DOI: 10.1002/ejoc.200600867

meso-5-Bromo-10,15,20-tri(*p*-tolyl)-21-thiaporphyrin as a Precursor for the Synthesis of Novel Compounds

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Keywords: 21-Thiaporphyrin / Building blocks / Palladium(0) coupling / *meso*-*meso*-Linked dyad / Energy transfer

The synthesis of eight novel compounds with *meso*-5-bromo-10,15,20-tri(*p*-tolyl)-21-thiaporphyrin as a key synthon under mild Pd-coupling conditions is reported. The title compound was prepared easily by treating the readily available 10,15,20-tri(*p*-tolyl)-21-thiaporphyrin with *N*-bromosuccinimide at room temperature for 10 min. The use of the title compound was demonstrated by synthesizing 21-thiaporphyrin-based complex systems such as ethyne-bridged N_3S-N_3S dyad, phenylethyne-bridged N_3S-N_3O dyad, N_3S-N_2S_2 dyad, *meso*-*meso*-linked ZnN_4-N_3S dyad and ZnN_4-N_3S-ZnN_4 triad under mild Pd-mediated coupling conditions. The steady-state fluorescence studies indicated a possibility of an efficient energy transfer between the two porphyrin subunits in the dyads and triad.

Introduction

21-Thiaporphyrins (STPPHs) are a class of macrocyclic compounds structurally related to tetraphenylporphyrin (H_2TPP), which result from replacing one nitrogen atom of the coordination core in the latter by sulfur.[1] These porphyrins have been explored, specially by the research group of Latos–Grazynski, for their metal coordination chemistry, and it was shown that STPPHs can stabilize metals in uncommon oxidation states (e.g. nickel in the +1 oxidation state).[2,3] Latos–Grazynski and coworkers have also shown that the metallo-STPPHs can provide a suitable platform for organometallic chemistry with an organometallic bond located in the axial position(s).[2,3] Porphyrins with one *meso*-unsubstituted carbon are very important precursors in synthetic porphyrin chemistry since the free *meso* carbon can be activated for the synthesis of several interesting compounds with special physical and chemical properties.[4] However, the methods available for the synthesis of mono-*meso*-unsubstituted porphyrins are very few, and the available synthetic routes are long and tedious.[5] We recently developed simple synthetic routes for the preparation of a series of mono-*meso*-unsubstituted porphyrins with six different porphyrin cores such as N_3S, N_3O, N_2S_2, N_2O_2, N_2SO and N_2OS cores.[6] These compounds now give a wide access to desired complex systems since the *meso*-unsubstituted carbon is highly reactive towards electrophilic and nucleophilic substitution reactions.[7] In continuation of our efforts to prepare novel heteroatom-substituted porphyrin-based complex systems,[8] in this paper, we show the use of *meso*-5-bromo-10,15,20-tri(*p*-tolyl)-21-thiaporphyrin (**2**) as a simple precursor, which can be obtained easily from 10,15,20-tri(*p*-tolyl)-21-thiaporphyrin (**1**),[6] for the synthesis of a range of novel compounds, which were not accessible earlier as heteroatom-substituted porphyrin cores.

Results and Discussion

The *meso*-bromo-21-thiaporphyrin **2** was obtained in 66% yield by treating **1** with 1.2 equiv. of *N*-bromosuccinimide at room temperature for 10 min (Scheme 1), followed by purification on a silica gel column with petroleum ether/dichloromethane (3:1) as the eluent.[9] Compound **2** was characterized by ESI-MS, NMR and UV/Vis spectroscopy and elemental analysis. The *m*/*z* peaks at 676.2 (Br^{79}) and 678.3 (Br^{81}) in the mass spectrum, matching the elemental analysis and the disappearance of the *meso*-H signal at $\delta \approx 10.6$ ppm in the ^1H NMR spectrum, confirmed the identity of compound **2**. The ^1H NMR spectroscopic data indicate that the NH and β-thiophene protons of **2** experienced mostly downfield shifts as compared to those of **1** (Table 1). The absorption spectrum of **2** showed four Q-bands and one Soret band (Figure 1), which were red shifted relative to those of **1** (Table 2). Compound **2** is a very important precursor for the synthesis of several complicated STPPH-based systems **3**–**10** with interesting physico-chemical properties, as shown in Scheme 2. These compounds were not previously accessible with N_3S or any other core-modified porphyrin, which prohibited the study of their novel properties for potential applications.

The mono *meso*-ethynyl N_3S porphyrin **3**, which can be used as a key building block for the synthesis of thiaporphyrin-based systems, was prepared in two steps from **2**.[10] In the first step, a trimethylsilylacetyl-substituted N_3S porphyrin derivative of **3** was prepared in 78% yield by treating **2**

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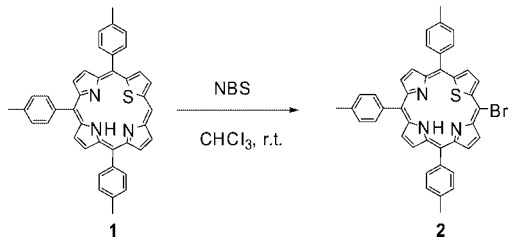


Scheme 1. Synthetic scheme for the preparation of *meso*-bromo-21-thiaporphyrin **2**.

Table 1. Comparison of ^{1}H NMR chemical shifts of β-thiophene and NH protons for compounds **1**–**10**, recorded in $CDCl_3$.

	^{1}H NMR chemical shift [ppm]	
	β-Thiophene	NH
1[a]	9.95 (s), 10.0 (s)	–2.91 (s)
2	9.79 (d), 10.14 (d)	–2.62 (s)
3	9.78 (d), 10.25 (d)	–2.32 (s)
4	9.81 (d), 10.29 (d)	–2.21 (s)
5[b]	10.37 (m), 10.61 (s)	–2.19 (s)
6	9.76 (d), 10.21 (d)	–2.29 (s)
7	9.91 (d), 10.52 (d)	–2.26 (s), –2.14 (s)
8	9.57 (s), 9.83 (m) 9.90 (m), 10.57 (m)	–2.24 (s)
9	9.45 (m)	–2.15 (s)
10	10.00 (m)	–2.18 (s)

[a] Data taken from ref.[3] [b] Recorded in C_6D_6.

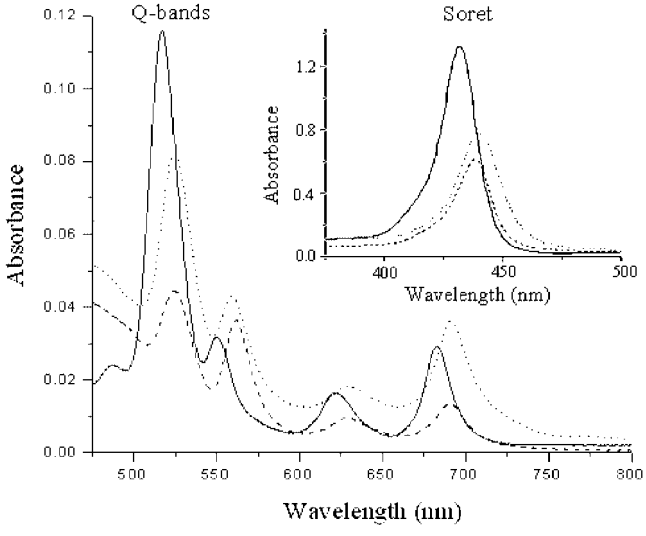


Figure 1. Comparison of Q-bands and Soret band (inset) absorption spectra of **2** (– – –), **3** (---------) and **5** (·····) recorded in toluene. The concentrations used were 5×10^{-5} M for Q-band spectra and 5×10^{-6} M for Soret band spectra.

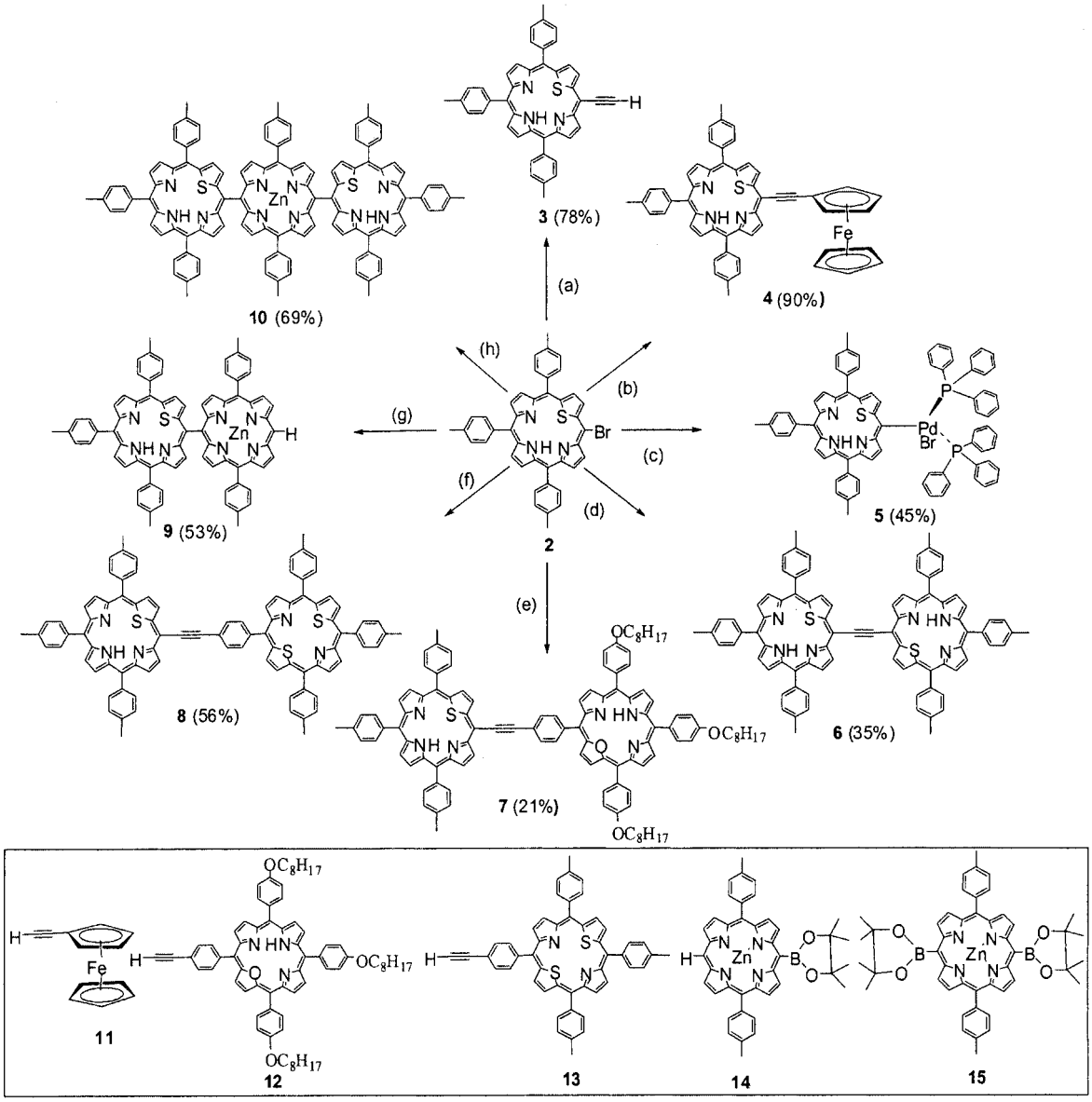
in triethylamine with trimethylsilyacetylene in the presence of a catalytic amount of $Pd_2(dba)_3/AsPh_3$ at 35 °C for 15 h, followed by purification through a silica gel column. In the second step, the trimethylsilyl group was deprotected with K_2CO_3 in THF/CH_3OH, affording the *meso*-ethynyl N_3S porphyrin **3** as a purple solid in 78% yield. The presence of a trimethylsilylethynyl group was confirmed by a ^{1}H NMR signal at δ = 0.57 ppm, and the deprotection of the trimethylsilylethynyl group to yield ethynyl derivative **3** was

Table 2. Absorption data for compounds **1**–**10**, recorded in toluene.

	Soret band λ [nm] (logε)	Absorption Q-bands λ [nm] (logε)
1[a]	424 (5.31)	508 (4.26), 542 (3.62), 609 (3.41), 669 (3.37)
2	430 (5.18)	516 (4.05), 551 (3.45), 620 (3.11), 681 (3.23)
3	438 (4.82)	524 (3.49), 563 (3.36), 629 (3.15), 693 (3.02)
4	440 (5.39)	513 (4.15), 583 (4.28), 641 (3.70), 706 (3.91)
5	440 (5.0)	525 (4.00), 560 (3.74), 631 (3.41), 692 (3.65)
6	429 (5.4)	514 (4.31), 548 (3.81), 618 (3.30), 679 (3.60)
7	428 (5.38) 449 (5.46)	513 (4.49), 543 (sh), 638 (3.79), 680 (3.85) 578 (4.51), 700 (3.00)
8	436 (5.22) 447 (5.38)	517 (4.30), 576 (4.41), 631 (3.57), 693 (3.70) 698 (3.86)
9	423 (4.3) 450 (4.14)	517 (3.75), 544 (3.74), 617 (3.51), 681 (3.48)
10	426 (4.99) 452 (4.81)	519 (4.28), 554 (4.26), 617 (3.71), 682 (3.60)

[a] Data taken from ref.[3]

confirmed by the presence of the ethynyl proton signal at δ = 3.65 ppm. The mass spectra showed the expected molecular ion peaks for **3** and the trimethylsilylacetyl derivative of **3**. In the ^{1}H NMR spectrum, the NH and β-thiophene signals of **3** were shifted downfield as compared to those of **2** (Table 1). The absorption spectrum of **3** showed four Q-bands and one Soret band, and the absorption bands were red shifted relative to those of **2** (Figure 1). The ethynyl-bridged STPPH-ferrocene conjugate **4** was synthesized in 90% yield by coupling **2** with α-ethynylferrocene **11** under Pd-coupling conditions similar to those used for the preparation of 5-(trimethylsilylacetyl)-10,15,20-tri(*p*-tolyl)-21-thiaporphyrin[11] and purifying the product by column chromatography. The molecular ion peak at *m*/*z* = 806.2 (Figure 2, a) and clean ^{1}H NMR spectrum, showing the peaks of both STPPH and ferrocene subunits, confirmed the formation of **4**. The β-thiophene and NH protons were shifted downfield relative to those of **2** (Table 1). The absorption bands of **4** also showed red shifts relative to those of **2**. The organopalladioporphyrin complex **5**, having a direct σ-bond between the Pd metal and the *meso* carbon of the N_3S porphyrin, was prepared by adopting the methodology of Arnold et al.[4] The palladioporphyrin **5** was obtained in 45% yield by treating porphyrin **2** with one equiv. of $Pd_2(dba)_3/PPh_3$ in toluene at 105 °C (Scheme 2), followed by recrystallization from toluene/hexane. Compound **5** was characterized by ESI-MS, ^{1}H, ^{13}C and ^{31}P NMR and absorption spectroscopy. The downfield shifts of the NH and β-thiophene protons in ^{1}H NMR spectrum and the red shifts in the absorption bands of **5** relative to those of **2** (Figure 1) indicated the formation of palladioporphyrin complex **5**. The ^{31}P NMR spectrum of **5** exhibited a single sharp peak at δ = 25.6 ppm. In the ESI-MS of **5**, we observed the molecular ion peak at *m*/*z* = 1307.4 and also a peak at *m*/*z* = 1263.3 due to a chloro complex, which is formed because of the use of dichloromethane as solvent. The *meso*-bromo N_3S porphyrin **2** was further used to synthesize symmetrical and unsymmetrical porphyrin dyads containing two porphyrin subunits connected by various kinds of linkers. The ethynyl–bridged, symmetrical, N_3S-



Scheme 2. Synthetic scheme for the preparation of 21-thiaporphyrin-based complex systems with *meso*-bromo-21-thiaporphyrin **2** as a key precursor. Reaction conditions: (a) 1. TMSA, $Pd_2(dba)_3$, TEA, 35 °C; 2. K_2CO_3, THF/CH_3OH, 60 °C. (b) **11**, $Pd_2(dba)_3/AsPh_3$, toluene/TEA, 35 °C. (c) $Pd_2(dba)_3/PPh_3$, toluene, 105 °C. (d) **3**, $Pd_2(dba)_3/AsPh_3$, toluene/TEA, 35 °C. (e) **12**, $Pd_2(dba)_3/AsPh_3$, toluene/TEA, 35 °C. (f) **13**, $Pd_2(dba)_3/AsPh_3$, Toluene/TEA, 35 °C. (g) **14**, $Pd_2(dba)_3/PPh_3/Cs_2CO_3$, Toluene/DMSO, 85 °C. (h) **15**, $Pd_2(dba)_3/PPh_3/Cs_2CO_3$, toluene/DMSO, 85 °C.

N_3S porphyrin dyad **6** was synthesized by coupling **2** and **3** in toluene/triethylamine in the presence of $Pd_2(dba)_3/AsPh_3$ at 35 °C overnight,[11] followed by silica gel column chromatography with CH_2Cl_2 as the eluent. Compound **6** was characterized by ESI-MS and NMR and absorption spectroscopy, and the spectral features of dyad **6** closely resembled those of *meso*-ethynyl N_3S porphyrin **3**. The molecular ion peak at m/z = 1217.5 in the mass spectrum confirmed the identity of compound **6**. The NH and β-thiophene protons of **6** in the ^1H NMR spectrum were shifted downfield relative to those of **2**. The absorption spectrum of porphyrin dyad **6** showed one Soret band and four Q-bands, and peak maxima closely matched those of compound **3**.

The phenylethyne-bridged, unsymmetrical, N_3S-N_3O porphyrin dyad **7** was synthesized by coupling **2** with 5-(4-ethynylphenyl)-10,15,20-tris(*p*-octyloxyphenyl)-21-oxaporphyrin (**12**)[12] under mild Pd-coupling conditions.[11] The crude compound was purified by silica gel column chromatography and afforded **7** in 21% yield. The identity of the dyad **7** was confirmed by the molecular ion peak in the mass spectrum. In the ^1H NMR spectrum, the NH and β-thiophene protons of the N_3S porphyrin subunit of dyad **7** showed downfield shifts relative to those of the parent porphyrin **2**. The absorption spectra of **7** showed a split Soret band and six Q-bands. The absorption bands corresponding to the N_3S porphyrin subunit were red shifted, whereas the absorption bands of the N_3O porphyrin sub-

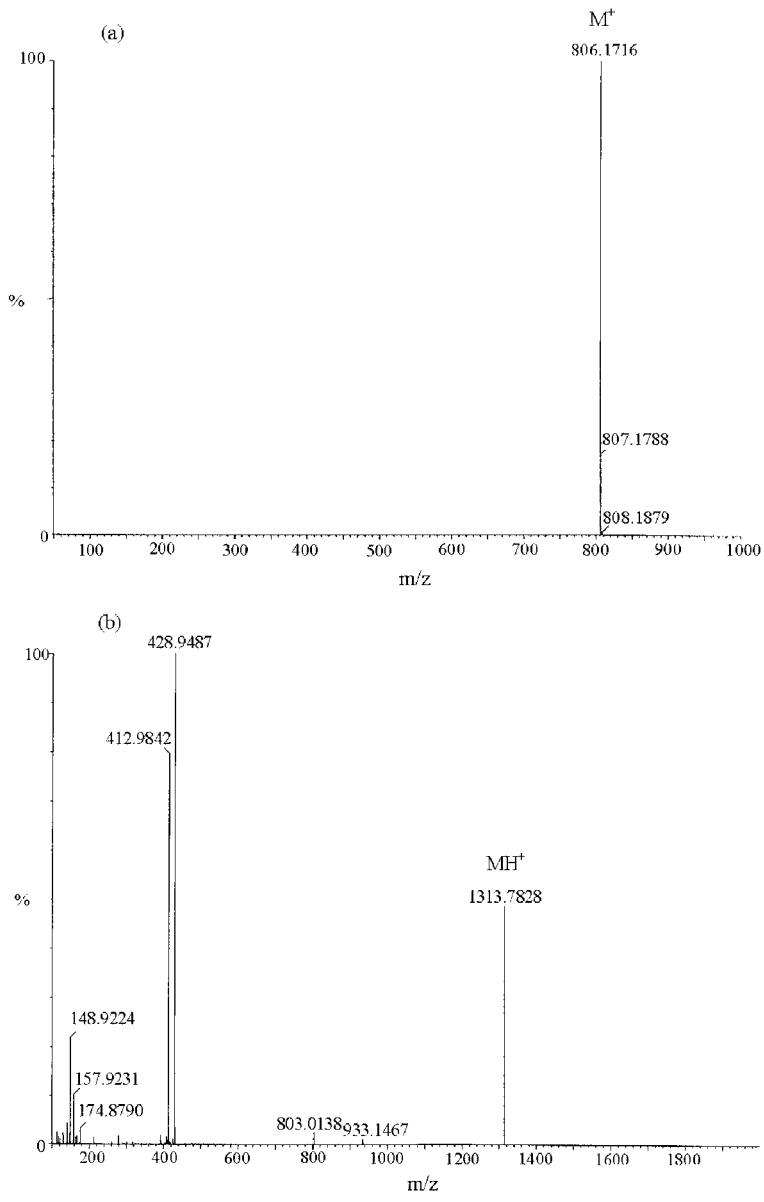


Figure 2. ESI-MS of **4** (a) and **8** (b).

unit did not show much shifting in the absorption peak maxima compared to those of their corresponding monomers. These observations indicate that in dyad **7**, a strong interaction between the two porphyrin subunits is present. Preliminary steady-state fluorescence studies (Table 3) were carried out for dyad **7** at 420 nm, where the N_3O porphyrin subunit absorbs strongly. The expected emission of the N_3O porphyrin subunit was quenched by 91.6% (ϕ = 0.0063), and the major emission was observed from the N_3S porphyrin subunit (Figure 3, a). However, when a 1:1 mixture of the corresponding monomers was excited at 420 nm, the major emission was observed mainly from the N_3O porphyrin. These results indicated that there is an efficient energy transfer from the N_3O porphyrin subunit to the N_3S porphyrin subunit in dyad **7**. Furthermore, the excitation spectrum recorded for dyad **7** at λ_{em} = 700 nm closely matched that of the absorption spectrum of the dyad (Figure 3, a), further confirming the efficient energy transfer between the subunits.

Table 3. Steady-state fluorescence data for compounds **7**–**10**, recorded in toluene.

		ϕ	ϕ % donor emission quenched
7	N_3O em[a]	0.0063	91.6
8	N_2S_2 em[b]	0.0064	94.2
9	N_3S em[c]	0.0027	90.9
10	N_3S em[c]	0.0015	95.6

[a] λ_{ex} = 420 nm. [b] λ_{ex} = 450 nm. [c] λ_{ex} = 550 nm.

The phenylethyne-bridged N_3S-N_2S_2 porphyrin dyad **8** was prepared similarly by coupling **2** with 5-(4-ethynylphenyl)-10,15,20-tri(*p*-tolyl)-21,23-dithiaporphyrin **13**[13] under the same mild Pd-coupling conditions as described above. After purification of the crude compound by column

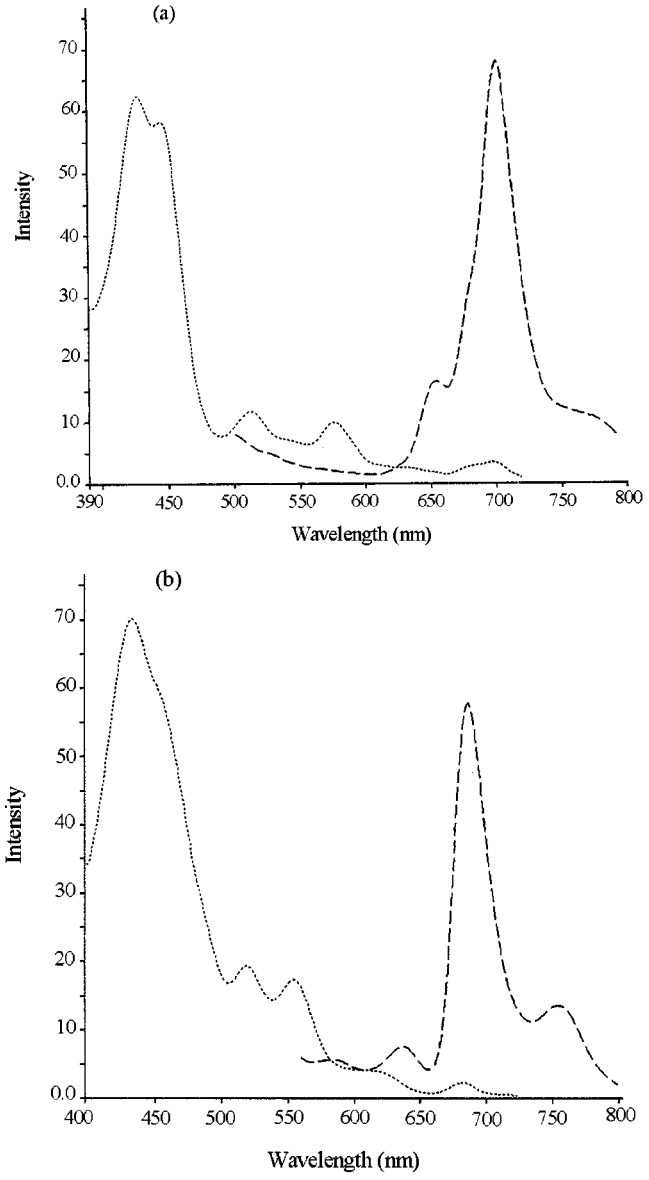


Figure 3. (a) Steady-state emission (·····) (λ_{ex} = 420 nm) and excitation (---------) (λ_{em} = 700 nm) spectra of **7** and (b) Steady-state emission (·····) (λ_{ex} = 550 nm) and excitation (---------) (λ_{em} = 750 nm) spectra of **10**, recorded in toluene. Concentrations used were 2×10^{-6} M.

chromatography, pure dyad **8** was obtained as a purple solid in 56% yield and was identified by its molecular ion peak at *m*/*z* = 1313.8 in the ESI-MS (Figure 2, b). In the ^{1}H NMR spectrum, the β-thiophene protons of both porphyrin subunits of dyad **8** were shifted mostly downfield relative to those of **2**. The absorption spectrum of dyad **8** showed five Q-bands and a broad, split Soret band. The absorption bands corresponding to the N_3S porphyrin subunit were red shifted, and the absorption bands corresponding to the N_2S_2 porphyrin subunit did not show significant shifts. The steady-state fluorescence spectra were recorded for dyad **8** at different wavelengths, and emission was mainly observed from the N_2S_2 porphyrin subunit with negligible emission from the N_3S porphyrin subunit, indicating an energy transfer from the N_3S porphyrin subunit to the N_2S_2 porphyrin subunit. Thus, in this dyad, the N_3S porphyrin subunit is an energy donor.

The *meso*-bromoporphyrin **2** is also a suitable precursor for the synthesis of a *meso*-*meso*-linked dyad containing two different porphyrin subunits. Interestingly, to the best of our knowledge, there are no reports of *meso*-*meso*-linked, unsymmetrical porphyrin arrays containing two different types of macrocyclic units. Osuka and coworkers[14] pioneered the synthesis of *meso*-*meso*-linked porphyrin arrays, and they successfully synthesized *meso*-*meso*-linked arrays as long as a 128-mer with their Ag^I salt-promoted, oxidative, *meso*-*meso*-coupling reaction methodology. However, this methodology is very effective only for synthesizing homogeneous porphyrin arrays. Recently, Osuka and coworkers[15] have shown that the *meso*-*meso*-linked hybrid, porphyrin arrays, such as the porphyrin dimer containing N_4 and ZnN_4 porphyrin subunits, can be synthesized in high yield with metal-catalysed Suzuki–Miyura cross-coupling methodology. We adopted this approach and synthesized *meso*-*meso*-linked, unsymmetrical porphyrin dyad **9** containing ZnN_4 and N_3S porphyrin subunits. The required porphyrin boronate building block **14** was prepared by following the procedure of Therien et al.[16] The coupling of **2** and **14** was carried out in toluene/DMSO at 85 °C in the presence of PPh_3, Cs_2CO_3 and $Pd_2(dba)_3$ for 16 h, followed by column chromatography on silica, giving *meso*-*meso*-linked ZnN_4-N_3S dyad **9** in 53% yield. The *meso*-*meso*-linked dyad **9** was characterized by mass spectrometry and ^{1}H NMR, absorption and fluorescence spectroscopy. The molecular ion peak at *m*/*z* = 1148.6 in the MALDI-TOF mass spectrum confirmed the identity of dyad **9**. In the ^{1}H NMR spectrum of the dyad, the free *meso* proton appeared as a singlet at δ = 10.41 ppm, and the inner NH proton of the N_3S porphyrin subunit appeared as a singlet in the high-field region. The inner NH proton of the N_3S porphyrin subunit in dyad **9** was shifted downfield relative to those of **2**. The steady-state fluorescence study of dyad **9** at wavelengths where the ZnN_4 porphyrin subunit absorbs strongly showed emission bands mainly due to the N_3S porphyrin subunit, and the emission of the ZnN_4 porphyrin subunit was quenched to a greater extent, supporting the efficient energy transfer from the ZnN_4 porphyrin subunit to the N_3S porphyrin subunit.

The *meso*-*meso*-linked porphyrin triad **10**, containing two N_3S porphyrin subunits and one ZnN_4 porphyrin subunit, was synthesized similarly by coupling **2** with porphyrin diboronate building block **15**[16] under similar coupling conditions as mentioned for dyad **9**. The crude compound was purified by silica gel column chromatography, which afforded the ZnN_4-N_3S-ZnN_4 triad **10** as a purple solid in 69% yield. The triad **10** was characterized by MALDI-TOF mass spectrometry and NMR, absorption and fluorescence spectroscopy. The molecular ion peak at *m*/*z* = 1745.9 in the MALDI-TOF spectrum confirmed the identity of the compound. The ^{1}H NMR spectrum showed signals corresponding to both the N_3S and ZnN_4 porphyrin subunits. In the ^{1}H NMR spectrum, the NH proton of the N_3S porphy-

rin subunits of **10** was shifted downfield relative to those of **2**. The absorption spectrum of **10** showed four Q-bands and a broad, split Soret band. In the steady-state fluorescence spectrum of **10**, recorded at 550 nm where the ZnN_4 porphyrin subunit absorbs strongly, the emission of the ZnN_4 porphyrin subunit was quenched 95.6%, extent and the main emission was observed from the N_3S porphyrin subunit (Figure 3, b). Furthermore the excitation spectrum of triad **10**, recorded at λ_{max} = 750 nm, matched exactly the absorption spectrum (Figure 3, b). These results confirm an efficient energy transfer from the middle ZnN_4 porphyrin subunit to the peripheral N_3S porphyrin subunits. Thus, in *meso*-*meso*-linked dyad **9** and triad **10**, the N_3S porphyrin subunit was an energy acceptor.

In conclusion, we have shown the use of 5-bromo-10,15,20-tri(*p*-tolyl)-21-thiaporphyrin as a key synthon for the preparation of several novel compounds by adopting well-established methodologies. These compounds were not previously known in core-modified porphyrin chemistry due to the inaccessibility of suitable precursors. Though we have demonstrated the synthesis of a series of interesting compounds, which will have potential applications with *meso*-bromo-21-thiaporphyrin as a key precursor, it is now possible to synthesize any desired complex system containing heteroatom-substituted porphyrins, such as N_3O, N_2S_2, N_2O_2, N_2SO and N_2OS porphyrins, with the mono-*meso*-free heteroporphyrins reported by our laboratory recently.[6]

Experimental Section

5-Bromo-10,15,20-tri(*p*-tolyl)-21-thiaporphyrin (2): To a stirred solution of 10,15,20-tri(*p*-tolyl)-21-thiaporphyrin (**1**) (35.0 mg, 0.055 mmol) in chloroform (15 mL) at room temperature, *N*-bromosuccinimide (10.0 mg, 0.055 mmol) was added. The progress of the reaction was monitored by TLC and absorption spectroscopy. After complete consumption of the porphyrin **1** (as confirmed by TLC), the reaction was quenched by adding acetone/methanol (10 mL, 1:1), and the solvent was removed on a rotary evaporator under vacuum. The crude reaction mixture was purified by silica gel column chromatography with petroleum ether/dichloromethane (90:10) as the eluent, and the pure bromoporphyrin **2** was obtained as a purple solid in 66% yield (26.2 mg). M.p. >300 °C. IR (KBr film): $\tilde{\nu}$ = 2926, 2850, 1966, 1645, 1464, 960, 800, 656 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = –2.62 (s, 1 H, NH), 2.65 (s, 9 H, CH_3), 7.47–7.59 (m, 6 H, aryl), 7.99–8.09 (m, 6 H, aryl), 8.55 (d, ^1J = 4.8 Hz, 1 H, β-pyrrole), 8.60 (d, ^1J = 4.8 Hz, 2 H, β-pyrrole), 8.88 (s, 2 H, β-pyrrole), 9.25 (d, ^1J = 4.6 Hz, 1 H, β-pyrrole), 9.79 (d, ^1J = 4.8 Hz, 1 H, β-thiophene), 10.14 (d, ^1J = 4.8 Hz, 1 H, β-thiophene) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 21.6, 110.4, 125.0, 127.5, 128.6, 129.3, 132.1, 133.3, 134.5, 135.0, 136.0, 136.6, 137.8, 139.1, 139.4, 145.2, 147.7, 154.9, 157.6, 158.0 ppm. ESI-MS: *m*/*z* (%) = 676.2 (100) $[M]^+$ (Br^{79}) and 678.3 (98) $[M + 2]^+$ (Br^{81}). $C_{41}H_{30}BrN_3S$ (676.7): calcd. C 72.77, H 4.47, N 6.21; found C 72.94, H 4.55, N 6.44.

5-(Trimethylsilylacetyl)-10,15,20-tri(*p*-tolyl)-21-thiaporphyrin: To a solution of porphyrin **2** (10.0 mg, 0.015 mmol) in triethylamine (15 mL), (trimethylsilyl)acetylene (0.10 mL, 0.020 mmol), $AsPh_3$ (10.0 mg, 0.035 mmol) and $Pd_2(dba)_3$, (4.2 mg, 0.004 mmol) were added in sequence, and the mixture was stirred at 35 °C under a nitrogen atmosphere for 15 h. [Note that the vessel must be sealed effectively due to the high volatility of (trimethylsilyl)acetylene (b.p. 53 °C).] The progress of reaction was monitored by TLC and UV visible spectroscopy. Upon completion of the reaction as judged by TLC, the solvent was removed under reduced pressure, and the crude compound was purified by silica gel column chromatography with petroleum ether/dichloromethane (80:20) to afford a dark purple solid in 78% yield (8.2 mg). M.p. >300 °C. IR (KBr film): $\tilde{\nu}$ = 3060, 2934, 2844, 1648, 1458, 962, 805, 650 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = –2.28 (s, 1 H, NH), 0.57 (s, 9 H, TMS-CH_3), 2.69 (s, 9 H, CH_3), 7.49–7.62 (m, 6 H, aryl), 8.00–8.12 (m, 6 H, aryl), 8.52 (d, ^1J = 4.6 Hz, 1 H, β-pyrrole), 8.58–8.62 (m, 2 H, β-pyrrole), 8.84 (s, 2 H, β-pyrrole), 9.26 (d, ^1J = 4.8 Hz, 1 H, β-pyrrole), 9.79 (d, ^1J = 4.8 Hz, 1 H, β-thiophene), 10.24 (d, ^1J = 4.8 Hz, 1 H, β-thiophene) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 16.2, 21.6, 116.1, 123.6, 124.6, 127.4, 127.5, 128.6, 129.3, 131.4, 132.9, 133.4, 134.1, 134.4, 134.9, 135.8, 138.1, 138.8, 139.4, 139.5, 146.6, 148.4, 154.1, 155.0, 157.0, 157.6 ppm. ESI-MS: *m*/*z* (%) = 694.2 (100) $[M]^+$. $C_{46}H_{39}N_3SSi$ (693.9): calcd. C 79.61, H 5.66, N 6.06; found C 79.43, H 5.82, N 5.99.

5-Ethynyl-10,15,20-tri(*p*-tolyl)-21-thiaporphyrin (3): To a solution of 5-(trimethylsilylacetyl)-10,15,20-tri(*p*-tolyl)-21-thiaporphyrin (10.0 mg, 0.014 mmol) in THF/CH_3OH (20 mL, 3:1), an excess of K_2CO_3 was added. The reaction mixture was refluxed with stirring for 3 h, and the progress of the reaction was monitored by TLC. After complete disappearance of the starting material as judged by TLC, the solvent was removed on rotary evaporator under vacuum. The crude product was purified by silica column chromatography with petroleum ether/dichloromethane (75:25) to afford pure **3** as a purple solid in 78% yield (7.1 mg). M.p. >300 °C. IR (KBr film): $\tilde{\nu}$ = 3310, 3050, 2932, 2854, 2210, 1640, 1456, 954, 804, 650 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = –2.32 (s, 1 H, NH), 2.68 (s, 9 H, CH_3), 3.65 (s, 1 H, CCH), 7.48–7.60 (m, 6 H, aryl), 8.00–8.13 (m, 6 H, aryl), 8.53 (d, ^1J = 4.6 Hz, 1 H, β-pyrrole), 8.62–8.65 (m, 2 H, β-pyrrole), 8.86 (s, 2 H, β-pyrrole), 9.28 (d, ^1J = 4.6 Hz, 1 H, β-pyrrole), 9.78 (d, ^1J = 4.8 Hz, 1 H, β-thiophene), 10.25 (d, ^1J = 4.8 Hz, 1 H, β-thiophene) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 21.6, 23.6, 116.2, 122.5, 124.6, 126.3, 127.5, 128.6, 129.2, 130.4, 132.0, 133.2, 134.2, 134.9, 135.7, 137.1, 138.1, 139.3, 139.6, 145.9, 147.9, 154.0, 155.0, 157.1, 157.6 ppm. ESI-MS: *m*/*z* (%) = 622.2 (100) $[M]^+$. $C_{43}H_{31}N_3S$ (621.8): calcd. C 83.06, H 5.03, N 6.76; found C 83.15, H 5.18, N 6.78.

N_3S Porphyrin-Ferrocene Conjugate 4: *meso*-Bromo-21-thiaporphyrin **2** (20.0 mg, 0.029 mmol) and α-ethynylferrocene **11** (6.2 mg, 0.029 mmol) were placed in a 100 mL three-necked round-bottomed flask, which was purged with nitrogen for 10 min. Toluene/TEA (40 mL, 3:1) was added, and the solution was stirred under nitrogen for another 10 min. $Pd_2(dba)_3$ (3.7 mg, 0.001 mmol) and $AsPh_3$ (10.0 mg, 0.003 mmol) were added, and the reaction mixture was stirred at 35 °C for 12 h. The progress of the reaction was monitored by TLC. TLC analysis of the reaction indicated the virtual disappearance of spots corresponding to starting materials and the appearance of a new spot corresponding to conjugate. The reaction mixture was concentrated to dryness, and the resulting residue was subjected to silica gel column chromatography, from which the desired product **4** was purified with petroleum ether/dichloromethane (70:30) as the eluent 90% yield (22.2 mg). M.p. >300 °C. IR (KBr film): $\tilde{\nu}$ = 3044, 2930, 2852, 1640, 1458, 958, 800, 654 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = –2.21 (s, 1 H, NH), 2.69 (s, 9 H, CH_3), 4.45 (s, 7 H, ferrocenyl), 4.95 (s, 2 H, ferrocenyl), 7.50–7.63 (m, 6 H, aryl), 8.02–8.14 (m, 6 H, aryl), 8.53–8.63 (m, 3 H, β-pyrrole), 8.85 (s, 2 H, β-pyrrole), 9.32 (d, ^1J = 4.4 Hz, 1 H, β-pyrrole), 9.81 (d, ^1J = 4.8 Hz, 1 H, β-thiophene), 10.29 (d, ^1J = 4.4 Hz, 1 H, β-thiophene) ppm. ^{13}C NMR (100 MHz, C_6D_6,

25 °C): δ = 21.7, 65.8, 69.7, 70.4, 72.1, 76.7, 76.9, 86.9, 98.9, 111.5, 124.8, 125.0, 127.6, 127.6, 128.6, 128.9, 129.2, 132.0, 132.2, 133.7, 134.3, 134.4, 134.5, 134.8, 135.8, 136.0, 137.8, 137.8, 137.9, 138.0, 139.3, 139.3, 139.5, 139.6, 146.7, 149.6, 154.3, 154.6, 157.9, 159.1 ppm. ESI-MS: *m*/*z* (%) = 806.1 (100) $[M]^+$.

Palladio-Porphyrin 5: Toluene (20 mL) was added to a Schlenk flask and heated under a stream of nitrogen. Triphenylphosphane (31.4 mg, 0.012 mmol) was added, followed by $Pd_2(dba)_3$ (27.8 mg, 0.003 mmol). The dark purple colour of the Pd starting material faded rapidly, leaving a clear yellow solution. After stirring for 10 min, **2** (20.0 mg, 0.029 mmol) was added, and the mixture was stirred at 105 °C for a further 1 h, and the reaction progress was monitored by TLC with dichloromethane/petroleum ether (50:50) as the eluent. The *meso*-bromoporphyrin **2** was consumed within 45 min, and the product precipitated directly from the hot reaction mixture. The desired palladioporphyrin **5** was obtained as a dark brown powder after cooling, thorough washing with cold toluene and hexane and vacuum drying for 1 h (17.4 mg, 45%). M.p. >200 °C. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = –2.19 (s, 1 H, NH), 6.94–7.08 (m, 18 H, aryl), 7.70–7.78 (m, 18 H, aryl), 8.55–8.60 (m, 6 H, aryl), 8.72–8.80 (m, 3 H, β-pyrrole), 8.85–8.88 (m, 1 H, β-pyrrole), 9.26–9.29 (m, 1 H, β-pyrrole), 9.48 (d, *J* = 3.4 Hz, 1 H, β-pyrrole), 10.36–10.38 (m, 1 H, β-thiophene), 10.61 (br. s, 1 H, β-thiophene) ppm. ^{31}P NMR (161.8 MHz, C_6D_6, 25 °C): δ = 25.6 ppm. ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ = 21.5, 22.7, 23.6, 126.5, 128.2, 128.3, 128.4, 128.5, 128.89, 128.9, 129.0, 129.0, 129.4, 130.6, 131.0, 132.0, 132.7, 132.8, 133.4, 134.0, 134.3, 134.8, 135.1, 135.6, 135.7, 136.3, 136.4, 143.1 ppm. ESI-MS: *m*/*z* (%) = 1307.4 (60) $[M]^+$.

Ethyne-Bridged N_3S-N_3S Porphyrin Dyad 6: A solution of N_3S bromoporphyrin **2** (10.0 mg, 0.015 mmol) and 5-(4-ethynyl)-10,15,20 tri(*p*-tolyl)-21-thiaporphyrin (**3**) (9.2 mg, 0.015 mmol) in dry toluene/triethylamine (40 mL, 3:1) was placed in a 100 mL two-necked round-bottomed flask. The flask was fitted with a reflux condenser, gas inlet and gas outlet tubes for nitrogen purging. The reaction vessel was placed in an oil bath preheated to 35 °C. After purging with nitrogen for 15 min, $AsPh_3$ (5.0 mg, 0.003 mmol) followed by $Pd_2(dba)_3$ (1.8 mg, 0.001 mmol) was added, and the reaction was stirred at 35 °C for 12 h. TLC analysis of the reaction mixture indicated the appearance of a dark new spot apart from the faded two starting monomeric porphyrins spots. The solvent was removed under vacuum, and the crude compound was purified by silica gel chromatography with petroleum ether/dichloromethane (50:50) to remove the excess $AsPh_3$ and the small amounts of monomeric porphyrins. The desired dyad **6** was then collected with dichloromethane as a violet solid (4.6 mg, 35% yield). M.p. >300 °C. IR (KBr film): ν̃ = 3046, 2915, 2840, 2211, 1641, 1458, 967, 820, 654 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = –2.29 ppm(s, 1 H, NH), 2.63 (s, 18 H, CH_3), 7.44–7.48 (m, 8 H, aryl), 7.55 (d, ^1J = 7.2 Hz, 4 H, aryl), 7.95–7.97 (m, 8 H, aryl), 8.04 (d, ^1J = 7.2 Hz, 4 H, aryl), 8.49 (d, ^1J = 4.0 Hz, 2 H, β-pyrrole), 8.54–8.57 (m, 3 H, β-pyrrole), 8.82 (s, 5 H, β-pyrrole), 9.21 (d, ^1J = 4.0 Hz, 2 H, β-pyrrole), 9.76 (d, ^1J = 5.2 Hz, 2 H, β-thiophene), 10.21 (d, ^1J = 5.2 Hz, 2 H, β-thiophene) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 23.7, 126.3, 128.5, 128.3, 129.0, 129.4, 130.6, 132.0, 132.7, 133.6, 134.4, 135.2, 135.7, 136.3, 143.1, 155.5 ppm. ESI-MS: *m*/*z* (%) = 1217.5 (60) $[M]^+$.

Phenylethyne-Bridged N_3S-N_3O Porphyrin Dyad 7: A solution of **2** (20.0 mg, 0.003 mmol) and 5-(4-ethynylphenyl)-10,15,20-tris(*p*-octyloxyphenyl)-21-oxaporphyrin (**12**) (33.1 mg, 0.003 mmol) in dry toluene/triethylamine (40 mL, 3:1) was purged with argon for 10 min. To this solution, $Pd_2(dba)_3$ (4.0 mg, 0.001 mmol) and $AsPh_3$ (10.8 mg, 0.003 mmol) were added, and the reaction mixture was stirred under a nitrogen atmosphere at 35 °C for 15 h. The progress of the reaction was monitored by TLC. The solution was concentrated on a rotary evaporator in vacuo, and the resulting crude product was purified by neutral alumina column chromatography. Compound **7** was collected with petroleum ether/dichloromethane (20:80) as a violet-brown solid in 21% yield (11.2 mg). M.p. >300 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = –2.26 (s, 1 H, NH), –2.14 (s, 1 H, NH), 0.94–0.99 (m, 9 H, CH_3), 1.29–1.46 (m, 30 H, CH_2), 1.63–1.66 (m, 6 H, CH_2), 1.99–2.04 (m, 6 H, CH_2), 2.72–2.76 (m, 9 H, CH_3), 4.28–4.33 (m, 6 H, OCH_2), 7.34–7.39 (m, 5 H, aryl), 7.57–7.61 (m, 5 H, aryl), 7.67 (d, ^1J = 7.8 Hz, 3 H, aryl), 8.07–8.11 (m, 6 H, aryl), 8.17–8.20 (m, 3 H, aryl), 8.35–8.40 (m, 6 H, aryl), 8.59–8.63 (m, 5 H, β-pyrrole), 8.65 (d, ^1J = 4.2 Hz, 1 H, β-pyrrole), 8.76–8.79 (m, 4 H, β-pyrrole), 8.89 (s, 2 H, β-pyrrole), 9.69 (d, ^1J = 4.2 Hz, 2 H, β-furan), 9.91 (d, ^1J = 5.1 Hz, 1 H, β-thiophene), 10.52 (d, ^1J = 5.1 Hz, 1 H, β-thiophene) ppm. ESI-MS: *m*/*z* (%) = 1620.8 (55) $[M]^+$.

N_3S-N_2S_2 Phenylethyne-Bridged Porphyrin Dyad 8: A solution of **2** (20.0 mg, 0.029 mmol) and 5-(4-ethynylphenyl)-10,15,20-tri(*p*-tolyl)-21,23-dithiaporphyrin (**13**) (24 mg, 0.029 mmol) in dry toluene/triethylamine (40 mL, 3:1) was purged with nitrogen for 10 min. The coupling was initiated by adding $AsPh_3$ (10.0 mg, 0.003 mmol) followed by $Pd_2(dba)_3$ (3.7 mg, 0.001 mmol), and the reaction was stirred at 35 °C for 12 h. Formation of dyad **8** was confirmed by the appearance of a new spot by TLC as well as from the characteristic splitting pattern of the bands observed in the UV/Vis spectrum. The solvent was removed under vacuum, and the crude compound was purified by silica gel chromatography with petroleum ether/dichloromethane as the eluent. The desired dyad **8** was collected with petroleum ether/dichloromethane (40:60) as a purple solid (16.7 mg, 56% yield). M.p. >300 °C. IR (KBr film): ν̃ = 3051, 2932, 2848, 1964, 2118, 1649, 1455, 955, 812, 644, 618 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = –2.24 (s,1 H, NH), 2.80 (s, 18 H, CH_3), 7.50–7.70 (m, 14 H, aryl), 7.80–7.82 (m, 2 H, aryl), 8.14–8.48 (m, 12 H, aryl), 8.42–8.51 (m, 6 H, β-pyrrole), 8.78–8.81 (m, 3 H, β-pyrrole), 9.30 (s, 1 H, β-pyrrole), 9.57 (s, 1 H, β-thiophene), 9.81–9.85 (m, 3 H, β-thiophene), 9.89–9.91 (m, 1 H, β-thiophene), 10.56–10.58 (m, 1 H, β-thiophene) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 26.4, 29.5, 29.6, 66.0, 68.5, 112.8, 113.8, 122.4, 123.9, 124.2, 129.2, 130.0, 131.0, 131.7, 132.8, 133.3, 133.9, 134.3, 134.8, 135.7, 141.3, 147.2 ppm. ESI-MS: *m*/*z* (%) = 1313.7 (50) $[M + H]^+$.

***meso*-*meso*-Linked N_3S-ZnN_4 Porphyrin Dyad 9:** To a solution of **2** (7.0 mg, 0.010 mmol) and (*meso*-monoborylporphyrin)zinc(II) **14** (10.0 mg, 0.015 mmol) in toluene/DMSO (9 mL, 2:1), triphenylphosphane (0.50 mg, 0.002 mmol), Cs_2CO_3 (3.0 mg, 0.017 mmol) and $Pd_2(dba)_3$ (0.45 mg, 0.001 mmol) were added, and the reaction mixture was refluxed at 85 °C for 16 h under an argon atmosphere. The reaction mixture was poured into water and extracted with dichloromethane. The crude product was purified by silica gel column chromatography with hexane/dichloromethane (50:50) as the eluent to afford **9** as a purple solid in 53% yield (9.1 mg). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = –2.15 (s, 1 H, NH), 2.66 (s, 15 H, CH_3), 7.48–7.64 (m, 12 H, aryl), 7.83 (d, ^1J = 4.5 Hz, 1 H, β-pyrrole), 8.11–8.18 (m, 8 H, aryl), 8.19 (d, ^1J = 4.5 Hz, 2 H, β-pyrrole), 8.36 (d, ^1J = 4.4 Hz, 2 H, β-pyrrole), 8.68 (d, ^1J = 4.4 Hz, 1 H, β-pyrrole), 8.70–8.75 (m, 3 H, β-pyrrole), 8.91 (d, ^1J = 4.4 Hz, 2 H, β-pyrrole), 8.94–9.05 (m, 2 H, β-pyrrole), 9.24 (d, ^1J = 4.4 Hz, 1 H, β-pyrrole), 9.43–9.47 (m, 2 H, β-thiophene), 10.41 (s, 1 H, *meso*-H) ppm. MALDI-TOF-MS: *m*/*z* (%) = 1148.6 (100) $[M]^+$.

***meso-meso*-Linked N_3S-ZnN_4-N_3S Porphyrin Triad 10:** To a solution of **2** (13.5 mg, 0.020 mmol) and (*meso*-diborylporphyrin)-zinc(II) **14** (8.7 mg, 0.001 mmol) in toluene/DMSO (18 mL, 2:1), triphenylphosphane (1.0 mg, 0.004 mmol), Cs_2CO_3 (6.0 mg, 0.033 mmol) and $Pd_2(dba)_3$ (1.0 mg, 0.001 mmol) were added, and the reaction mixture was purged with argon. The resulting reaction mixture was refluxed at 85 °C for 20 h. The reaction mixture was poured into water and extracted with dichloromethane. The crude product was purified by silica gel column chromatography with hexane/dichloromethane (20:80) as the eluent to afford triad **10** as a purple solid in 69% yield (13.4 mg). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = –2.18 (s, 2 H, NH), 2.65 (s, 24 H, CH_3), 7.48–7.55 (m, 12 H, aryl), 7.86 (d, ^1J = 4.6 Hz, 2 H, β-pyrrole), 8.11–8.18 (m, 12 H, aryl), 8.28 (d, ^1J = 4.5 Hz, 4 H, β-pyrrole), 8.38 (d, ^1J = 4.6 Hz, 2 H, β-pyrrole), 8.68–8.76 (m, 8 H, aryl), 8.98–9.05 (m, 6 H, β-pyrrole), 9.19 (d, ^1J = 4.5 Hz, 4 H, β-pyrrole), 9.48 (d, ^1J = 4.5 Hz, 2 H, β-pyrrole), 10.00 (d, ^1J = 4.8 Hz, 4 H, β-thiophene) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C): δ = 21.4, 21.5, 25.4, 29.7, 85.3, 119.2, 121.7, 124.8, 124.9, 127.2, 127.3, 127.4, 128.2, 128.6, 128.9, 130.0, 131.9, 132.3, 132.9, 132.9, 133.7, 134.0, 134.3, 134.4, 135.3, 135.6, 137.0, 137.5, 137.5, 137.6, 138.0, 139.1, 139.4, 139.6, 139.7, 139.8, 146.5, 150.3, 150.6, 151.6, 153.2, 154.1, 154.2, 154.6, 157.9, 162.0 ppm. MALDI-TOF-MS: *m*/*z* (%) = 1745.9 (100) $[M]^+$.

Acknowledgments

M. R. thanks DST and DAE, Government of India for supporting the project and S. P. thanks CSIR for a fellowship.

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Received: October 3, 2006
Published Online: January 8, 2007

