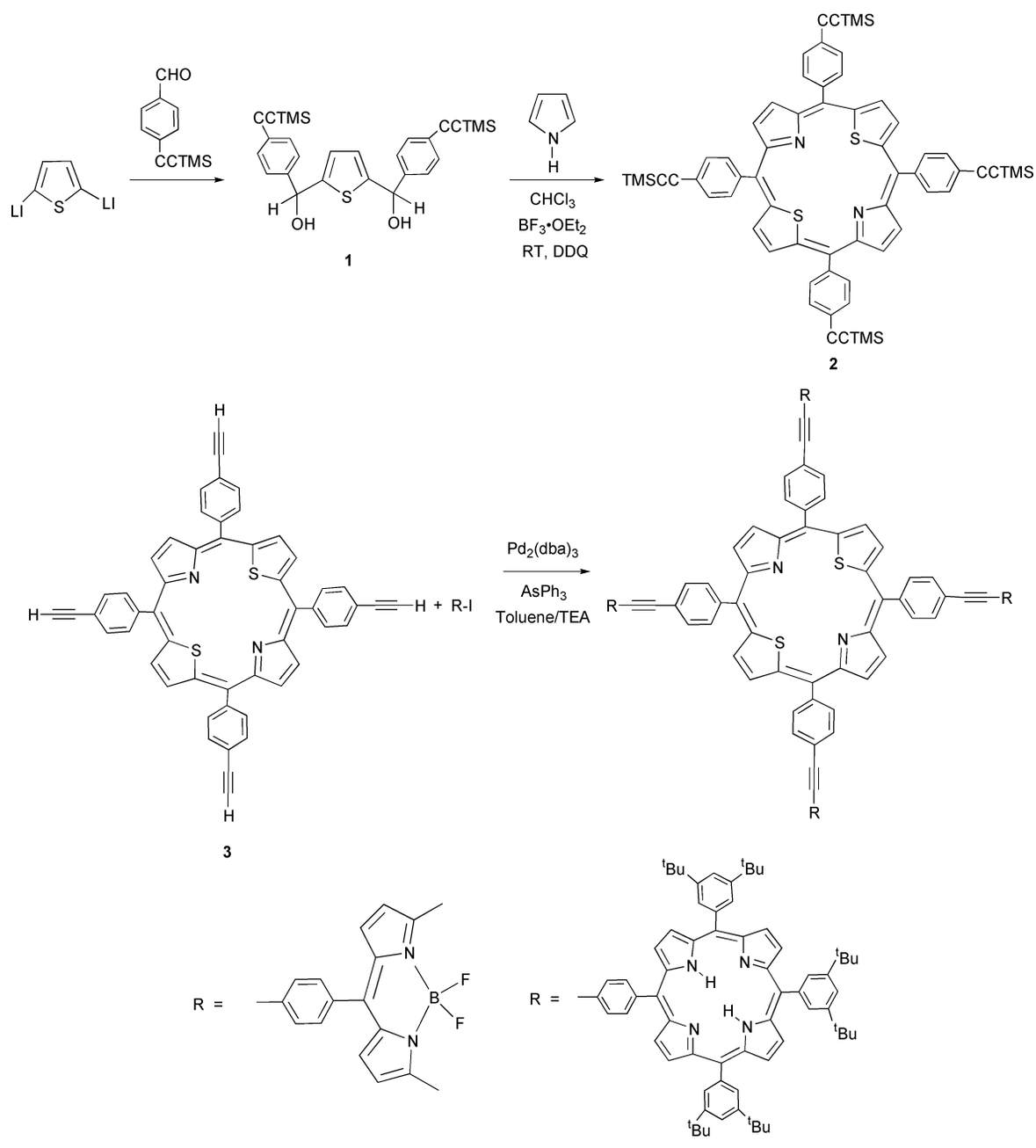
to four BDPY units, $H_2TPP(BDPY)_4$, (**5**), which exhibited similar characteristic features in its absorption spectrum.[14] The emission spectrum of **4**, along with that of **5**, recorded at 485 nm is shown as an inset in Fig. 2. As is evident from Fig. 2, in the case of **4**, excitation at 485 nm (where BDPY is the predominant absorber) resulted in emission from both the units with a strong emission from the BDPY unit, indicating that there is no energy transfer from the BDPY unit to the thiaporphyrin unit. The quantum yield of the BDPY ($\varphi = 0.16$) component in **4** is similar to that of the free BDPY unit ($\varphi = 0.18$), which supports the lack of energy transfer from the BDPY unit to the dithiaporphyrin unit. On the other hand, in the case of **5**, excitation at 485 nm resulted in a strong quenching of the BDPY emission ($\varphi = 0.006$) and increased emission from the N_4 porphyrin unit suggesting that there is energy transfer from the BDPY unit to the N_4 porphyrin unit. The energy transfer that occurred in **5** was independent of the excitation wavelength.

To understand the failure of the energy transfer from the BDPY unit to the dithiaporphyrin unit in **4**, we synthesized a dithiaporphyrin unit appended to N_4 porphyrin units in place of the BDPY units. In this system, we expected the N_4 porphyrin unit to act as an energy donor and transfer energy to the central N_2S_2 unit. The desired N_4 porphyrin building block, 5,10,15-tris(3,5-di-*tert*-butylphenyl)-20-(4-iodophenyl)-porphyrin (**6**), was synthesized by following the building-block approach.[15] The reaction of one equivalent of **3** with 4.5 equivalents of **6** was carried out in toluene–triethylamine (5 : 1) in the presence of a catalytic amount of $AsPh_3$ and $Pd_2(dba)_3$. The progress of the reaction was monitored by analytical size exclusion chromatography (SEC) and TLC.[16,17] The reaction mixture remained homogeneous throughout the coupling process. After 20 hours, the peak from the starting material had decreased and the pentamer peak had reached a maximum with a small amount of higher oligomers (Fig. 3). The reaction was stopped and solvents were removed *in vacuo*. The crude pentamer was passed through a silica gel column to remove unreacted materials and was subjected to SEC chromatography.



Scheme 1 Synthetic scheme for the 21,23-dithiaporphyrin building block and its donor-appended systems.

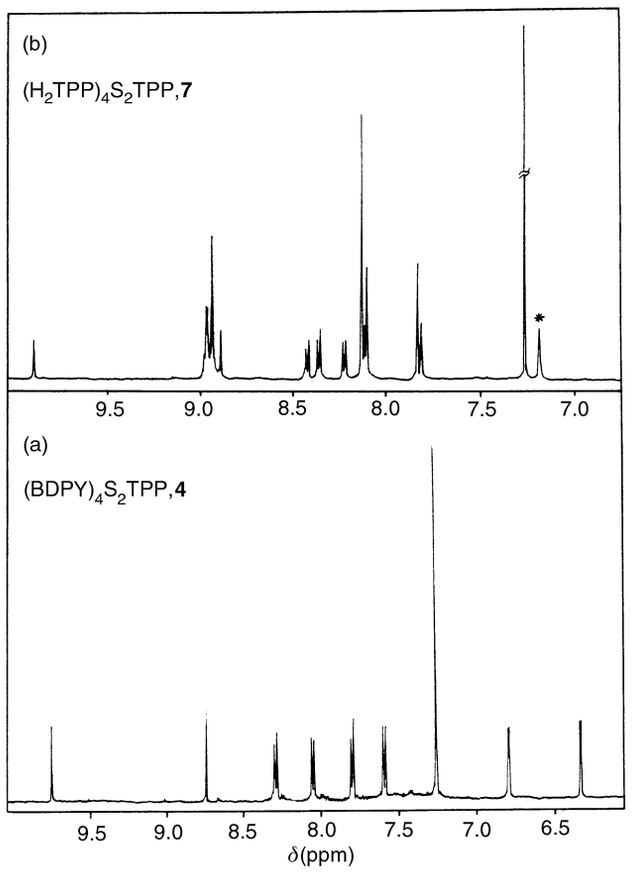


Fig. 1 ^{1}H NMR spectra of (a) **4** and (b) **7** recorded in $CDCl_3$. The peak marked by an asterisk corresponds to an impurity present in the solvent.

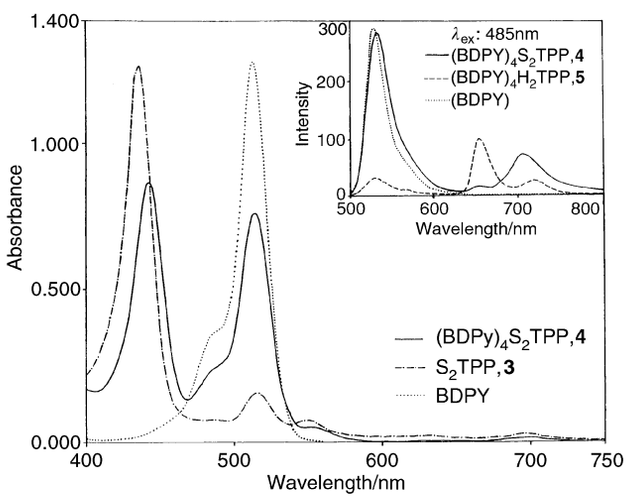


Fig. 2 Absorption spectra of **4**, **3** and BDPY recorded in toluene. The concentration used was ~2×10^{-6} M. The inset shows the emission spectra of **4**, **5** and BDPY in toluene.

The pentamer obtained from the SEC column contained small amounts of impurities of higher and lower porphyrin oligomers and, hence, it was further subjected to preparative HPLC to afford the pure pentaporphyrin $(H_2TPP)_4S_2TPP$ (**7**), comprising one free base N_2S_2 sub-unit and four N_4 sub-units, in 37% yield. The pentaporphyrin, **7** was characterized by ^{1}H NMR, absorption and emission spectroscopies and by MALDI mass spectrometry. The ^{1}H NMR spectrum of **7** in the 7–10 ppm region is shown in Fig. 1(b). The thiophene protons appeared as a singlet, indicating the symmetric nature of the pentamer. The pyrrole protons and aryl protons appeared as a multiplet due to overlap of the N_2S_2 porphyrin unit and N_4 porphyrin unit

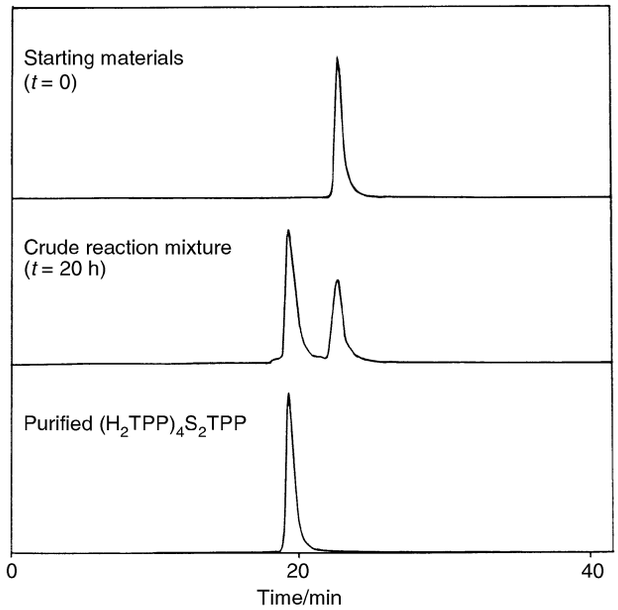


Fig. 3 Size exclusion chromatograms of the reaction solution of **3** with **6** under palladium coupling conditions to synthesize **7** and chromatogram of **7** after purification.

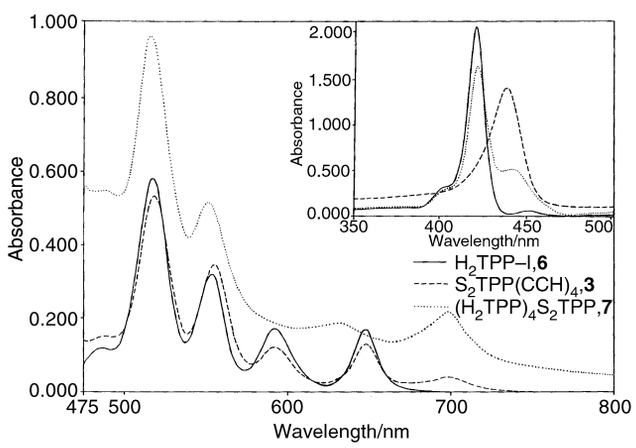


Fig. 4 Q-bands and Soret band (inset) absorption spectra of **7** along with those of its monomers. The concentrations used were: Soret band (inset), ~2×10^{-6} M; and Q-bands, 5×10^{-5} M.

protons. The absorption spectra of **7**, along with those of the two monomers, in both the Q-band and the Soret region are shown in Fig. 4. The absorption spectrum of **7** resembles, but does not equal, the sum of the spectra of the corresponding monomeric units. The absorption spectrum was dominated by the intense Soret band (inset in Fig. 4) of the four N_4 porphyrin constituents. The weaker five Q-bands of the porphyrins lie between 500 and 750 nm. Both the Q-bands and the Soret band exhibited slight red shifts and broadening, indicating a weak interaction between the normal and the dithiaporphyrin sub-units. The emission spectrum of **7** along with those of its corresponding monomers (recorded at 420 nm) are shown in Fig. 5. Upon excitation of **7** at 420 nm (where the N_4 porphyrin unit is the dominant absorber), fluorescence was observed exclusively from the N_2S_2 unit. The quantum yield of the N_4 unit in **7** ($\varphi_f = 0.002$) was greatly diminished compared to that of the corresponding N_4 monomer and the intensity of the fluorescence bands of the N_2S_2 unit was enhanced, which strongly supports the occurrence of energy transfer from the N_4 unit to the N_2S_2 unit. Similar emission spectra were observed at different wavelengths at which the N_4 porphyrin is a strong absorber. These results indicate that very efficient energy transfer occurs from the N_4 porphyrins to the central N_2S_2 porphyrin

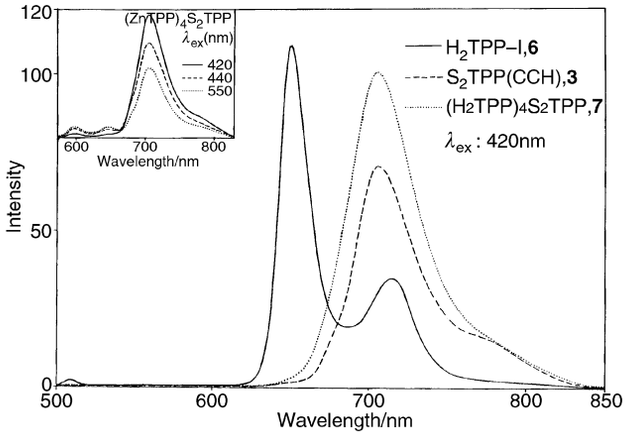


Fig. 5 Emission spectra of **7** along with those of its monomers. The inset shows the emission spectra of **8** recorded at different wavelengths.

unit. To further confirm the energy transfer in pentaporphyrin **7**, we introduced Zn^{2+} into the four peripheral N_4 units by the standard $Zn(OAc)_2$ method to give $(ZnTPP)_4S_2TPP$ (**8**) and recorded the steady state fluorescence spectra at different wavelengths. Excitation at 550 nm, where zinc porphyrin absorbs four times as much as the free base porphyrin, resulted in emission exclusively from the central N_2S_2 unit, indicating an efficient energy transfer from zinc porphyrin to the N_2S_2 porphyrin unit. This kind of efficient energy transfer is not possible in pentaporphyrins comprising only N_4 free base subunits where all the porphyrin units are the same and absorb in the same region. Thus, the pentaporphyrin **7** reported here is unique in the sense that it can be excited selectively and it shows an efficient energy transfer from the central N_2S_2 unit. The synthesis and detailed photodynamics of several such pentaporphyrins containing N_2O_2, N_3O, N_3S and N_3SO as central cores are presently under investigation in our laboratory.

Experimental

^{1}H NMR spectra were recorded on a Varian 300 MHz using tetramethylsilane as internal standard. Absorption and fluorescence spectra were obtained with Shimadzu-160 and Spex Fluoromax respectively. Mass spectra were obtained for samples in neat form by laser desorption mass spectrometry using a Bruker Proflex II. Toluene, THF and triethylamine were obtained from S.D. Fine chemicals, India, and dried by standard procedures before use. All general chemicals were obtained from Qualigens, India. Aldehydes and pyrrole were obtained from Lancaster. Column chromatography was performed using 60–120 mesh silica obtained from Sisco Research Laboratories, India. Size exclusion chromatography was performed using Bio-Beads SX-1 in toluene obtained from Biorad, USA.

2,5-Bis[4-(2-trimethylsilylethynyl)phenyl(hydroxy)methyl]-thiophene, 1

Dried and distilled *n*-hexane (13 ml) was added to a 250 ml three-necked, round-bottomed flask that was equipped with a gas inlet tube, a reflux condenser and a rubber septum. *N*,*N*,*N* ′,*N* ′-Tetramethylethylenediamine (0.924 g, 7.95 mmol, 1.2 ml) and *n*-butyllithium (5 ml of a 1.6 M solution in hexane) were injected into the stirred solution. Thiophene (0.263 g, 4.12 mmol, 0.250 ml) was injected and the solution was refluxed gently for 1 h. The reaction mixture was then allowed to attain room temperature. 4-(2-Trimethylsilylethynyl)benzaldehyde (1.6 g, 7.91 mmol) in dry tetrahydrofuran (16 ml) was added dropwise to the ice-cooled reaction flask. After addition was complete, the reaction mixture was allowed to attain room temperature, saturated ammonium chloride solution was added and it was then extracted with ether (3 × 50 ml). The organic layers were combined and washed with brine and dried over anhydrous Na_2SO_4. The crude product obtained on evaporation of the solvent was recrystallized from toluene and afforded the pure diol as a white solid (1.35 g, 69%). ^{1}H NMR ($CDCl_3$, δ in ppm) 0.34 (s, 18H), 2.12 (br s, 2H), 6.03 (s, 2H), 6.76 (s, 2H), 7.44 (m, 4H), 7.53 (m, 4H). Calcd for $C_{27}H_{32}Si_2O_2S$: C, 68.8; H, 6.59; found: C, 68.5; H, 6.61%. Mp 115 °C.

5,10,15,20-Tetrakis[4-(2-trimethylsilylethynyl)phenyl]-21,23-dithiaporphyrin, 2

A stream of argon was passed through chloroform (25 ml) in a 100 ml one-necked, round-bottomed flask for 10 min. Compound **1** (100 mg, 0.205 mmol) and pyrrole (0.040 ml, 0.575 mmol) were added and argon purging was continued for an additional 10 min. $BF_3{\cdot}OEt_2$ (0.040 ml of a 2.5 M stock solution) was added and the reaction mixture was stirred for 1 h. During this period the colour of the reaction mixture was slowly turned from colourless to dark brown. DDQ (100 mg, 0.441 mmol) was then added and the reaction mixture was stirred in open air for an additional 1 h. The solvent was removed *in vacuo* and the crude compound was purified by silica column using CH_2Cl_2. The desired compound **2** was obtained as a purple solid (17 mg, 17%). ^{1}H NMR ($CDCl_3$, δ in ppm) 0.39 (s, 36H, CH_3), 7.92 (AA′BB′, 8H, Ar), 8.17 (AA′BB′, 8H, Ar), 8.65 (s, 4H, β-pyrrole), 9.65 (s, 4H, β-thiophene). LD-MS $C_{64}H_{60}N_2S_2Si_4$ calcd. av. mass 1033.7, obsd. *m*/*z* 1033.1. Anal. calcd: C, 74.4; H, 5.76; N, 2.71; found: C, 75.2; H, 5.82; N, 2.75%. UV–Vis λ_{max}/nm (ε/mol^{-1} dm^3 cm^{-1}) 439 (159000), 516 (10200), 551 (5600), 632 (1500), 698 (1900).

5,10,15,20-Tetrakis(4-ethynylphenyl)-21,23-dithiaporphyrin, 3

To a solution of **2** (80 mg, 0.077 mmol) in 16 ml of THF–methanol (3 : 1) K_2CO_3 (42 mg, 0.304 mmol) was added and the reaction mixture was stirred at room temperature for 4 h. The progress of the reaction mixture was monitored by TLC. The reaction mixture was rotary-evaporated to dryness and the greenish purple powder thus obtained was dissolved in 50 ml of CH_2Cl_2. The organic layer was washed with 10% $NaHCO_3$ (2 × 50 ml), dried (Na_2SO_4), filtered and rotary-evaporated to dryness. Column chromatography (silica, CH_2Cl_2) afforded 45.9 mg (0.0616 mmol, 80%) of porphyrin **3**. ^{1}H NMR ($CDCl_3$, δ in ppm) 3.33 (s, 4H, CCH), 7.95 (AA′BB′, 8H, Ar), 8.20 (AA′BB′, 8H, Ar), 8.67 (s, 4H, β-pyrrole), 9.67 (s, 4H, β-thiophene). LD-MS $C_{52}H_{28}N_2S_2$ calcd. av. mass 744.9, obsd. *m*/*z* 746.4. Anal. calcd: C, 82.1; H, 3.79; N, 3.76; found: C, 82.1; H, 3.71; N, 3.79%. UV–Vis λ_{max}/nm (ε/mol^{-1} dm^3 cm^{-1}) 439 (168000), 516 (12200), 552 (4600), 633 (1000), 698 (1900).

$(BDPY)_4S_2TPP$, 4

Samples of **3** (10 mg, 0.0139 mmol) and BDPY-I (35 mg, 0.0839 mmol) were dissolved in 12 ml of toluene–triethylamine (5 : 1). $AsPh_3$ (40 mg, 0.131 mmol) was then added and the solution was deaerated with argon for 15 min. The coupling reaction was initiated by the addition of a catalytic amount of $Pd_2(dba)_3$ (16 mg, 0.017 mmol). The reaction mixture was stirred under argon at 35 °C. After 3 h, the solvent was removed *in vacuo*; the crude material was dissolved in dichloromethane and passed through a short silica column to remove the palladium species, triphenylarsine and other side products. The desired compound was then eluted with CH_2Cl_2–5% ether in 58% yield (20 mg). ^{1}H NMR ($CDCl_3$, δ in ppm) 1.54 (s, 24H, CH_3), 6.13 (d, J = 4.5 Hz, 8H, BDPY pyrrole), 6.79 (d, J = 4.5 Hz, 8H, BDPY pyrrole), 7.59 (AA′BB′, 8H, Ar), 7.80 (AA′BB′, 8H, Ar), 8.05 (AA′BB′, 8H, Ar), 8.29 (AA′BB′, 8H, Ar), 8.75 (s, 4H, β-pyrrole), 9.75 (s, 4H, β-thiophene). LD-MS

$C_{120}H_{80}N_{10}S_2B_4F_8$ calcd. av. mass 1921.4, obsd. *m*/*z* 1921.3. UV–Vis λ_{max}/nm (ε/mol^{-1} dm^3 cm^{-1}) 442 (375000), 514 (154700), 552 (13000), 698 (2900).

(BDPY)$_4$H$_2$TPP, 5

Compound **5** was prepared by following the method described for **4**. The coupling of 5,10,15,20-tetrakis(4-ethynylphenyl)-porphyrin (10 mg, 0.0139 mmol) and BDPY-I (35 mg, 0.0839 mmol) in toluene–triethylamine (5 : 1) under palladium-coupling conditions, as described above, resulted in **5** (36%, 9.5 mg) after column chromatography. ^{1}H NMR ($CDCl_3$, δ in ppm) −2.73 (s, 2H, NH), 1.54 (s, 24H, CH_3), 6.33 (d, J = 4.5 Hz, 8H, BDPY pyrrole), 6.79 (d, J = 4.5 Hz, 8H, BDPY pyrrole), 7.59 (AA′BB′, 8H, Ar), 7.79 (AA′BB′, 8H, Ar), 7.99 (AA′BB′, 8H, Ar), 8.26 (AA′BB′, 8H, Ar), 8.92 (s, 8H, β-pyrrole). LD-MS $C_{120}H_{82}N_{12}B_4F_8$ calcd. av. mass 1887.4, obsd. *m*/*z* 1887.1. UV–Vis λ_{max}/nm (ε/mol^{-1} dm^3 cm^{-1}) 425 (874316), 514 (214200), 554 (21730), 592 (11051), 648 (6705).

5,10,15-Tris(3,5-di-*tert*-butylphenyl)-20-(4-iodophenyl)-porphyrin, 6

Compound **6** was prepared by following the procedure reported earlier.[15]

(H$_2$TPP)$_4$S$_2$TPP, 7

5,10,15,20-Tetrakis(4-ethynylphenyl)-21,23-dithiaporphyrin (11 mg, 0.0148 mmol) and 5,10,15-tris(3,5-di-*tert*-butylphenyl)-20-(4-iodophenyl)porphyrin (80 mg, 0.074 mmol) were dissolved in toluene–triethylamine (5 : 1, 12 ml) in a 25 ml round-bottomed flask. The flask was fitted with a reflux condenser and a glass pipette was inserted through the top of the condenser into the solution for argon purging. The reaction vessel was placed in an oil bath preheated to 35 °C. The argon was purged for 15 min. $AsPh_3$ (34 mg, 0.111 mmol) and $Pd_2(dba)_3$ (18 mg, 0.019 mmol) were then added and the reaction was stirred at 35 °C until HPLC analyses showed the absence of starting materials (20 h). The solvents were removed *in vacuo* and the crude compound was passed through a small silica column using CH_2Cl_2 to remove the excess of $AsPh_3$ and the palladium impurities. The porphyrin mixture containing unreacted monomeric materials, the desired pentamer and higher molecular weight material was dissolved in the minimum amount of toluene and loaded on to the top of a preparative size exclusion chromatography column (Bio-Beads SX-1 poured into toluene) and eluted with toluene. On slow elution, the higher oligomers, desired pentamer and lower molecular weight materials were clearly separated. The required pentamer was collected and then subjected to another SEC column to furnish the pure (H$_2$TPP)$_4$S$_2$TPP in 37% yield. ^{1}H NMR ($CDCl_3$, δ in ppm) −2.63 (s, 8H, NH), 1.54 (m, 216H, -CH_3), 7.83 (m, 12H, Ar), 8.05 (m, 24H, Ar), 8.13 (m, 8H, Ar), 8.22 (d, J = 8 Hz, 8H, Ar), 8.34 (d, J = 8 Hz, 8H, Ar), 8.41 (d, J = 8 Hz, 8H, Ar), 8.88–8.97 (m, 36H, β-pyrrole), 9.89 (s, 4H, β-thiophene). LD-MS $C_{324}H_{332}N_{18}S_2$ calcd. av. mass 4542.5, obsd. *m*/*z* 4543.9. UV–Vis λ_{max}/nm (ε/mol^{-1} dm^3 cm^{-1}) 421 (770000), 441 (240000), 518 (28600), 555 (16900), 592 (6200), 648 (5600), 698 (2300).

(ZnTPP)$_4$S$_2$TPP, 8

A solution of **7** (10 mg, 0.002 mmol) in 10 ml of CH_2Cl_2 was treated with methanolic $Zn(OAc)_2$ (25 mg, 0.114) and the reaction mixture was stirred for 2 h. The solvent was removed under vacuum and the resulting solid was purified on a silica gel column using CH_2Cl_2 to give a purple solid in 90% yield. ^{1}H NMR ($CDCl_3$, δ in ppm) 1.55 (m, 216H, -CH_3), 8.10 (m, 44H, Ar), 8.21 (d, J = 8 Hz, 8H, Ar), 8.34 (d, J = 8 Hz, 8H, Ar), 8.41 (d, J = 8 Hz, 8H, Ar), 8.88–8.97 (m, 36H, β-pyrrole), 9.88 (s, 4H, β-thiophene). LD-MS $C_{324}H_{324}N_{18}S_2Zn_4$ calcd. av. mass 4795.9, obsd. *m*/*z* 4796.2. UV–Vis λ_{max}/nm (ε/mol^{-1} dm^3 cm^{-1}) 423 (623723), 440 (195495), 518 (13213), 551 (25683), 589 (7913), 633 (743), 699 (1762).

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