A Simple Route to Prepare Monofunctionalised 21-Thia-, 21,23-Dithia-, and 21-Thia-23-oxaporphyrins from Unsymmetrical Thiophene Diols and Their Use in the Synthesis of Covalently Linked Unsymmetrical Porphyrin Dimers

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A series of unsymmetrical thiophene diols has been prepared in two steps from thiophene in 16–46 % yields. The unsymmetrical thiophene diols containing functionalised aryl groups were then used as key synthons for the synthesis of a series of monofunctionalised 21-thia (N_3S), 21,23-dithia (N_2S_2) and 21-thia-23-oxaporphyrins (N_2SO). Condensation of one equivalent of unsymmetrical diol with either two equivalents of aldehyde and three equivalents of pyrrole, one equivalent of symmetrical 16-thiatripyrrane or one equivalent of symmetrical 16-oxatripyrrane under standard porphyrin-forming conditions resulted in monofunctionalised 21-thia-, 21,23-dithia- or 21-thia-23-oxaporphyrins in decent yields. This unsymmetrical diol method is simple, versatile and gives an access for the first time to any desired monofunctionalised porphyrins with N_3S, N_2S_2 and N_2SO porphyrin cores. The use of monofunctionalised N_3S, N_2S_2 and N_2SO porphyrins is further demonstrated by synthesising the first examples of three new covalently linked diarylethyne-bridged unsymmetrical dimers containing two different porphyrin cores such as N_2S_2-N_4, N_2S_2-N_3S and N_2S_2-N_2SO.

Introduction

Unsymmetrical porphyrin dimers that consist of two different porphyrin sub-units are suitable models for mimicking electron- and energy-transfer processes of photosynthesis. In the recent past attention has been directed towards synthesising covalently linked unsymmetrical dimers such as porphyrin-chlorin, porphyrin-corrole, porphyrin-pheophorbide and porphyrin-phthalocyanine to study the photosynthesis processes.[1] A common feature among the various unsymmetrical dimers mentioned above is that they all have similar pyrrole nitrogens as donor atoms. Unsymmetrical porphyrin dimers containing two dissimilar cores having different donor atoms are expected to possess interesting structural and electronic properties. However, this area of porphyrin chemistry has largely remained unexplored due to the unavailability of suitable functionalised porphyrin building blocks. The replacement of one or two inner pyrrole nitrogens of porphyrin with heteroatoms such as S, O, Se and Te gives heteroatom-substituted porphyrins which possess quite different properties from normal porphyrins (N_4 core) in terms of both aromatic character and their ability to stabilize metals in unusual oxidation states.[2] The assembly of such a heteroatom-substituted porphyrin (N_3S, N_3O, N_2S_2, N_2O_2, N_2SO etc) and normal porphyrin (N_4 core) or an assembly of two different heteroatom-substituted porphyrins would offer unique dimers which are expected to have unusual electronic structure and interesting properties. However, very few examples of unsymmetrical porphyrin arrays containing heteroatom-substituted porphyrins have appeared in the literature[3] due to the unavailability of the functionalised heteroporphyrin building blocks. Heteroporphyrins with one functional group at the *meso* position are ideal building blocks for the synthesis of covalently linked unsymmetrical porphyrin dimers. To the best of our knowledge, there are only two methods available in the literature to synthesise monofunctionalised heteroatom-substituted porphyrin building blocks. Lindsey and co-workers[4] have developed a novel and efficient method to prepare monofunctionalised 21-thia- and 21-oxaporphyrins with ethyne and iodo functional groups at the *para* position of the *meso*-phenyl groups, as shown in Scheme 1. As noted in Scheme 1, the two key precursors involved in the synthesis are not easily available, and the method involves multi-step synthesis, extensive chromatography and vacuum distillations to purify the precursors. We have recently developed[5] a rapid, one-pot synthetic route (Scheme 2) to prepare monofunctionalised 21-thia- and 21-oxaporphyrins from 2-(arylhydroxymethyl)thiophene or -furan (thiophene or furan mono-ol). In this mono-ol method, two equivalents of thiophene or furan mono-ol containing the functionalised aryl group are condensed with two equivalents of aldehyde and three equivalents of pyrrole under acid-catalysed conditions followed by simple column chromatography to give the desired monofunctionalised 21-thia- or

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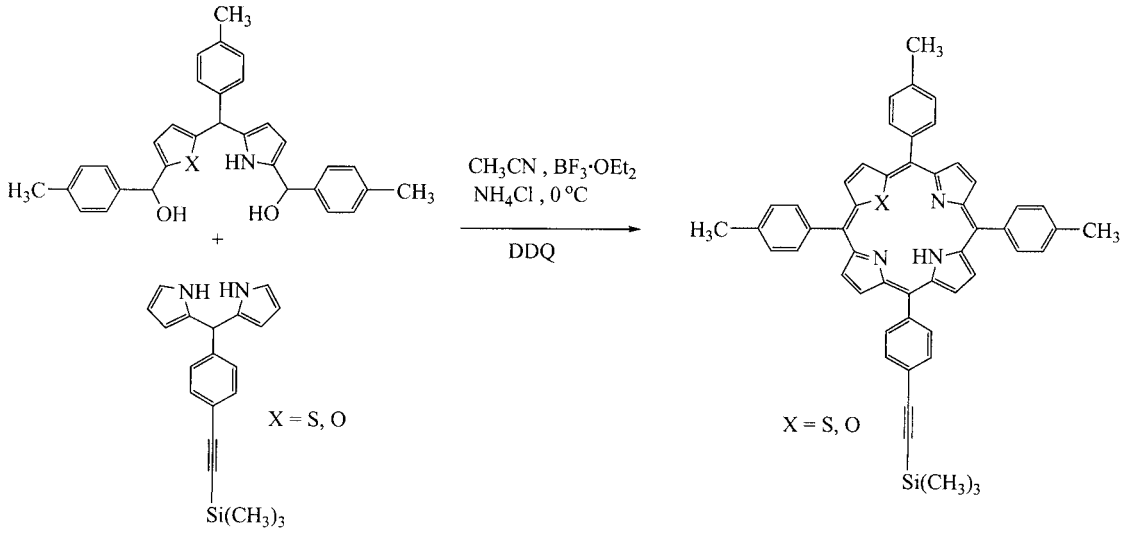
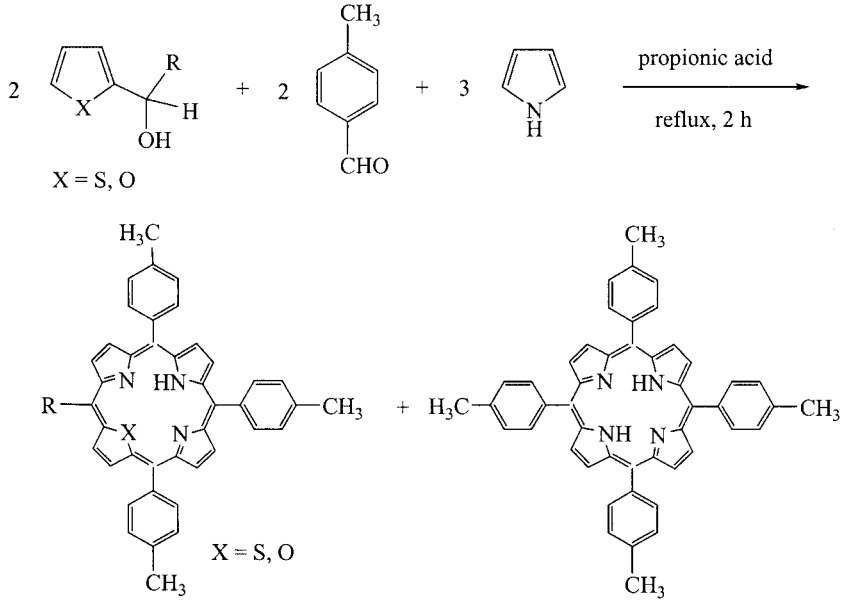
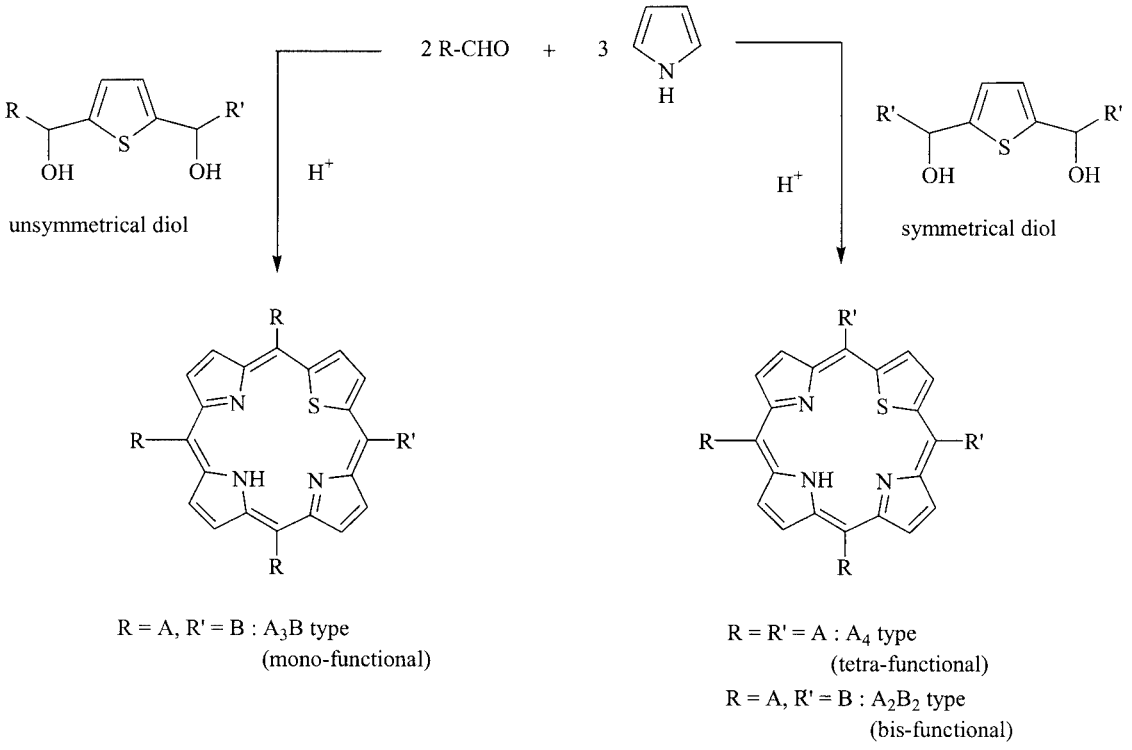
21-oxaporphyrins (Scheme 2). Although the mono-ol method is very simple, the yields of porphyrins are quite low (2–6%). Furthermore, using this method, one can synthesise only the monofunctionalised 21-thia- and 21-oxaporphyrins. Hence we have developed an alternate method using unsymmetrical thiophene diols[5b] to improve the yields of monofunctionalised 21-thiaporphyrins. The unsymmetrical diol method is based on the well-established synthetic strategy used for the synthesis of 21-thiaporphyrins. The 21-thiaporphyrins can be synthesised[6] by condensing 2,5-bis(arylhydroxymethyl)thiophene (symmetrical thiophene diol) with an aldehyde and pyrrole under standard porphyrin-forming conditions (Scheme 3). The symmetrical thiophene diol method[6] is useful to prepare 21-thiaporphyrins bearing only one type of *meso* substituent (A_4 type) or two types of *meso* substituents in a *cis* configuration (*cis*-A_2B_2 type). In addition to the synthesis of 21-thiaporphyrins, the symmetrical thiophene diols have been explored for the synthesis of several novel macrocycles.[7] There was no method available based on thiophene diols to synthesise monofunctionalised 21-thiaporphyrins until our recent communication,[5b] in which we used an unsymmetrical thiophene diol in place of the symmetrical thiophene diol and synthesised for the first time a series of monofunctionalised 21-thiaporphyrins. In this paper, we describe in detail the further importance of the unsymmetrical thiophene diols as key synthons to synthesise the desired monofunctionalised heteroporphyrins with three different types of heteroatom-substituted cores (N_3S, N_2S_2 and N_2SO). We elaborate the synthesis and characterisation of a series of unsymmetrical thiophene diols and a series of monofunctionalised 21-thia- (N_3S), 21,23-dithia- (N_2S_2) and 21-thia-23-oxapor-



Scheme 1. Synthetic scheme of Lindsey and co-workers for the preparation of monofunctionalised 21-thia- and 21-oxaporphyrins.



Scheme 2. Mono-ol method for the synthesis of monofunctionalised 21-thia- and 21-oxaporphyrins.



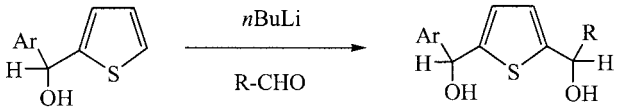
Scheme 3. Symmetrical and unsymmetrical thiophene diol methods for the preparation of functionalised 21-thiaporphyrins.

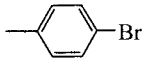
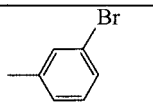
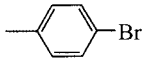
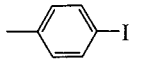
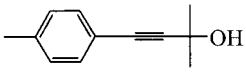
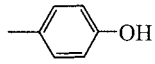
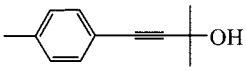
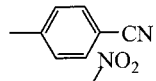
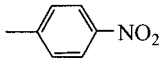
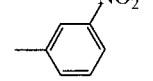
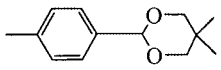
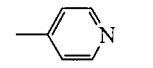
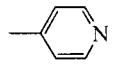
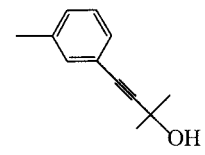
phyrin (N_2SO) building blocks. This method is simple and versatile and the required monofunctionalised heteroporphyrin building blocks with N_3S, N_2S_2 or N_2SO cores can be prepared in 100 mg batches in a one-pot reaction. We also show the use of the monofunctionalised heteroporphyrins in the synthesis of the first examples of three covalently linked diarylethyne-bridged unsymmetrical dimers with different combinations of porphyrin cores such as N_2S_2-N_4, N_2S_2-N_3S and N_2S_2-N_2SO.

Results and Discussion

Synthesis of Unsymmetrical Thiophene Diols 1–14

The required thiophene mono-ols 2-(phenylhydroxymethyl)thiophene and 2-(*p*-tolylhydroxymethyl)thiophene were prepared in 65–70% yields by treating thiophene with 1.2 equivalents of *n*BuLi followed by 1.2 equivalents of benzaldehyde or *p*-tolualdehyde in THF at 0 °C and subsequent purification by silica-gel column chromatography.[5a] The unsymmetrical thiophene diols **1**–**14** were prepared by treating the 2-(phenyl or *p*-tolylhydroxymethyl)-thiophene with two equivalents of *n*BuLi followed by 1.2 equivalents of functionalised aromatic aldehyde in THF at 0 °C (Scheme 4). TLC analysis of the crude reaction mixture showed two fast moving minor spots corresponding to the unchanged aldehyde and mono-ol, respectively, followed by one very minor and one major spot which were close to each other and correspond to the desired thiophene diol. Since the unsymmetrical diols have two chiral centres, the additional minor spot observed above the major spot could be due to its diastereomer.[8] We collected only the major spot in all diol reactions and used the compound isolated for the porphyrin reactions. Because the chirality is lost on porphyrin formation,[8] no attempts were made to characterise the very minor spot. We varied the number of *n*BuLi equivalents to optimise the conditions for unsymmetrical thiophene diols. The reaction requires a minimum of two equivalents of *n*BuLi to get decent yields of unsymmetrical thiophene diols because the hydroxyl group of the thiophene mono-ol is also lithiated during the reactions. Although the yields of unsymmetrical thiophene diols are moderate (Scheme 4), large quantities of unsymmetrical diols can be prepared easily by this method. Furthermore, since the aryl group containing the functional group is introduced at the unsymmetrical thiophene diol stage, this allows an easy access to prepare monofunctionalised heteroporphyrins containing a desired functional group. The unsymmetrical thiophene diols **1**–**14** were characterised by NMR and IR spectroscopy, mass spectrometry and elemental analysis. The unsymmetrical nature of the diols is clearly evident in their ^{1}H NMR spectra: the thiophene protons in the ^{1}H NMR spectra, which generally appear as a singlet in 2,5-bis(arylhydroxymethyl)thiophene (symmetrical diol), appear as a multiplet or two sets of doublets in diols **1**–**14**. Furthermore, the presence of a broad singlet at around δ = 2.00–5.00 ppm in the ^{1}NMR spectrum and a very strong broad peak at about 3400 cm^{-1} in the spectra IR indicate the presence of hydroxyl groups. The ES mass spectra of **1**–**14** show [M$^+$], [M$^+$ – OH] or [M$^+$ + Na] peaks, thus con-



Ar	R	Thiophene diol	Yield %	Ar	R	Thiophene diol	Yield %
Ph		**1**	40	Tolyl		**8**	38
Tolyl		**2**	39	Tolyl		**9**	36
Ph		**3**	16	Tolyl		**10**	32
Tolyl		**4**	46	Tolyl		**11**	40
Ph		**5**	29	Tolyl		**12**	41
Ph		**6**	35	Tolyl		**13**	45
Ph		**7**	30	Tolyl		**14**	44

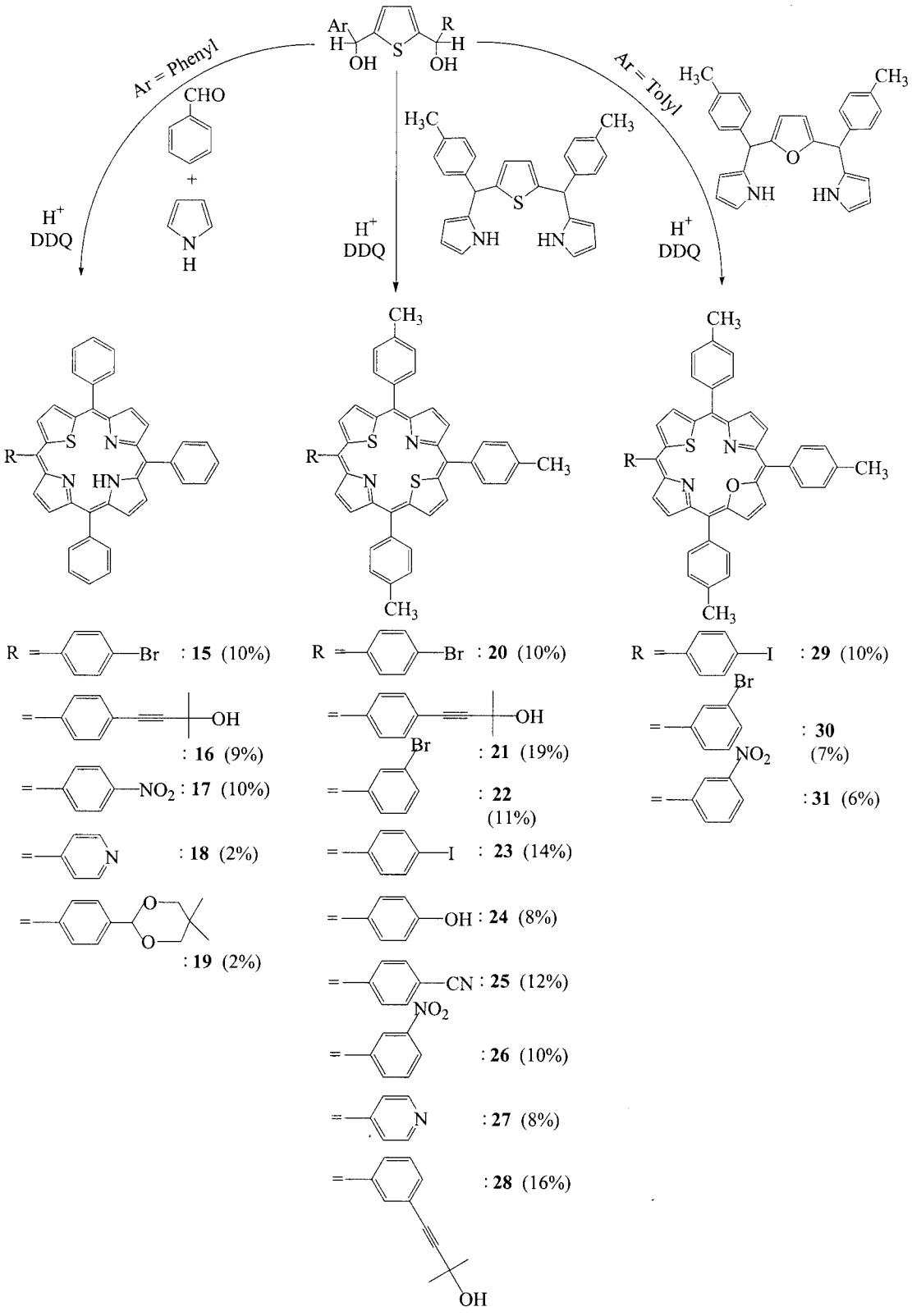
Scheme 4. Synthesis of unsymmetrical thiophene diols **1**–**14**.

firming the identities of the unsymmetrical thiophene diols. The elemental analyses were also in agreement with the composition of the diols **1**–**14**.

Synthesis of Monofunctionalised 21-Thiaporphyrins

The monofunctionalised 21-thiaporphyrins were synthesised by condensing one equivalent of the appropriately functionalised unsymmetrical thiophene diol with two equivalents of benzaldehyde and three equivalents of pyrrole under Lindsey's[9] or Adler's[10] porphyrin-forming conditions (Scheme 5). The condensation is expected to result in the formation of a mixture of four porphyrins: 5,10,15,20-tetraphenylporphyrin (H_2TPP), the desired monofunctionalised 21-thiaporphyrin and a *cis* and *trans* mixture of difunctionalised 21,23-dithiaporphyrins.[5b] The TLC analysis clearly showed three spots corresponding to H_2TPP, the desired 21-thiaporphyrin and the *cis* and *trans* mixture of 21,23-dithiaporphyrins. The mixture of porphyrins was separated by silica gel column chromatography; the desired monofunctionalised 21-thiaporphyrin was always obtained as the second band. Two chromatographic purifications were required to separate the mixture of porphyrins, and the pure porphyrins **15**–**19** were afforded in 2–10% yields. The low yields in the case of **18** and **19** are due to the low solubility of the aldehydes under our reaction conditions. Some of these monofunctionalised 21-thiaporphyrins were recently prepared by us[5a] using the "mono-ol method". However, the yields of the monofunctionalised21-thiaporphyrin building blocks from the "mono-ol method" are quite low. Although we have not demonstrated the unsymmetrical diol method with several examples of monofunctionalised 21-thiaporphyrins, we note that the unsymmetrical diol method is much superior and more versatile than than the mono-ol method for preparing the desired monofunctionalised 21-thiaporphyrins in decent yields. Furthermore, separation of the mixture of porphyrins is very straightforward. Absorption spectroscopy is the best technique to follow the purification of porphyrins on silica gel column and also to identify the desired 21-thiaporphyrin fraction easily, since the absorption spectrum of 21-thiaporphyrin is quite different from that of H_2TPP and 21,23-dithiaporphyrin.[11] We have not made any attempts to separate the *cis* and *trans* mixture of 21,23-dithiaporphyrin. Allporphyrin condensation reactions work well under either Lindsey's or Adler's reaction conditions, and no scramblingor any other additional porphyrin products were noted in these reactions.

The porphyrins **15**–**19** were characterised by NMR and absorption spectroscopy, mass spectrometry and elemental



Scheme 5. Synthesis of monofunctionalised heteroporphyrins **15**–**31**.

analysis. All porphyrins show the [M^+] ion peak in the ES mass spectra and the elemental analyses confirm the composition of the monofunctionalised 21-thiaporphyrins. In the ^{1}H NMR spectra, the two thiophene protons, which generally appear as a singlet in the symmetrically substituted 21-thiaporphyrin[2] 5,10,15,20-tetraphenyl-21-thiaporphyrin (STPPH), appear as two sets of signals or a complex multiplet in **15**–**19** due to the unsymmetrical substitution of

monofunctionalised 21-thiaporphyrins. The absorption spectra of **15**–**19** show four Q-bands and one Soret band whose peak positions closely match those of STPPH.[2]

Synthesis of Monofunctionalised 21,23-Dithiaporphyrins

Interestingly, there are very few reports of unsymmetrical porphyrin arrays containing 21,23-dithiaporphyrin as one of the sub-units. In 2001, we reported the first synthesis of a covalently linked unsymmetrical porphyrin pentamer containing one 21,23-dithiaporphyrin unit and four normal porphyrin units using the tetra-functionalised 21,23-dithiaporphyrin building block and demonstrated an efficient energy transfer from a peripheral normal porphyrin unit to the central 21,23-dithiaporphyrin unit.[3c] Recently, we synthesised a series of mono *meso*-pyridyl 21,23-dithiaporphyrin building blocks[12] and used them for the synthesis of non-covalent unsymmetrical dimers. However, there are no monofunctionalised 21,23-dithiaporphyrin building blocks available for the synthesis of covalently linked unsymmetrical porphyrin dimers. We have shown here the use of unsymmetrical thiophene diols in the synthesis of nine monofunctionalised 21,23-dithiaporphyrin building blocks having a range of functionalities such as iodo, hydroxy, bromo, cyano, ethynyl and nitrophenyl groups at the *meso* position. The condensation of one equivalent of the appropriate unsymmetrical thiophene diol with one equivalent of known 16-thiatripyrrane[13] under Lindsey's[9] or Adler's[10] porphyrin-forming conditions resulted in the formation of the desired monofunctionalised 21,23-dithiaporphyrin as a single product (Scheme 5). TLC analysis of the crude reaction mixture clearly showed a single spot corresponding to the required monofunctionalised 21,23-dithiaporphyrin and lot of polymeric material at the base. After standard work-up of the reaction mixture, the crude porphyrins were purified by one simple silica gel column chromatography and afforded 21,23-dithiaporphyrins **20**–**28** in 8–19% yields. No scrambling was noted in these reactions as we did not observe the formation of any other porphyrin other than the required monofunctionalised 21,23-dithiaporphyrins. Thus, the present method of using unsymmetrical thiophene diols gives an easy access to any desired monofunctionalised 21,23-dithiaporphyrin building block in very decent yields. The porphyrins **20**–**28** were characterised by NMR and absorption spectroscopy, mass spectrometry and elemental analysis. In the ^{1}H NMR spectra, unlike the symmetrically substituted 5,10,15,20-tetraphenyl-21,23-dithiaporphyrin[2] (S_2TPP), which shows a singlet each for the thiophene and pyrrole protons, the monofunctionalised 21,23-dithiaporphyrins show two or more signals for the thiophene and pyrrole protons due to the unsymmetrical substitution pattern. All porphyrins show an [M$^+$] ion peak in the ES mass spectra and the elemental analyses are in agreement with the composition of the porphyrins **20**–**28**. The absorption spectra of **20**–**28** show the typical four Q-bands and one Soret band with peak positions matching those of S_2TPP.[2]

Synthesis of Monofunctionalised 21-Thia-23-oxaporphyrins

To the best of our knowledge, there is no report of unsymmetrical porphyrin arrays containing 21-thia-23-oxaporphyrin as one of the sub-units. This may be because of the unavailability of suitable 21-thia-23-oxaporphyrin building blocks. In general, the reports of heteroporphyrins having two different heteroatoms such as S and O in the core are too few to be able to understand the physico-chemical properties of such systems.[14] We have used the unsymmetrical thiophene diols to synthesise for the first time three monofunctionalised 21-thia-23-oxaporphyrin building blocks **29**–**31**. The condensation of one equivalent of the appropriate unsymmetrical thiophene diol with one equivalent of 16-oxatripyrrane[14b] under Adler's or Lindsey's porphyrin-forming conditions gave the desired 21-thia-23-oxaporphyrin building blocks as the sole product. Since no other porphyrin was formed due to scrambling, a simple silica gel column chromatography was used to purify the porphyrins. The porphyrins **29**–**31** were isolated in 6–10% yields and characterised by various spectroscopic techniques. The [M$^+$] ion in the ES mass spectra and acceptable elemental analysis confirmed the nature of the porphyrins **29**–**31**. In the ^{1}H NMR spectra of **29**–**31**, the protons corresponding to both thiophene and furan rings are present at δ = 9.65–9.80 and δ = 9.19–9.26 ppm, respectively, further confirming the identity of the compounds. The furan and thiophene protons in 5,10,15,20-tetraphenyl-21-thia-23-oxaporphyrin[2] (OSTPP) appear as singlets. However, in monofunctionalised 21-thia-23-oxaporphyrins **29**–**31** the furan protons appear as a singlet but the thiophene protons appear always as two sets of signals or a complex multiplet due to the unsymmetrical substitution around the thiophene ring. The pyrrole protons in **29**–**31**, also appear as three sets of doublets or multiplets due to this unsymmetrical substitution. The absorption spectra of **29**–**31** show four Q-bands and one Soret band with peak positions matching those of OSTPP.[2]

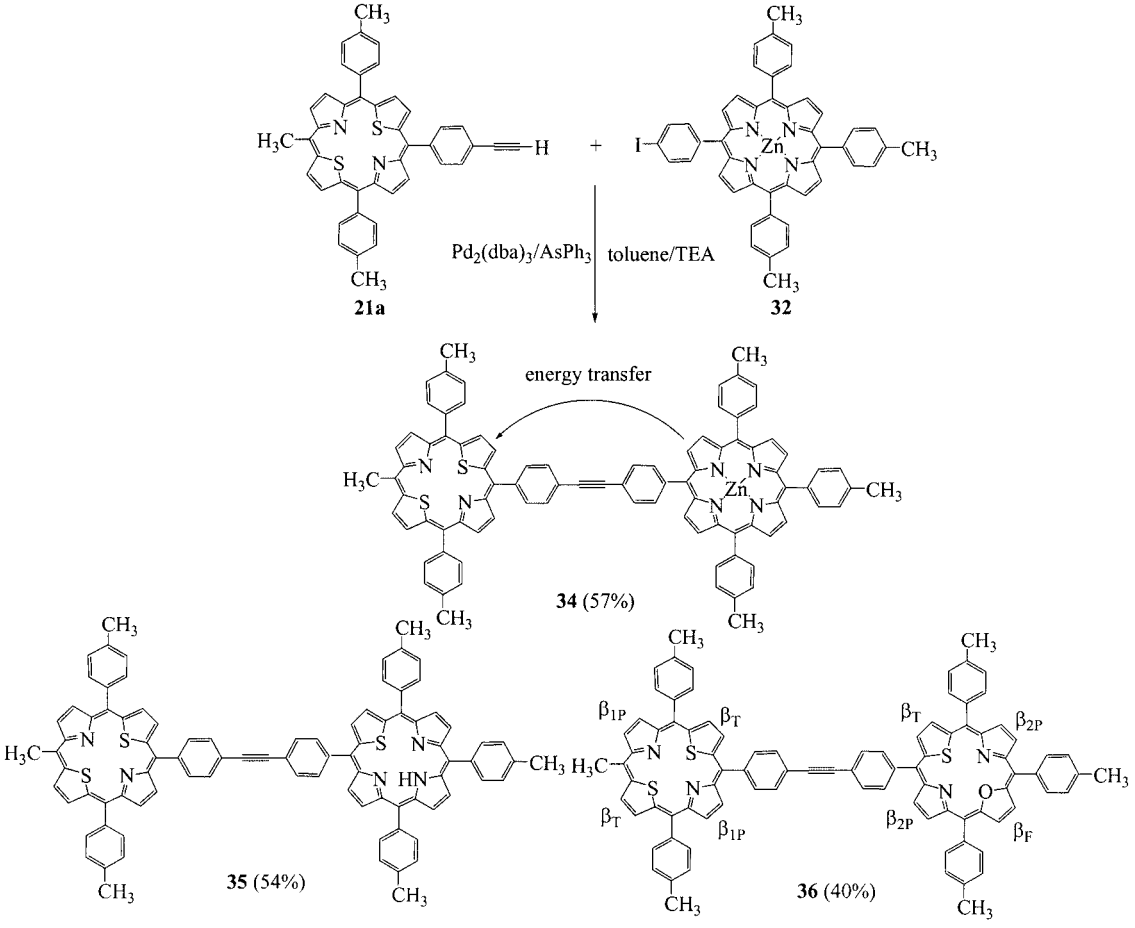
Covalently Linked Unsymmetrical Porphyrin Dimers

The monofunctionalised 21-thia-, 21,23-dithia- and 21-thia-23-oxaporphyrins are suitable building blocks to synthesise a variety of unsymmetrical porphyrin dimers. As mentioned above, there have been very few reports[3] of unsymmetrical dimers containing heteroporphyrins as one of the sub-units, and this has limited our understanding of the physico-chemical properties of these systems. Recently, we reported the synthesis of five covalently linked unsymmetrical porphyrin dimers containing mainly 21-thia- and 21-oxaporphyrin subunits.[5a] Interestingly, there is no report of covalently linked dimers containing 21,23-dithia- or 21-thia-23-oxaporphyrins as one of the sub-units. We therefore synthesised for the first time three covalently linked unsymmetrical dimers (**34**–**36**) having two different porphyrin sub-units − dimer **34** contains N_2S_2 and N_4 sub-units, dimer **35** contains N_2S_2 and N_3S sub-units and dimer **36** contains N_2S_2 and N_2SO porphyrin sub-units − from the monofunc-

tionalised heteroporphyrins synthesised in this report. These three diphenylethyne-bridged dimers were synthesised using Lindsey's conditions[15] for the Sonogashira coupling of an ethynylphenyl porphyrin and an iodophenyl porphyrin. Under these conditions, the coupling of an equimolar quantity of ethynylphenyl porphyrin and iodophenyl porphyrin in dilute conditions can be carried out at very low temperature and in the absence of copper. The low temperature conditions are needed to prevent side reactions, such as the formation of ethyne oligomerisation products, and the absence of copper is important since the free-base porphyrins are easily metallated.

The required ethynylphenyl porphyrin building block with an N_2S_2 core (**21a**) was prepared by deprotection of **21** with KOH in benzene/methanol at 80 °C.[16] The 5-(4-iodophenyl)-10,15,20-tri(*p*-tolyl)zinc(II) porphyrin[16] **32** and 5-(4-iodophenyl)-10,15,20-tri(*p*-tolyl)-21-monothiaporphyrin[5a] **33** were prepared by literature methods. The N_2S_2-N_4 **34** dimer was synthesised by coupling of **21a** and **32** in toluene/triethylamine at 35 °C in the presence of a catalytic amount of $Pd_2(dba)_3/AsPh_3$ (Scheme 6). TLC monitoring after 12 h showed two very minor spots corresponding to the starting materials and one major spot corresponding to the required dimer **34**. After standard work-up, the crude reaction mixture was subjected to silica gel column chromatography with petroleum ether/dichloromethane as eluent. The excess $AsPh_3$ and the small amounts of unreacted starting monomeric porphyrins were removed with petroleum ether/dichloromethane (80:20) as eluent and the desired dimer, with a small amount of impurities, was collected with petroleum ether/dichloromethane (65:35) as eluent. The impure dimer was subjected to a second silica gel column chromatography with the same solvent mixture to give the pure dimer **34** as a purple solid in 57% yield. Similarly, the N_2S_2-N_3S dimer **35** was prepared by the coupling of **21a** and **33**, and the N_2S_2-N_2SO dimer **36** by coupling of **21a** and **29** under the same coupling conditions as used for dimer **34**. All three dimer reactions worked smoothly and required two straightforward silica gel column chromatographic purifications. Dimers **34**–**36** are highly soluble in all common organic solvents and were characterised by NMR and absorption spectroscopy, mass spectrometry and elemental analysis.

The ES mass spectra show the expected [M^+] ion peak and the elemental analyses closely match the expected compositions of the dimers **34**–**36**. The ^{1}H NMR spectra of dimers **34**–**36** are very clean and the resonances of the dimers were assigned on the basis of the spectra observed for the corresponding monomers taken independently. A representative spectrum of dimer **36**, along with the spectra of



Scheme 6. Synthesis of unsymmetrical covalent dimer **34** and the structures of dimers **35** and **36**.

the corresponding monomers, are shown in Figure 1. In the ^{1}H NMR spectra of the dimers, the resonances corresponding to both the porphyrinic sub-units and the bridging groups are present. In the N_2S_2-N_4 dimer **34**, the four thiophene protons appear as one multiplet resonance in the region δ = 9.73–9.76 ppm. The twelve pyrrole protons, four belonging to the N_2S_2 porphyrin sub-unit and eight belonging to the ZnN_4 porphyrin sub-unit, appear as four sets of overlapping signals in the δ = 8.69–9.07 ppm region. The *ortho* and *meta* protons of the *meso* tolyl groups and the bridging phenyl groups appear in the region δ = 7.42–8.32 ppm and the methyl groups appear at around δ = 2.70 ppm. Dimers **35** and **36** were also characterised by comparing the ^{1}H NMR spectra with their corresponding monomeric porphyrin units. In N_2S_2-N_3S dimer **35**, the four thiophene protons of the N_2S_2 porphyrin unit appeared as a multiplet in the region δ = 9.68–9.78 ppm and the two thiophene protons of the N_3S porphyrin sub-unit also appear as a multiplet in the region δ = 9.48–9.51 ppm. The ten pyrrole protons of both the porphyrin units appear as two sets of signals. A broad singlet at δ = 8.94 ppm was assigned to two pyrrole protons and a complex multiplet in the region δ = 8.58–8.72 ppm was assigned to eight pyrrole protons. The aryl protons appear in the region δ = 7.32–8.28 ppm and the inner NH proton of the N_3S porphyrin sub-unit appears as a broad singlet at δ = –2.65 ppm. In ^{1}H NMR spectrum of N_2S_2-N_2SO dimer **36**, two multiplet resonances in the region δ = 9.70–9.73 ppm and δ = 9.61–9.64 ppm are observed for four and two thiophene protons of the N_2S_2 and N_2SO porphyrin sub-units, respectively. The two furan protons of the N_2SO porphyrin sub-unit appear as a singlet at δ = 9.18 ppm. The eight pyrrole protons, four belonging to the N_2S_2 porphyrin sub-unit and the other four belonging to the N_3S porphyrin sub-unit, appear as six sets of signals at δ = 8.73 (d, 1 H), 8.70 (s, 2 H), 8.64 (d, 1 H), 8.55 (d, 1 H), 8.51 (d, 1 H) and 8.40–8.43 ppm (m, 2 H). The aryl protons appear in the region δ = 7.50–8.18 ppm. A comparison of the chemical shifts of the various protons of dimers **34**–**36** with those of the corresponding individual monomeric porphyrin units indicate only minor differences, which suggests that the two porphyrin sub-units in the dimers interact very weakly. This is consistent with earlier reports on covalently linked tetraphenylporphyrin dimers.[17]

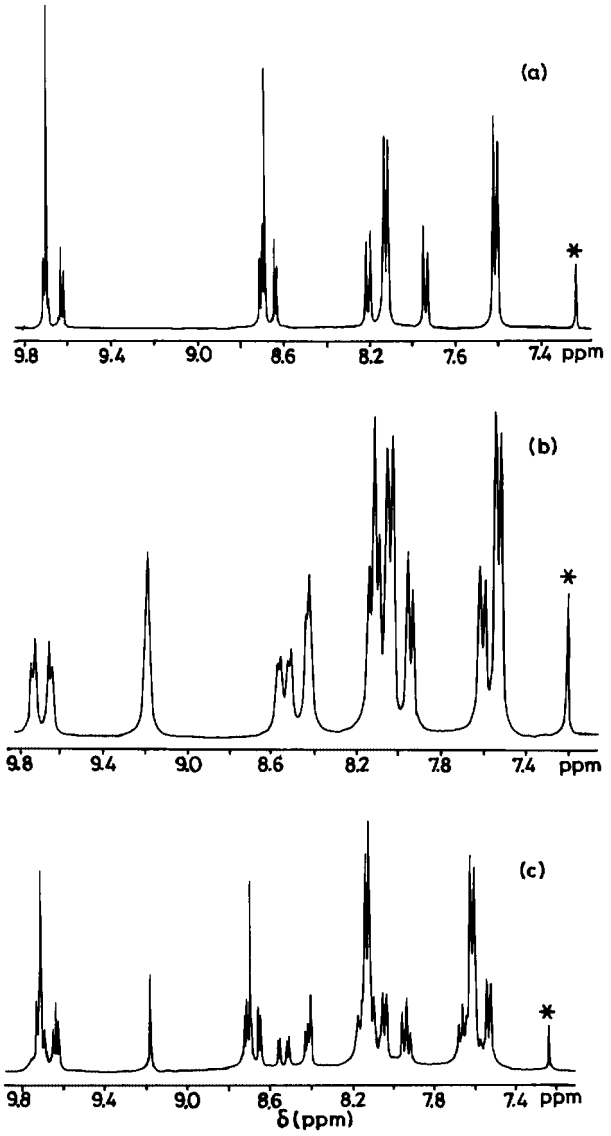


Figure 1. ^{1}H NMR spectra of **21a** (a) **29** (b) and **36** (c) recorded in $CDCl_3$.

Absorption and Fluorescence Properties of Dimers 34–36

The absorption spectra of dimers **34**–**36** and the corresponding monomers in toluene were measured at room temperature; the results are tabulated in Table 1. A comparison of the absorption spectra of dimers **34**–**36** along

Table 1. Absorption data of dimers **34**–**36** and their corresponding monomers recorded in toluene.

Porphyrin	Soret band λ [nm] ($\varepsilon \times 10^{-4}$)	Absorption Q-bands λ [nm] ($\varepsilon \times 10^{-3}$)
21a	437 (22.3)	514 (22.0), 548 (8.0), 634 (1.6), 697 (4.0)
32	423 (40.6)	550 (16.6), 588 (1.9)
33	431 (27.0)	515 (20.9), 550 (6.9), 617 (2.8), 677 (5.4)
29	432 (18.2)	512 (23.7), 545 (5.4), 645 (1.6), 710 (6.0)
34	425 (22.9), 439 (20.7)	516 (18.9), 551 (13.7) 592 (3.1), 636 (1.6), 699(3.4)
35	432 (38.7)	514 (33.3), 548 (9.7), 619 (2.6), 633 (2.1), 678 (3.6), 697 (3.5)
36	435 (44.3)	514 (51.0), 547 (13.4), 639 (3.1), 696 (6.6), 708 (8.8)

with their corresponding monomers is shown in Figure 2 (see a–c). Dimer **34**, which contains N_2S_2 porphyrin and ZnN_4 porphyrin sub-units, shows a split Soret band at 425 and 439 nm and Q-bands at 516, 551, 592, 636 and 699 nm. This spectrum is essentially a linear combination of the spectra of the corresponding monomers with only minor differences in wavelength maxima and band shapes. The Soret band in dimer **34** is split because of the large difference between the Soret absorption peak maxima of the corresponding monomers. Similarly, the absorption spectra of other two dimers **35** and **36** are nearly the sum of the two corresponding monomers. The Soret absorption peak maxima of these two dimers is not split but appears as a broad band due to the overlap of the Soret band maxima of the corresponding monomers. Thus, the absorption spectral studies of dimers **34**–**36** indicate a weak interaction between the two moieties and the two chromophores mostly retain their individual identities.

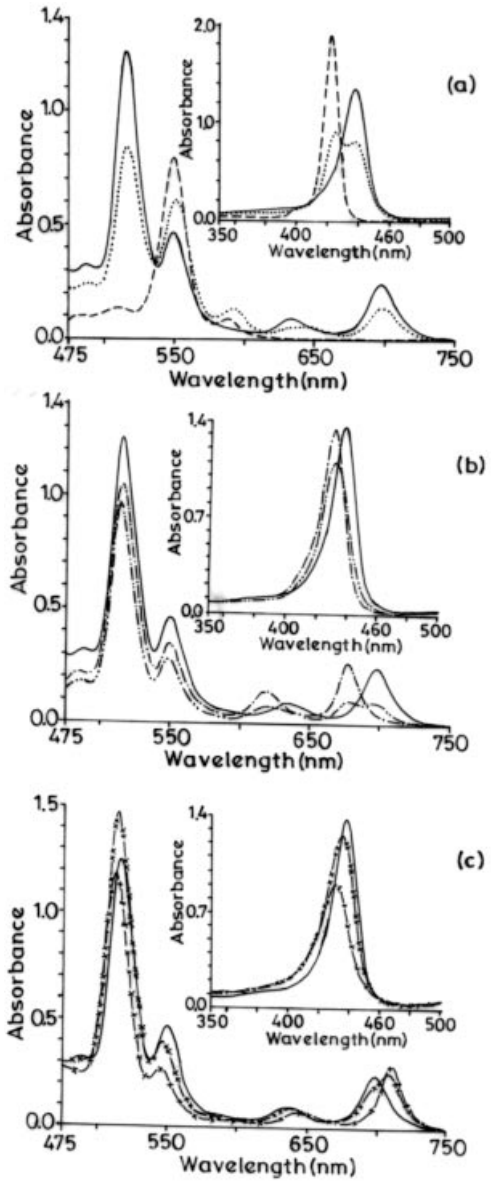


Figure 2. Q-band absorption spectra of: (a) **21a** (), **32** (----), **34** (····); (b) **21a** (), **33** (-·-·-), **35** (-··-··-); (c) **21a** (), **29** (-*-*-), **36** (-**-**-) recorded in toluene. Their corresponding Soret band absorption spectra are shown in the insets. The concentrations used for Q-band spectra was 5×10^{-5} M and for Soret band was 5×10^{-6} M.

The fluorescence properties of dimers **34**–**36** and the appropriate reference compounds were recorded in toluene at room temperature. The emission spectra of dimer **34** and a 1:1 mixture of the corresponding monomers **21a** and **32** recorded at 550 nm are shown in Figure 3. As is evident from this figure, in the dimer **34**, excitation at 550 nm, where the ZnN_4 porphyrin sub-unit absorbs strongly (φ = 0.033 for ZnTPP), the emission of the ZnN_4 porphyrin sub-unit is quenched by 93.5% (φ = 0.00213) and the strong emission from the N_2S_2 porphyrin sub-unit is observed. However, when a 1:1 mixture of **21a** and **32** was irradiated at 550 nm, a strong emission was observed mainly from the ZnN_4 porphyrin sub-unit (Figure 3). These results indicate that there is an efficient energy transfer from the ZnN_4 porphyrin sub-unit to the N_2S_2 porphyrin sub-unit in dimer **34**. The energy transfer that occurs in **34** is independent of the excitation wavelength. The excitation spectrum recorded for **34** at λ_{em} = 730 nm matches exactly with the absorption spectrum, further confirming the efficient energy transfer between the sub-units. However, in the case of dimers **35** and **36**, it is difficult to study the energy-transfer properties since the porphyrin sub-units of **35** (N_2S_2 and N_3S porphyrin sub-units) and **36** (N_2S_2 and N_2SO porphyrin sub-units) exhibit overlapping emission spectra, hence no further studies were carried out on these dimers.

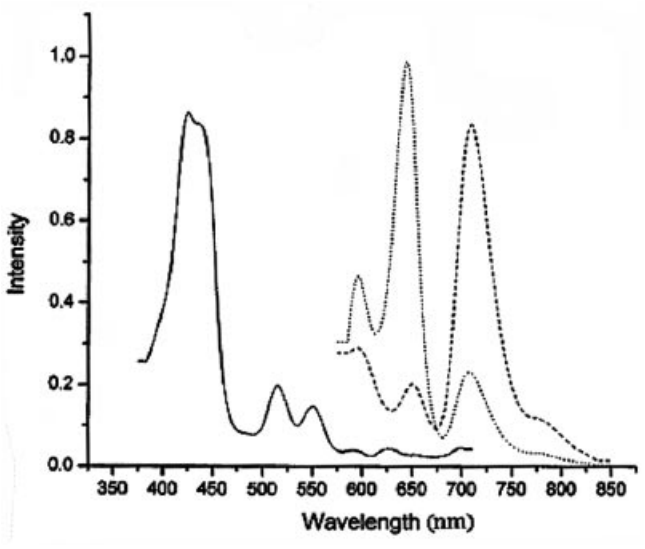


Figure 3. Comparison of emission spectra of dimer **34** (----) and a 1:1 mixture of **21a** and **32** (·····) recorded at an excitation wavelength of 550 nm in toluene. The excitation spectrum of dimer **34** () recorded at an emission wavelength of 750 nm is also shown.

We realized from the steady-state fluorescence study of dimer **34** that there is an efficient energy transfer between the sub-units, hence we carried out time-resolved fluorescence measurements on dimer **34** and its reference compounds ZnTPP and **21a** by exciting at λ = 406 nm in toluene at room temperature. The lifetimes of monomers

ZnTPP (τ = 2.1 ns) and **21a** (τ = 1.26 ns) were measured at 600 and 700 nm, respectively, and the observed lifetimes were closely matched with the reported literature values.[2] The fluorescence lifetime of dimer **34** was measured by monitoring the decay at 600 nm as well as 700 nm corresponding to the ZnN_4 and N_2S_2 porphyrin sub-units, respectively. When the emission decay of dimer **34** is monitored at 700 nm the decay is monophasic and exhibits a lifetime (τ = 1.27 ns) which matches closely that of **21a**. However, when the decay of dimer **34** is monitored at 600 nm, the fluorescence decay curve is biphasic (Figure 4). The shorter lifetime component (142 ps) accounts for the major emission of decay (96%) along with the minor longer-component decay at 2.1 ns. The minor lifetime component at 2.1 ns is attributed to the ZnN_4 porphyrin impurity present in the dimer **34**, and the major component at 142 ps is the decreased lifetime of the ZnN_4 porphyrin sub-unit because of the transfer of energy to N_2S_2 porphyrin sub-unit. From the measured lifetime of the ZnN_4 porphyrin sub-unit in dimer **34** ($\tau_{donor-acceptor}$) and the lifetime of ZnTPP (τ_{donor}), the rate constant for energy transfer (K_{ENT}) and the yield of energy transfer (φ_{ENT}) from the ZnN_4 porphyrin sub-unit to the N_2S_2 porphyrin sub-unit can be calculated from Equations (1) and (2).[17c]

$$K_{ENT} = 1/\tau_{donor-acceptor} - 1/\tau_{donor} \quad (1)$$

$$\varphi_{ENT} = K_{ENT} \times \tau_{donor-acceptor} \quad (2)$$

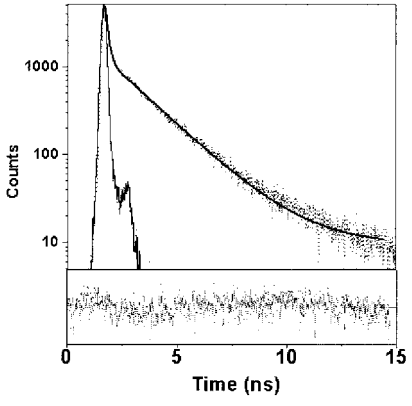


Figure 4. Fluorescence decay profile and the weighted residuals distribution fit of dimer **34**. The excitation wavelength used was 406 nm and emission was detected at 600 nm.

For dimer **34**, the rate of excitation energy transfer, K_{ENT}, is 152 ps and the yield of energy transfer, φ_{ENT}, is 93%. These results supports the energy transfer from the ZnN_4 porphyrin sub-unit to N_2S_2 porphyrin sub-unit. However, compared to other diarylethyne-bridged porphyrin dimers reported in the literature,[17] the rate of energy transfer in dimer **34** is slow. This may be due to the presence of two sulfur atoms in one of the porphyrin sub-unit of the dimer, which enhances the contribution of non-radiative decay channels.

Conclusions

In summary, a series of unsymmetrical thiophene diols have been synthesised in two steps by modifying a known synthetic strategy. The unsymmetrical thiophene diols, which can easily be synthesised in 5–7 g batches, were used as key synthons to prepare the monofunctionalised 21-thia- (five porphyrins) 21,23-dithia- (nine porphyrins) and 21-thia-23-oxaporphyrins (three porphyrins) upon condensation with readily available appropriate precursors under standard porphyrin-forming conditions. The unsymmetrical thiophene diol method is versatile and applicable to the synthesis of monofunctionalised 21-thia-, 21,23-dithia- and 21-thia-23-oxaporphyrins containing a required functional group such as iodophenyl, ethynylphenyl, nitrophenyl, bromophenyl, hydroxyphenyl and pyridyl groups at the *meso* position. To demonstrate the importance of the monofunctionalised heteroporphyrins, we synthesised three novel covalently linked unsymmetrical porphyrin dimers containing two different porphyrin cores. Thus, the unsymmetrical diol method reported in this paper gives an access to a variety of unsymmetrical porphyrin dimers containing two different porphyrin cores. The metallation, optical, electrochemical and photophysical properties of these dimers should be interesting and such studies are currently in progress in our laboratory.

Experimental Section

General: ^1H and ^{13}C NMR spectra were recorded on a Varian 400 MHz spectrometer using tetramethylsilane as an internal standard and are reported in δ (ppm) relative to the residual ^1H (of residual proton; δ = 7.26 ppm) and ^{13}C (δ = 77.0 ppm) signals of $CDCl_3$. Absorption and fluorescence spectra were obtained with Perkin–Elmer Lambda 35 and Perkin–Elmer Lambda 55 models, respectively. IR spectra were recorded on a Nicolet Impact-400 FT-IR spectrometer and the ES mass spectra were recorded with a Q-Tof micro (YA-105) mass spectrometer. Elemental analyses were conducted with a Thermo Finnigan Flash EA 1112. Diethyl ether, *n*-hexane, THF and toluene were obtained from S.D Fine chemicals, India, and dried with sodium benzophenone ketyl and distilled prior to use. Triethylamine was dried over CaH_2 and distilled prior to use. $BF_3{\cdot}OEt_2$, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) were used as obtained from Sigma–Aldrich Chemical Co. All other chemicals used for the synthesis were reagent grade, unless otherwise specified. Column chromatography was performed on silica (Merck, 60–120 mesh) obtained from Sisco Research Laboratories, India. The mono-ols 2-[hydroxy(phenyl)methyl]thiophene [mono-ol (a)] and 2-[hydroxy(*p*-tolyl)methyl]thiophene [mono-ol (b)][1] and the symmetrical tripyrranes 15,17-dihydro-5,10-ditolyl-16-thiatripyrrane (16-thiatripyrrane)[2] and 15,17-dihydro-5,10-ditolyl-16-oxatripyrrane (16-oxatripyrrane)[2] were synthesised by the reported methods.

2-[(4-Bromophenyl)hydroxymethyl]-5-[hydroxy(phenyl)methyl]thiophene (1): Freshly distilled dry diethyl ether (20 mL) was added to a three-necked, round-bottomed flask equipped with a rubber septum, gas inlet and gas outlet tube. A positive pressure of nitrogen was maintained and, after purging nitrogen for 15 min, mono-ol (a) (0.57 g, 2.91 mmol) was added to it. The temperature of the

reaction flask was maintained at 0 °C. TMEDA (0.88 mL, 5.81 mmol) followed by *n*BuLi (3.63 mL of ca. 15% solution in hexane) were added dropwise over 10 min to the stirred solution. The reaction mixture was allowed to stir for 30 min at 0 °C. An ice-cold solution of 4-bromobenzaldehyde (0.65 g, 3.49 mmol) in dry THF (15 mL) was added from another round-bottomed flask using a siphon apparatus. The mixture was stirred for 15 min and an ice-cold solution of NH_4Cl (50 mL, ca. 1 M) was added to quench the excess *n*BuLi. The organic layer was separated from the aqueous layer and the aqueous layer was extracted several times with diethyl ether. All the organic layers were combined and washed with water and brine and dried with anhydrous Na_2SO_4. The solvent was removed on a rotary evaporator under reduced pressure to afford the crude compound. TLC analysis showed three major spots corresponding to the unreacted mono-ol, unreacted 4-bromobenzaldehyde, and the desired diol **1**. In addition to the major spot of the diol, we also noted one minor spot just above the major diol spot, which was not characterised. The aldehyde, the mono-ol and the minor unidentified fractions were removed by silica gel column chromatography with petroleum ether/ethyl acetate (90:10) as eluent as eluent, and the major diol fraction **1** was collected with petroleum ether/ethyl acetate (85:15) as eluent. The solvent was removed on a rotary evaporator under reduced pressure to afford the diol **1** as an off-white solid (0.44 g, 40%). M.p. 106–107 °C. IR (KBr film): $\tilde{\nu}$ = 3414 cm^{-1}, 3010, 2960, 1596, 1489, 1403, 1266, 1123, 1077, 1021, 827, 705, 690. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.34 (br. s, 2 H, OH), 5.92 (s, 1 H, CH), 5.97 (s, 1 H, CH), 6.70–6.74 (m, 2 H, thiophene), 7.28–7.48 (m, 9 H, aryl) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 121.92, 124.54, 124.73, 126.31, 127.17, 127.47, 128.15, 128.66, 131.67, 141.90, 142.85 ppm. ES-MS for $C_{18}H_{15}BrO_2S$ (375.3): *m*/*z* (%) = 356.99 (48) [M^+ – 17], 359.02 (50). $C_{18}H_{15}BrO_2S$ (375.3): calcd. C 57.61, H 4.03, S 8.54; found C 57.89, H 3.83, S 8.50.

2-[(4-Bromophenyl)hydroxymethyl]-5-[hydroxy(*p*-tolyl)methyl]-thiophene (2): Dry, distilled diethyl ether (30 mL) was placed in a dry, 250-mL, three-necked, round-bottomed flask fitted with a rubber septum, gas inlet and gas outlet tube and a positive pressure of nitrogen was maintained. After purging nitrogen for 15 min, mono-ol (b) (1.00 g, 4.90 mmol) followed by TMEDA (1.48 mL, 9.79 mmol) and *n*BuLi (6.12 mL of ca. 15% solution in hexane) were added at 0 °C and stirring was continued for 1 h. Then, an ice-cold solution of 4-bromobenzaldehyde (1.09 g, 5.87 mmol) in dry THF (30 mL) was added to the stirred solution. The reaction mixture was stirred at 0 °C for a further 15 min and then brought to room temperature. The reaction was quenched by adding an ice-cold NH_4Cl solution (50 mL, ca. 1 M). The organic layer was washed with water and brine solution and dried with anhydrous Na_2SO_4. The solvent was removed on a rotary evaporator under reduced pressure to afford the crude compound. The crude compound was subjected to silica gel column chromatography for purification. The unreacted starting materials and the minor unidentified fractions were removed with petroleum ether/ethyl acetate (92:8) and the major diol fraction **2** was collected with petroleum ether/ethyl acetate (84:16) as eluent. The solvent was removed on a rotary evaporator under vacuum to afford pure diol **2** as a light-yellow liquid (0.76 g, 40%). IR (neat): $\tilde{\nu}$ = 3457 cm^{-1}, 3059, 2964, 2856, 1600, 1486, 1436, 1050, 810, 750, 690, 574. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.23 (s, 3 H, CH_3), 2.80 (br. s, 2 H, OH), 5.90–5.98 (m, 2 H, CH), 6.72 (m, 2 H, thiophene), 7.22–7.25 (m, 4 H, aryl), 7.44 (d, *J* = 8.2 Hz, 2 H, aryl), 7.60 (d, *J* = 8.2 Hz, 2 H, aryl) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.52, 70.60, 71.83, 120.33, 124.20, 124.55, 126.38, 126.57, 128.11, 129.37, 134.59, 136.00, 136.14, 140.22, 142.11, 142.45 ppm. ES-MS: *m*/*z* (%) = 411.1 (100) [M^+ + Na], 413.05 (92), 371.1 (98) [M^+ – 17], 373.06 (91). $C_{19}H_{17}BrO_2S$ (389.3): calcd. C 58.62, H 4.40, S 8.24; found C 58.41, H 4.31, S 8.32.

2-{Hydroxy[4-(3-hydroxy-3-methylbut-1-ynyl)phenyl]methyl}-5-[hydroxy(phenyl)methyl]thiophene (3): Dry diethyl ether (20 mL) was placed in a three-necked, round-bottomed flask. After purging nitrogen for 15 min, mono-ol (a) (0.57 g, 2.91 mmol) was added and stirred for 15 min while maintaining a positive pressure of nitrogen. TMEDA (0.88 mL, 5.81 mmol) followed by *n*BuLi (3.62 mL of ca. 15% solution in hexane) were then added dropwise over 10 min and the reaction mixture was allowed to stir for 30 min at 0 °C. An ice-cooled solution of 4-(3-hydroxy-3-methylbut-1-ynyl) benzaldehyde (0.66 g, 3.49 mmol) in dry THF (15 mL) was added and the mixture was stirred for 15 min. The reaction was quenched by adding an ice-cold NH_4Cl (50 mL, ca. 1 M) solution. After standard work up, all organic layers were combined and washed several times with water and brine and dried with anhydrous Na_2SO_4. The crude compound was subjected to silica gel column chromatography and the desired diol **3** collected with petroleum ether/ethyl acetate (80:20) as eluent. After removal of the solvent on a rotary evaporator under vacuum the pure diol **3** was isolated as a white solid (0.18 g, 16%). M.p. 170–175 °C. IR (KBr film): $\tilde{\nu}$ = 3421 cm^{-1}, 2942, 2868, 2110, 1480, 1484, 1266, 1123, 1077, 827, 705. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.56 (s, 6 H, CH_3), 2.04 (br. s, 3 H, OH), 5.94 (s, 1 H, CH), 5.97 (s, 1 H, CH), 6.68–6.70 (m, 2 H, thiophene), 7.29–7.43 (m, 9 H, aryl) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 31.45, 65.67, 71.86, 81.93, 94.02, 122.25, 125.09, 125.66, 126.22, 127.70, 131.78, 143.18, 147.71, 151.21 ppm. ES-MS: *m*/*z* (%) = 378.5 (18) [M^+], 361.4 (100) [M^+ – 17]. $C_{23}H_{22}O_3S$ (378.5): calcd. C 72.99, H 5.86, S 8.47; found C 73.43, H 5.77, S 8.30.

2-{Hydroxy[4-(3-hydroxy-3-methylbut-1-ynyl)phenyl]methyl}-5-[hydroxy(*p*-tolyl)methyl]thiophene (4): TMEDA (1.48 mL, 9.79 mmol) and *n*BuLi (6.12 mL of ca. 15% solution in hexane) were added, under the same experimental conditions as mentioned above, to a three-necked, 250-mL, round-bottomed flask containing mono-ol (b) (1.00 g, 4.90 mmol) in diethyl ether (30 mL). An ice-cold solution of 4-(3-hydroxy-3-methylbut-1-ynyl)benzaldehyde (1.10 g, 5.87 mmol) in dry THF (30 mL) was added slowly to the reaction mixture. The reaction was worked up in the standard way and the crude compound was purified by silica gel chromatography. The desired compound **4** was collected with petroleum ether/ethyl acetate (81:19) as eluent and the solvent was removed on a rotary evaporator under vacuum to afford pure diol **4** as a white solid in 46% yield (0.88 g). M.p. 122–123 °C. IR (KBr film): $\tilde{\nu}$ = 3372 cm^{-1}, 3010, 2960, 2870, 2115, 1486, 1436, 1050, 810, 750, 690. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.60 (s, 6 H, CH_3), 2.03 (s, 3 H, CH_3), 2.80 (br. s, 3 H, OH), 5.81–5.83 (m, 2 H, CH), 6.78 (m, 2 H, thiophene), 7.27 (m, 4 H, aryl), 7.52 (d, *J* = 8.2 Hz, 2 H, aryl), 7.80 (d, *J* = 8.2 Hz, 2 H, aryl) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.81, 25.83, 31.73, 70.67, 70.82, 81.73, 100.29, 124.40, 124.51, 125.51, 128.17, 129.35, 133.20, 134.52, 136.00, 136.55, 140.21, 146.04, 146.42, 146.47, 148.20, 150.71, 152.20 ppm. ES-MS: *m*/*z* (%) = 415.2 (22) [M^+ + Na], 375.2 (55) [M^+ – 17]. $C_{24}H_{24}O_3S$ (392.51): calcd. C 73.44, H 6.16, S 8.17; found C 73.41, H 6.32, S 8.32.

2-[Hydroxy(4-nitrophenyl)methyl]-5-[hydroxy(phenyl)methyl]thiophene (5): TMEDA (0.88 mL, 5.81 mmol) and *n*BuLi (3.63 mL of ca. 15% solution in hexane) were added to a three-necked, 250-mL, round-bottomed flask containing mono-ol (a) (0.57 g, 2.91 mmol) in diethyl ether (20 mL). An ice-cold solution of 4-nitrobenzaldehyde (0.40 g, 3.49 mmol) in dry THF (15 mL) was added slowly to the reaction mixture. Standard workup and

chromatography on silica with petroleum ether/ethyl acetate (85:15) as eluent afforded the desired diol **5** as a white solid (0.29 g, 29%). M.p. 145–148 °C. IR (KBr film): $\tilde{\nu}$ = 3348 cm^{-1}, 3083, 2859, 1642, 1596, 1525, 1454, 1352, 1275, 1204, 1011, 850, 706. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.62 (br. s, 2 H, OH), 6.20–6.22 (m, 2 H, CH), 6.90–6.92 (m, 2 H, thiophene), 7.42–8.16 (m, 9 H, aryl) ppm. ES-MS: *m*/*z* (%) = 341.0 (20) [M^+], 324.3 (100) [M^+ – 17]. $C_{18}H_{15}NO_4S$ (341.4): calcd. C 63.33, H 4.43, N 4.10, S 9.39; found C 63.61, H 4.27, N 4.36, S 9.20.

2-{[4-(5,5-Dimethyl-1,3-dioxan-2-yl)phenyl]hydroxymethyl}-5-[hydroxy(phenyl)methyl]thiophene (6): Mono-ol (a) (0.38 g, 1.94 mmol), TMEDA (0.58 mL, 3.87 mmol) and *n*BuLi (2.42 mL of ca. 15% solution in hexane) were added successively to dry distilled diethyl ether (20 mL) in a three-necked, round-bottomed flask under nitrogen, and the reaction mixture was stirred for 30 min at 0 °C. An ice-cold solution of 4-(5,5-dimethyl-1,3-dioxan-2-yl)benzaldehyde (0.51 g, 2.32 mmol) in dry THF (15 mL) was then added and the mixture was stirred for 15 min. Ice cold NH_4Cl (50 mL, ca. 1 M) was added to quench the reaction. After standard work-up, the crude compound was purified by silica gel column chromatography with petroleum ether/ethyl acetate (90:10) as eluent to afford diol **6** as a white solid (0.28 g, 35%). M.p. 141–143 °C. IR (KBr film): $\tilde{\nu}$ = 3383 cm^{-1}, 3011, 2936, 2869, 1480, 1494, 1246, 1047, 827, 705. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.90 (s, 3 H, CH_3), 0.88 (s, 3 H, CH_3), 3.24 (br. s, 2 H, OH), 3.64 (s, 2 H, OCH_2), 3.74 (s, 2 H, OCH_2), 5.49–5.53 (m, 2 H, CH), 5.60 (s, 1 H, CH), 6.50–6.54 (m, 2 H, thiophene), 7.31–7.47 (m, 9 H, aryl) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.35, 22.00, 23.18, 36.64, 101.69, 124.26, 125.23, 126.25, 127.43, 129.17, 130.07, 135.84, 138.08, 141.65, 146.13, 147.49, 148.63 ppm. ES-MS: *m*/*z* (%) = 393.5 (100) [M^+ – 17]. $C_{24}H_{26}O_4S$ (410.5): calcd. C 70.22, H 6.38, S 7.81; found C 70.65, H 6.51, S 7.60.

5-[Hydroxy(phenyl)methyl]-2-[hydroxy(4-pyridyl)methyl]-thiophene (7): The mono-ol (a) (0.57 g, 2.91 mmol) and *n*BuLi (3.63 mL of ca. 15% solution in hexane) were added successively to freshly distilled dry diethyl ether (20 mL) and stirred for 15 min under nitrogen at 0 °C. An ice-cold solution of 4-pyridinecarboxaldehyde (0.33 mL, 3.49 mmol) in dry THF (15 mL) was then added. The mixture was stirred for 15 min and ice-cold NH_4Cl (50 mL, ca. 1 M) was added. The aqueous layer was separated, washed with diethyl ether and mixed with the organic layer. All the organic layers were combined and washed several times with water and brine and dried with anhydrous Na_2SO_4. The crude compound was purified by silica gel column chromatography with dichloromethane/methanol (97:3) to give the diol **7** as a white solid (0.26 g, 30%). M.p. 79–80 °C. IR (KBr film): $\tilde{\nu}$ = 3362 cm^{-1}, 3011, 2860, 1596, 1429, 1403, 1021, 827, 705. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.70 (br. s, 2 H, OH), 5.82 (s, 1 H, CH), 6.02 (s, 1 H, CH), 6.70 (d, *J* = 5.2 Hz, 1 H, thiophene), 6.92 (d, *J* = 5.2 Hz, 1 H, thiophene), 7.21–7.29 (m, 5 H, aryl), 7.60 (d, *J* = 7.8 Hz, 2 H, pyridyl), 8.38 (d, *J* = 7.8 Hz, 2 H, pyridyl) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 70.41, 71.87, 121.38, 124.03, 126.25, 126.31, 126.44, 129.10, 129.43, 137.41, 140.33, 146.26, 148.63, 149.77, 153.22 ppm. ES-MS: *m*/*z* (%) = 298.1 (10) [M^+], 280.1 (100) [M^+ – 17]. $C_{17}H_{15}NO_2S$ (297.4): calcd. C 68.66, H 5.08, N 4.71, S 10.78; found C 68.75, H 5.22, N 4.59, S 10.60.

2-[(3-Bromophenyl)hydroxymethyl]-5-[hydroxy(*p*-tolyl)-methyl]thiophene (8): Mono-ol (b) (1.00 g, 4.90 mmol), TMEDA (1.48 mL, 9.79 mmol) and *n*BuLi (6.12 mL of ca. 15% solution in hexane) were added successively to dry, distilled diethyl ether (30 mL) in a three-necked, round-bottomed flask under nitrogen and the reaction mixture was stirred for 30 min at 0 °C. An ice-cold solution of 3-bromobenzaldehyde (1.09 g, 5.87 mmol) in dry THF (30 mL) was added to it and the reaction mixture was stirred for additional 15 min. An ice-cold NH_4Cl solution (50 mL ca.1 M) was added to quench the reaction. After standard workup, the crude compound was purified by silica gel column chromatography using petroleum ether/ethyl acetate (84:16) as eluent to give the diol **8** as a yellow oily liquid (0.72 g, 38%). IR (neat): $\tilde{\nu}$ = 3456 cm^{-1}, 3057, 2856, 1484, 1432, 1050, 810, 750, 690, 570. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.22 (s, 3 H, CH_3), 5.50 (s, 2 H, OH), 5.73 (s, 1 H, CH), 5.78 (s, 1 H, CH), 6.52 (d, *J* = 4.4 Hz, 1 H, thiophene), 6.58 (d, *J* = 4.4 Hz, 1 H, thiophene), 7.02–7.04 (m, 3 H, aryl), 7.18–7.20 (m, 2 H, aryl), 7.38–7.40 (m, 1 H, aryl), 7.52–7.54 (m, 1 H, aryl), 7.60 (s, 1 H, aryl) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.32, 70.60, 70.89, 124.22, 124.54, 126.84, 127.00, 128.15, 129.34, 132.55, 133.20, 134.59, 136.11, 136.23, 140.22, 142.72, 143.7 ppm. ES-MS: *m*/*z* (%) = 411.1 (100) [M^+ + Na], 413.1 (98), 371.1 (60) [M^+ – 17], 373.06 (57). $C_{19}H_{17}BrO_2S$ (389.3): calcd. C 58.62, H 4.40, S 8.24; found C 58.40, H 4.33, S 8.13.

2-[Hydroxy(4-iodophenyl)methyl]-5-[hydroxy(*p*-tolyl)methyl]thiophene (9): TMEDA (1.48 mL, 9.79 mmol) and *n*BuLi (6.12 mL of ca. 15% solution in hexane) were added under the same experimental conditions to a three-necked, 250-mL, round-bottomed flask containing mono-ol (b) (1.00 g, 4.90 mmol) in diethyl ether (30 mL). 4-Iodobenzaldehyde (1.36 g, 5.87 mmol) in dry THF (30 mL) was added slowly to the reaction mixture followed by workup and chromatography on silica with petroleum ether/ethyl acetate (82:18) as eluent to afford the desired diol **9** as a white solid (0.77 g, 36%). M.p. 117–118 °C. IR (KBr film): $\tilde{\nu}$ = 3450 cm^{-1}, 3059, 2852, 1484, 1432, 1050, 810, 750, 690, 574. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.62 (br. s, 2 H, OH), 2.30 (s, 3 H, CH_3), 5.90 (s, 1 H, CH), 5.93 (s, 1 H, CH), 6.72–6.75 (m, 2 H, thiophene), 7.18 (m, 4 H, aryl), 7.24 (d, *J* = 8.1 Hz, 2 H, aryl), 7.71 (d, *J* = 8.1 Hz, 2 H, aryl) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.85, 70.62, 70.85, 101.00, 105.32, 124.44, 124.57, 128.13, 129.33, 134.56, 136.04, 136.58, 140.29, 143.71, 146.00, 146.42, 146.91 ppm. ES-MS: *m*/*z* (%) = 459.0 (100) [M^+ + 23], 419.0 (98) [M^+ – 17]. $C_{19}H_{17}IO_2S$ (436.3): calcd. C 52.30, H 3.93, S 7.35; found C 52.41, H 3.01, S 7.32.

2-[Hydroxy(4-hydroxyphenyl)methyl)]-5-[hydroxy(*p*-tolyl)methyl]-thiophene (10): The diol **10** was prepared following the same method by adding TMEDA (1.48 mL, 9.79 mmol) and *n*BuLi (6.12 mL of ca. 15% solution in hexane) to mono-ol (b) (1.00 g, 4.90 mmol) in diethyl ether (30 mL) followed by an ice-cold solution of 4-hydroxybenzaldehyde (0.72 g, 5.87 mmol) in dry THF (30 mL). Purification of the crude product by silica gel column chromatography with petroleum ether/ethyl acetate (74:26) as eluent gave the desired diol **10** as a dark-yellow oily liquid (0.51 g, 32%). IR (neat): $\tilde{\nu}$ = 3380 cm^{-1}, 3058, 2850, 1486, 1436, 1050, 810, 750, 690. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.25 (s, 3 H, CH_3), 3.00 (s, 2 H, OH), 5.82–5.85 (m, 2 H, CH), 6.62–6.65 (m, 2 H, thiophene), 7.16 (d, *J* = 7.8 Hz, 2 H, aryl), 7.27 (d, *J* = 7.8 Hz, 2 H, aryl), 7.78 (d, *J* = 8.2 Hz, 2 H, aryl), 8.42 (d, *J* = 8.2 Hz, 2 H, aryl) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.53, 70.51, 71.55, 120.12, 124.33, 124.54, 128.17, 129.30, 134.57, 136.00, 139.45, 140.22, 143.73, 145.36, 146.07, 156.92 ppm. ES-MS: *m*/*z* (%) = 309.3 (65) [M^+ – 17]. $C_{19}H_{18}O_3S$ (326.4): calcd. C 58.62, H 4.40, S 8.24; found C 70.01, H 5.41, S 9.62.

2-[(4-Cyanophenyl)hydroxymethyl]-5-[hydroxy(*p*-tolyl)methyl]thiophene (11): Diol **11** was prepared by adding TMEDA (1.48 mL, 9.79 mmol) and *n*BuLi (6.12 mL of ca. 15% solution in hexane) to mono-ol (b) (1.00 g, 4.90 mmol) in diethyl ether (30 mL) followed by an ice-cold solution of 4-cyanobenzaldehyde (0.77 g, 5.87 mmol)

in dry THF (30 mL) under the same experimental conditions. Purification of the crude product by silica gel column chromatography with petroleum ether/ethyl acetate (81:19) as eluent gave the desired diol **11** as a white solid (0.66 g, 40%). M.p. 133–135 °C. IR (KBr film): $\tilde{\nu}$ = 3457 cm^{-1}, 3059, 2856, 1486, 1436, 1050, 810, 750, 690. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.24 (s, 3 H, CH_3), 4.00 (br. s, 2 H, OH), 5.80–5.83 (m, 2 H, CH), 6.72–6.75 (m, 2 H, thiophene), 7.16 (d, J = 7.8 Hz, 2 H, aryl), 7.30 (d, J = 7.8 Hz, 2 H, aryl), 7.61 (d, J = 8.2 Hz, 2 H, aryl), 8.28 (d, J = 8.2 Hz, 2 H, aryl) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.50, 70.55, 70.82, 111.01, 117.38, 124.34, 124.53, 128.16, 129.33, 134.51, 136.00, 136.56, 139.43, 140.25, 143.71, 145.35, 146.00, 147.45, 147.92 ppm. ES-MS: m/z (%) = 318.1 (100) [M^+ – 17]. $C_{20}H_{17}NO_2S$ (335.4): calcd. C 71.62, H 5.11, N 4.18, S 9.56; found C 71.41, H 5.31, N 4.11, S 9.32.

2-[Hydroxy(3-nitrophenyl)methyl]-5-[hydroxy(*p*-tolyl)methyl]thiophene (12): In a three-necked, 250-mL, round-bottomed flask, a solution of the mono-ol (b) (1.00 g, 4.90 mmol) in diethyl ether (30 mL) was treated with *n*BuLi (6.12 mL of ca. 15% solution in hexane) in the presence of TMEDA (1.48 mL, 9.79 mmol) under the same experimental conditions. An ice-cold solution of 3-nitrobenzaldehyde (0.68 g, 5.87 mmol) was added slowly to the reaction mixture followed by workup and chromatography on silica with petroleum ether/ethyl acetate (79:21) as eluent to afford the desired diol **12** as an oily yellow liquid (0.71 g, 41%). IR (neat): $\tilde{\nu}$ = 3457 cm^{-1}, 3059, 2856, 1520, 1486, 1436, 1346, 1050, 852, 810, 750, 690. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.30 (s, 3 H, CH_3), 2.81 (s, 2 H, OH), 5.88–6.01 (m, 2 H, CH), 6.68 (d, J = 4.4 Hz, 1 H, thiophene), 6.80 (d, J = 4.4 Hz, 1 H, thiophene), 7.15 (d, J = 7.8 Hz, 2 H, aryl), 7.22–7.25 (m, 4 H, aryl), 7.62 (t, J = 8.1 Hz, 1 H, aryl), 8.10 (s, 1 H, aryl) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.81, 70.53, 70.60, 124.32, 124.56, 128.17, 129.4, 134.55, 136.08, 136.52, 140.29, 143.74, 145.33, 146.07, 147.80, 148.44, 150.91 ppm. ES-MS: m/z (%) = 338.4 (100) [M^+ – 17]. $C_{19}H_{17}NO_4S$ (355.4): calcd. C 64.21, H 4.82, N 3.94, S 9.02; found C 64.41, H 4.71, N 4.08, S 9.22.

2-[Hydroxy(4-pyridyl)methyl]-5-[hydroxy(*p*-tolyl)methyl]thiophene (13):[12] Diol **13** was prepared by the same method from diethyl ether (30 mL), *n*BuLi (6.12 mL of a 15% solution in hexane) and mono-ol (b) (1.00 g, 4.90 mmol) to give the 2,5-dilithiothiophene salt, which was added to an ice-cold solution of 4-pyridinecarboxaldehyde (0.63 g, 5.87 mmol) in dry THF (20 mL). The crude diol was purified by column chromatography on silica with dichloromethane/methanol (96:4). The solvent was removed to afford the desired diol **13** as a white solid (0.68 g, 45%). M.p. 125–126 °C. IR (KBr film): $\tilde{\nu}$ = 3457 cm^{-1}, 3060, 2858, 1484, 1430, 1050, 810, 750, 690. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.27 (s, 3 H, CH_3), 4.81 (br. s, 2 H, OH), 5.82–5.85 (m, 2 H, CH), 6.59 (d, J = 5.2 Hz, 1 H, thiophene), 6.62 (d, J = 5.2 Hz, 1 H, thiophene), 7.06 (d, J = 8.8 Hz, 2 H, pyridyl), 7.21–7.25 (m, 4 H, aryl), 8.18 (d, J = 8.8 Hz, 2 H, pyridyl) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.14, 70.42, 71.88, 121.38, 123.11, 124.38, 124.68, 126.31, 129.43, 137.41, 140.73, 146.21, 146.46, 148.63, 149.77, 153.22 ppm. ES-MS: m/z (%) = 294.1 (100) [M^+ – 17]. $C_{18}H_{17}NO_2S$ (311.4): calcd. C 69.43, H 5.50, N 4.50, S 10.30; found C 69.28, H 5.41, N 4.30, S 10.18.

2-{Hydroxy[3-(3-hydroxy-3-methylbut-1-ynyl)phenyl]methyl}-5-[hydroxy(*p*-tolyl)methyl]thiophene (14): Diol **14** was prepared by adding TMEDA (1.48 mL, 9.79 mmol) and *n*BuLi (6.12 mL of ca. 15% solution in hexane) to mono-ol (b) (1.00 g, 4.90 mmol) in diethyl ether (30 mL) followed by an ice-cold solution of 3-(3-hydroxy-3-methylbut-1-ynyl)benzaldehyde (1.10 g, 5.87 mmol) in dry THF (30 mL) under the same experimental conditions. Purification of the crude product by silica gel column chromatography with petroleum ether/ethyl acetate (73:27) as eluent gave the desired diol **14** as a white solid (0.85 g, 44%). M.p. 120–122 °C. IR (KBr film): $\tilde{\nu}$ = 3370 cm^{-1}, 3008, 2954, 2870, 2110, 1484, 1432, 1050, 807, 750, 692. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.61 (s, 6 H, CH_3), 2.23 (s, 3 H, CH_3), 2.80 (s, 2 H, OH), 5.80–5.83 (m, 2 H, CH), 6.60 (d, J = 4.6 Hz, 1 H, thiophene), 6.74 (d, J = 4.6 Hz, 1 H, thiophene), 7.17 (d, J = 7.8 Hz, 2 H, aryl), 7.36–7.38 (m, 4 H, aryl), 7.78–7.80 (m, 1 H, aryl), 7.88 (s, 1 H, aryl) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.83, 25.80, 61.57, 70.67, 70.81, 81.73, 100.20, 124.44, 124.50, 125.52, 128.11, 129.34, 133.26, 134.59, 136.07, 136.51, 140.25, 146.08, 146.40, 148.30, 149.74, 152.84, 155.02 ppm. ES-MS: m/z (%) = 376.1 (100) [M^+ – 17]. $C_{24}H_{24}O_3S$ (392.5): calcd. C 73.44, H 6.16, S 8.17; found C 73.20, H 6.21, S 8.30.

5-(4-Bromophenyl)-10,15,20-triphenyl-21-monothiaporphyrin (15): Diol **1** (0.34 g, 0.90 mmol), benzaldehyde (0.20 mL, 1.98 mmol) and pyrrole (0.20 mL, 2.88 mmol) were dissolved in dichloromethane (120 mL) in a 250-mL, round-bottomed flask and nitrogen was purged for 10 min. $BF_3{\cdot}OEt_2$ (0.06 mL of a 2.5 M stock solution) was added to catalyze the reaction and the stirring was continued for 1 h. DDQ (0.21 g, 0.92 mmol) was added to oxidize the porphyrinogen to porphyrin and stirring was continued for an additional hour in air. TLC analysis indicated the formation of a mixture of four porphyrins: tetraphenylporphyrin (H_2TPP), the desired 21-thiaporphyrin **15** and *cis* and *trans* mixture of 21,23-dithiaporphyrins. The crude compound containing this mixture of four porphyrins was subjected to silica gel column chromatography and the desired N_3S porphyrin **15** with a small amount of impurities was obtained as the second band with petroleum ether/dichloromethane (75:25) as eluent. It was further subjected to a second chromatographic separation with the same solvent mixture to afford pure **15** as a purple solid (0.07 g, 10%). M.p. > 300 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = –2.70 (s, 1 H, NH), 7.70–7.80 (m, 9 H, aryl), 7.92 (d, J = 7.2 Hz, 2 H, aryl), 8.10 (d, J = 7.2 Hz, 2 H, aryl), 8.17–8.24 (m, 6 H, aryl), 8.60–8.62 (m, 2 H, β-pyrrole), 8.64 (d, J = 4.8 Hz, 1 H, β-pyrrole), 8.68 (d, J = 4.8 Hz, 1 H, β-pyrrole), 8.92 (s, 2 H, β-pyrrole), 9.68 (d, J = 5.5 Hz, 1 H, β-thiophene), 9.74 (d, J = 5.5 Hz, 1 H, β-thiophene) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 122.80, 124.14, 126.77, 127.70, 128.05, 129.75, 130.88, 132.90, 133.37, 134.03, 134.53, 137.74, 135.65, 139.21, 140.07, 141.05, 147.21, 154.66, 157.11, 157.65 ppm. ES-MS: m/z (%) = 710.1 (97) [M^+], 712.1 (100%). $C_{44}H_{28}BrN_3S$ (710.7): calcd. C 74.36, H 3.97, N 5.91, S 4.51; found C 74.82, H 5.14, N 5.75, S 4.41. UV/Vis (toluene): λ_{max} (ε) = 430 nm (363 078 $M^{-1}cm^{-1}$), 514 (28 840), 548 (7286), 617 (3631), 677 (5012).

5-[4-(3-Hydroxy-3-methylbut-1-ynyl)phenyl]-10,15,20-triphenyl-21-monothiaporphyrin (16): One equivalent of diol **3** (0.88 g, 2.31 mmol), two equivalents of benzaldehyde (0.55 mL, 5.39 mmol) and three equivalents of pyrrole (0.55 mL, 7.93 mmol) were dissolved in warm propionic acid (100 mL) and the temperature was increased slowly to reflux. The reaction mixture was refluxed for 2 h. The propionic acid was distilled off under reduced pressure and the crude solid was washed several times with water to remove any traces of acid. A dark slurry was then prepared by dissolving the crude solid in dichloromethane and loaded onto a silica gel column with dichloromethane as eluent. The N_4 porphyrin (H_2TPP) eluted as the first band and the desired N_3S porphyrin **16** as the second band in dichloromethane/methanol (98:2). The solvent was removed to afford **16** as a purple solid (0.15 g, 9%). M.p. > 300 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = –2.70 (s, 1 H, NH), 1.75 (s, 6 H, CH_3), 7.70–7.80 (m, 9 H, aryl), 7.92 (d, J = 7.2 Hz, 2 H, aryl), 8.10 (d, J = 7.2 Hz, 2 H, aryl), 8.17–8.24 (m, 6 H, aryl), 8.59–8.61 (m, 2 H, β-pyrrole), 8.64 (d, J = 4.8 Hz, 1 H, β-pyrrole), 8.68 (d, J = 4.8 Hz, 1 H, β-pyrrole), 8.92 (s, 2 H, β-pyrrole), 9.68

(d, J = 5.2 Hz, 1 H, β-thiophene), 9.74 (d, J = 5.2 Hz, 1 H, β-thiophene) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 122.80, 124.14, 126.77, 127.70, 129.75, 130.88, 132.90, 133.37, 134.03, 134.53, 137.74, 135.65, 139.21, 140.07, 141.05, 147.21, 154.66, 157.11, 157.65 ppm. ES-MS: m/z (%) = 714.4 (100) [M^+]. $C_{49}H_{35}N_3SO$ (713.9): calcd. C 82.44, H 4.94, N 5.89, S 4.49; found C 82.76, H 5.16, N 5.62, S; 4.30. UV/Vis (toluene): λ_{max} (ε) = 430 nm (186 209 $M^{-1}cm^{-1}$), 514 (15 488), 549 (5370), 617 (2399), 678 (3020).

5-(4-Ethynylphenyl)-10,15,20-triphenyl-21-monothiaporphyrin (16a): Porphyrin **16** (0.12 g, 0.17 mmol) was dissolved in benzene/methanol (3:1, 40 mL) and an excess of potassium hydroxide (0.02 g) was added. The reaction mixture was refluxed at 80 °C overnight in a Dean–Stark apparatus. TLC analysis showed the completion of reaction after 12 h. The crude compound was subjected to silica gel column chromatography with a petroleum ether/dichloromethane mixture (50:50) as eluent to afford the pure desired porphyrin **16a** as a purple solid (0.09 g, 80%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = –2.71 (s, 1 H, NH), 3.32 (s, 1 H, CH), 7.76–7.95 (m, 11 H, aryl), 8.20–8.24 (m, 8 H, aryl), 8.66 (m, 4 H, β-pyrrole), 8.93 (s, 2 H, β-pyrrole), 9.73–9.76 (m, 2 H, β-thiophene) ppm. ES-MS: m/z (%) = 656.2 (100) [M^+]. $C_{46}H_{29}N_3S$ (655.8): calcd. C 84.24, H 4.46, N 6.41, S 4.89; found C 84.57, H 4.71, N 6.26, S 4.70. UV/Vis (toluene): λ_{max} (ε) = 430 nm (281 838 $M^{-1}cm^{-1}$), 514 (23 442), 548 (6607), 618 (2884), 677 (3981).

5-(4-Nitrophenyl)-10,15,20-triphenyl-21-monothiaporphyrin (17): Diol **5** (0.25 g, 0.73 mmol), benzaldehyde (0.16 mL, 1.61 mmol) and pyrrole (0.16 mL, 2.30 mmol) were dissolved in dry dichloromethane (80 mL) in a 250-mL round-bottomed flask. After 10 min purging with nitrogen, $BF_3{\cdot}OEt_2$ (0.05 mL of a 2.5 M stock solution) was added to initiate the reaction. After 1 h stirring, DDQ (0.17 g, 0.74 mmol) was added and stirring was continued in air for an additional hour. The crude compound was subjected to silica gel chromatography and the desired N_3S porphyrin **17** was collected as the second band with petroleum ether/dichloromethane (65:35) as eluent. The solvent was removed to afford **17** as a purple solid (0.60 g, 12%). M.p. > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = –2.68 (s, 1 H, NH), 7.22–7.80 (m, 9 H, aryl), 8.17–8.24 (m, 6 H, aryl), 8.38 (d, J = 7.4 Hz, 2 H, aryl), 8.56 (d, J = 4.8 Hz, 1 H, β-pyrrole), 8.60–8.64 (m, 4 H, β-pyrrole and aryl), 8.68 (d, J = 4.8 Hz, 1 H, β-pyrrole), 8.94 (s, 2 H, β-pyrrole), 9.60 (d, J = 5.4 Hz, 1 H, β-thiophene), 9.77 (d, J = 5.4 Hz, 1 H, β-thiophene) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 122.74, 124.45, 124.84, 126.78, 127.73, 128.13, 129.30, 129.43, 132.33, 133.29, 134.48, 134.82, 135.13, 135.94, 136.28, 139.24, 139.40, 142.25, 146.74, 146.90, 147.76, 147.93 ppm. ES-MS: m/z (%) = 677.4 (100) [M^+]. $C_{44}H_{28}N_4O_2S$ (676.8): calcd. C 79.09, H 4.17, N 8.28, S 4.74; found C 79.34, H 4.29, N 8.11, S 4.60. UV/Vis (toluene): λ_{max} (ε) = 432 nm (316 228 $M^{-1}cm^{-1}$), 515 (29 512), 550 (9333), 616 (4365), 676 (5248).

10,15,20-Triphenyl-5-(4-pyridyl)-21-monothiaporphyrin (18): A solution of diol **7** (0.50 g, 1.67 mmol), benzaldehyde (0.40 mL, 3.92 mmol) and pyrrole (0.38 mL, 5.48 mmol) in hot propionic acid (70 mL) was refluxed for 2 h. The propionic acid was then removed under vacuum and the crude compound was loaded onto a silica gel chromatography column with dichloromethane as eluent. The N_4 porphyrin (H_2TPP) eluted as the first band and the desired N_3S porphyrin **18** eluted as the second band with dichloromethane/methanol (98:2) as eluent. The solvent was removed on a rotary evaporator to afford **18** as a purple solid (0.02 g, 2%). M.p. > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = –2.70 (s, 1 H, NH), 7.71–7.82 (m, 9 H, aryl), 8.16–8.20 (m, 6 H, aryl), 8.25 (d, J = 7.6 Hz, 2 H, pyridyl), 8.60–8.69 (m, 4 H, β-pyrrole), 8.94 (s, 2 H, β-pyrrole), 9.02 (d, J = 7.6 Hz, 2 H, pyridyl), 9.65 (d, J = 5.2 Hz, 1 H, β-thiophene), 9.77 (d, J = 5.2 Hz, 1 H, β-thiophene) ppm. ES-MS: m/z (%) = 633.3 (50) [M^+]. $C_{43}H_{28}N_4S$ (632.8): calcd. C 81.62, H 4.46, N 8.84, S 5.01; found C 81.95, H 4.69, N 8.59, S 5.20. UV/Vis (toluene): λ_{max} (ε) = 428 nm (95 499 $M^{-1}cm^{-1}$), 513 (8318), 547 (3236), 615 (1549), 675 (2512).

5-[4-(5,5-Dimethyl-1,3-dioxan-2-yl)phenyl]-10,15,20-triphenyl-21-monothiaporphyrin (19): Diol **6** (0.25 g, 0.61 mmol), benzaldehyde (0.14 mL, 1.34 mmol) and pyrrole (0.14 mL, 1.95 mmol) were condensed in dichloromethane (100 mL) in the presence of $BF_3{\cdot}OEt_2$ (0.03 mL of a 2.5 M stock solution) under nitrogen for 1 h. DDQ (0.21 g, 0.99 mmol) was added and reaction mixture was stirred for an additional hour in air. The solvent was removed on a rotary evaporator under vacuum and the crude solid was purified by column chromatography. The desired N_3S porphyrin **19** eluted with petroleum ether/dichloromethane (35:65) as eluent and the solvent was removed to afford **19** as a purple solid (0.01 g, 2%). M.p. > 300 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = –2.69 (s, 1 H, NH), 0.99 (s, 6 H, CH_3), 3.90 (s, 4 H, OCH_2), 5.65 (s, 1 H, CH), 7.72–7.80 (m, 11 H, aryl), 8.18–8.26 (m, 8 H, aryl), 8.66 (d, J = 4.2 Hz, 2 H, β-pyrrole), 8.83 (s, 2 H, β-pyrrole), 8.92–8.94 (m, 2 H, β-pyrrole), 9.72 (m, 2 H, β-thiophene) ppm. ES-MS: m/z (%) = 746.1 (100) [M^+] $C_{50}H_{39}N_3O_2S$ (745.9): calcd. C 80.51, H 5.27, N 5.63, S 4.30; found C 80.69, H 5.41, N 5.76, S 4.11. UV/Vis (toluene): λ_{max} (ε) = 439 nm (104 713 $M^{-1}cm^{-1}$), 513 (10 965), 551 (2951), 619 (2818), 680 (3388).

5-(4-Bromophenyl)-10,15,20-tri(*p*-tolyl)-21,23-dithiaporphyrin (20): A solution of diol **2** (0.50 g, 1.29 mmol) and 16-thiatripyrrane (0.54 g, 1.29 mmol) in dichloromethane (130 mL) was placed in a 250-mL, one-necked, round-bottomed flask fitted with a nitrogen gas bubbler. After purging nitrogen gas for 15 min, condensation of diol and tripyrrane was initiated at room temperature by the addition of a catalytic amount of $BF_3{\cdot}OEt_2$ (0.05 mL of a 2.5 M stock solution). The reaction mixture was stirred at room temperature for 1 h under nitrogen. DDQ (0.29 g, 1.10 mmol) was added and the reaction mixture was stirred in air for an additional hour. The progress of the reaction was checked by absorption spectroscopy, which showed bands characteristic of the desired porphyrin. TLC analysis showed the formation of the required compound as the sole product. The solvent was removed under reduced pressure and the crude compound was purified by silica gel column chromatography with petroleum ether/dichloromethane (63:37) as eluent to afford the desired porphyrin **20** as a purple solid (0.10 g, 10%). M.p. > 300 °C. IR (KBr film): $\tilde{\nu}$ = 3072 cm^{-1}, 2930, 2864, 1456, 970, 790, 585. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.71 (s, 9 H, CH_3), 7.60 (d, J = 7.8 Hz, 6 H, aryl), 7.72 (d, J = 8.1 Hz, 2 H, aryl), 7.92 (d, J = 8.1 Hz, 2 H, aryl), 8.11 (d, J = 7.8 Hz, 6 H, aryl), 8.62 (d, J = 4.5 Hz, 1 H, β-pyrrole), 8.68–8.70 (m, 3 H, β-pyrrole), 9.61 (d, J = 5.1 Hz, 1 H, β-thiophene), 9.66–9.70 (m, 3 H, β-thiophene) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.64, 122.54, 123.05, 123.47, 124.09, 124.42, 127.67, 128.81, 129.04, 131.22, 133.16, 135.09, 136.53, 138.44, 141.29, 144.65, 145.53, 147.65, 148.26 ppm. ES-MS: m/z (%) = 769.4 (85) [M^+], 771.3 (100%). $C_{47}H_{33}BrN_2S_2$ (769.8): calcd. C 73.33, H 4.32, N 3.64, S 8.33; found C 73.00, H 4.50, N 3.70, S 8.10. UV/Vis (toluene): λ_{max} (ε) = 437 nm (223 938 $M^{-1}cm^{-1}$), 515 (21 561), 548 (7138), 634 (1583), 697 (4104).

5-[4-(3-Hydroxy-3-methylbut-1-ynyl)phenyl]-10,15,20-tri(*p*-tolyl)-21,23-dithiaporphyrin (21): A solution of **4** (0.50 g, 1.28 mmol) and 16-thiatripyrrane (0.54 g, 1.28 mmol) in 125 mL of propionic acid was refluxed for 3 h. The progress of the reaction was checked by absorption spectroscopy, which showed bands characteristic of the desired porphyrin. The excess propionic acid was removed under

vacuum and the resultant black solid was washed several times with warm water and dried in an oven at 100 °C. The crude product was then purified by silica gel column chromatography with petroleum ether/dichloromethane (15:85) as eluent to afford the desired porphyrin **21** as a purple solid (0.19 g, 19%). M.p. > 300 °C. IR (KBr film): $\tilde{\nu}$ = 3360 cm^{-1}, 3070, 2942, 2860, 1520, 1456, 1050, 972, 790. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.44 (s, 6 H, CH_3), 2.73 (s, 9 H, CH_3), 7.62 (d, J = 7.2 Hz, 6 H, aryl), 7.86 (d, J = 8.0 Hz, 2 H, aryl), 8.12 (d, J = 7.2 Hz, 6 H, aryl), 8.21 (d, J = 8.0 Hz, 2 H, aryl), 8.63 (d, J = 4.6 Hz, 1 H, β-pyrrole), 8.72 (m, 3 H, β-pyrrole), 9.63 (d, J = 4.6 Hz, I H, β-thiophene), 9.69–9.72 (m, 3 H, β-thiophene) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.61, 29.79, 31.68, 65.90, 121.6, 123.2, 127.1, 128.32, 130.80, 132.75, 134.21, 134.75, 135.01, 135.63, 137.97, 138.27, 141.34, 148.06, 155.90, 156.41 ppm. ES-MS: m/z (%) = 773.5 (100) [M^+]. $C_{52}H_{40}N_2OS_2$ (773.0): calcd. C 80.80, H 5.22, N 3.62, S 8.30; found C 80.90, H 5.32, N 3.51, S 8.52. UV/Vis (toluene): λ_{max} (ε) = 438 nm (265 964 $M^{-1}cm^{-1}$), 515 (24 193), 549 (8949), 635 (1870), 698 (4830).

5-(4-Ethynylphenyl)-10,15,20-tri(*p*-tolyl)-21,23-dithiaporphyrin (21a): Porphyrin **21** (0.05 g, 0.07 mmol) was dissolved in benzene/methanol (3:1, 40 mL) in a 250-mL, round bottomed flask and excess potassium hydroxide (0.02 g) was added. The reaction mixture was refluxed at 80 °C in a Dean–Stark apparatus. TLC analysis confirmed completion of the reaction after 12 h. The excess solvent was removed under vacuum and the crude compound was subjected to silica gel column chromatography with petroleum ether/dichloromethane (60:40) as eluent to afford the pure desired porphyrin **21a** as a purple solid (0.05 g, 80%). M.p. > 300 °C. IR (KBr film): $\tilde{\nu}$ = 3311 cm^{-1}, 3070, 2942, 2860, 2120, 1520, 1456, 1240, 1050, 972, 790, 630. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.70 (s, 9 H, CH_3), 7.61 (d, J = 7.2 Hz, 6 H, aryl), 7.94 (d, J = 8.0 Hz, 2 H, aryl), 8.12 (d, J = 7.2 Hz, 6 H, aryl), 8.20 (d, J = 8.0 Hz, 2 H, aryl), 8.64 (d, J = 4.4 Hz, 1 H, β-pyrrole), 8.69–8.71 (m, 3 H, β-pyrrole), 9.62 (d, J = 4.4 Hz, I H, β-thiophene), 9.68–9.71 (m, 3 H, β-thiophene) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.61, 78.59, 121.95, 128.31, 131.29, 132.54, 134.18, 134.55, 134.92, 135.75, 135.93, 138.32, 141.98, 147.52, 147.80, 148.19, 155.95, 156.54, 156.60, 156.67 ppm. ES-MS: m/z (%) = 715.2 (100) [M^+]. $C_{49}H_{34}N_2S_2$ (714.9): calcd. C 82.31, H 4.79, N 3.92, S 8.97; found C 82.40, H 4.62, N 3.91, S 8.92. UV/Vis (toluene): λ_{max} (ε) = 437 nm (222 831 $M^{-1}cm^{-1}$), 514 (21 966), 548 (7963), 633 (1603), 697 (4002).

5-(3-Bromophenyl)-10,15,20-tri(*p*-tolyl)-21,23-dithiaporphyrin (22): Diol **8** (0.50 g, 1.29 mmol), 16-thiatripyrrane (0.54 g, 1.29 mmol), $BF_3{\cdot}OEt_2$ (0.05 mL of a 2.5 M stock solution) and DDQ (0.29 g, 1.41 mmol) in 130 mL of dichloromethane under similar reaction conditions as mentioned above gave **22** as a purple lustrous solid (0.14 g, 11%). M.p. > 250 °C. IR (KBr film): $\tilde{\nu}$ = 3069 cm^{-1}, 2928, 2860, 1456, 972, 790, 580. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.71 (s, 9 H, CH_3), 7.58 (d, J = 7.6 Hz, 6 H, aryl), 7.62 (m, 1 H, aryl), 7.86 (m, 2 H, aryl), 8.11 (d, J = 7.6 Hz, 6 H, aryl), 8.39 (s, 1 H, aryl), 8.64 (d, J = 5.2 Hz, 1 H, β-pyrrole), 8.68–8.70 (m, 3 H, β-pyrrole), 9.61 (d, J = 5.2 Hz, I H, β-thiophene), 9.69–9.70 (m, 3 H, β-thiophene) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.62, 122.54, 123.08, 123.43, 124.08, 124.49, 127.60, 128.85, 129.09, 131.22, 133.15, 135.00, 136.56, 138.48, 141.22, 144.65, 145.58, 147.69, 148.24 ppm. ES-MS: m/z (%) = 769.1 (74) [M^+], 771.1 (100%). $C_{47}H_{33}BrN_2S_2$ (769.82): calcd. C 73.33, H 4.32, N 3.64, S 8.33; found C 73.10, H 4.42, N 3.62, S 8.11. UV/Vis (toluene): λ_{max} (ε) = 437 nm (231 705 $M^{-1}cm^{-1}$), 514 (22 366), 548 (6708), 633 (1553), 697 (4060).

5-(4-Iodophenyl)-10,15,20-tri(*p*-tolyl)-21,23-dithiaporphyrin (23): Diol **9** (0.50 g, 1.15 mmol) and 16-thiatripyrrane (0.48 g, 1.15 mmol) were condensed in 115 mL of dichloromethane under nitrogen in the presence of a catalytic amount of $BF_3{\cdot}OEt_2$ (0.05 mL of a 2.5 M stock solution) for 1 h under nitrogen followed by oxidation with DDQ (0.26 g, 1.15 mmol) in air for an additional hour. The crude mixture was purified by silica gel column chromatography with petroleum ether/dichloromethane (70:30) as eluent. The desired porphyrin was collected as a purple solid (0.13 g, 14%). M.p. > 250 °C. IR (KBr film): $\tilde{\nu}$ = 3070 cm^{-1}, 2942, 2860, 1456, 972, 790, 555. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.68 (s, 9 H, CH_3), 7.60 (d, J = 7.6 Hz, 6 H, aryl), 7.94 (d, J = 7.8 Hz, 2 H, aryl), 8.10 (d, J = 7.6 Hz, 6 H, aryl), 8.38 (d, J = 7.8 Hz, 2 H, aryl), 8.63 (d, J = 4.4 Hz, 1 H, β-pyrrole), 8.68–8.70 (m, 3 H, β-pyrrole), 9.61 (d, J = 4.4 Hz, 1 H, β-thiophene), 9.68–9.70 (m, 3 H, β-thiophene) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.62, 100.51, 123.00, 123.44, 123.62, 124.09, 127.45, 128.05, 129.56, 131.23, 133.12, 136.06, 137.53, 138.37, 142.28, 145.13, 146.58, 149.24 ppm. ES-MS: m/z (%) = 817.2 (100) [M^+]. $C_{47}H_{33}IN_2S_2$ (816.8): calcd. C 69.11, H 4.07, N 3.43, S 7.85; found C 69.30, H 4.40, N 3.20, S 7.68. UV/Vis (toluene): λ_{max} (ε) = 437 nm (212 508 $M^{-1}cm^{-1}$), 514 (19 313), 548 (5837), 633 (1356), 697 (3473).

5-(4-Hydroxyphenyl)-10,15,20-tri(*p*-tolyl)-21,23-dithiaporphyrin (24): Diol **10** (0.50 g, 1.53 mmol) was condensed with 16-thiatripyrrane (0.65 g, 1.53 mmol) in propionic acid (125 mL) and the mixture was refluxed for 2 h. The crude compound was purified by silica gel column chromatography with petroleum ether/dichloromethane (15:85) as eluent to afford porphyrin **24** as a purple solid (0.09 g, 8%). M.p. > 300 °C. IR (KBr film): $\tilde{\nu}$ = 3372 cm^{-1}, 3070, 2942, 2860, 1456, 1220, 1050, 972, 790. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.73 (s, 9 H, CH_3), 7.64 (d, J = 7.4 Hz, 6 H, aryl), 7.96 (d, J = 8.0 Hz, 2 H, aryl), 8.14 (d, J = 7.4 Hz, 6 H, aryl), 8.44 (d, J = 8.0 Hz, 2 H, aryl), 8.66 (d, J = 4.8 Hz, 1 H, β-pyrrole), 8.72–8.74 (m, 3 H, β-pyrrole), 9.63 (d, J = 4.8 Hz, I H, β-thiophene), 9.71–9.73 (m, 3 H, β-thiophene) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.65, 123.67, 124.08, 127.44, 128.08, 130.00, 134.29, 135.16, 136.02, 137.51, 138.31, 142.26, 146.27, 147.55, 149.19, 152.24, 154.28 ppm. ES-MS: m/z (%) = 707.2 (100) [M^+]. $C_{47}H_{34}N_2OS_2$ (706.9): calcd. C 79.85, H 4.85, N 3.96, S 9.07; found C 79.95, H 4.70, N 4.10, S 9.05. UV/Vis (toluene): λ_{max} (ε) = 438 nm (144 369 $M^{-1}cm^{-1}$), 514 (16 150), 549 (5626), 634 (1180), 698 (2245).

5-(4-Cyanophenyl)-10,15,20-tri(*p*-tolyl)-21,23-dithiaporphyrin (25): Porphyrin **25** was prepared by the [3+1] condensation of diol **11** (0.50 g, 1.49 mmol) with 16-thiatripyrrane (0.63 g, 1.49 mmol) in dry dichloromethane (150 mL) in the presence of a catalytic amount of $BF_3{\cdot}OEt_2$ (0.06 mL of a 2.5 M stock solution) for 1 h under nitrogen followed by oxidation with DDQ (0.34 g, 1.49 mmol) in air for an additional hour. The crude product was purified by silica gel column chromatography with petroleum ether/dichloromethane (50:50) as eluent to give **25** as a purple solid in 12% yield (0.13 g). M.p. > 250 °C. IR (KBr film): $\tilde{\nu}$ = 3068 cm^{-1}, 2960, 2858, 2220, 1454, 972, 760. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.72 (s, 9 H, CH_3), 7.62 (d, J = 7.2 Hz, 6 H, aryl), 7.90 (d, J = 7.6 Hz, 2 H, aryl), 8.12 (d, J = 7.2 Hz, 6 H, aryl), 8.34 (d, J = 7.6 Hz, 2 H, aryl), 8.54 (d, J = 4.6 Hz, 1 H, β-pyrrole), 8.70–8.72 (m, 3 H, β-pyrrole), 9.52 (d, J = 4.8 Hz, 1 H, β-thiophene), 9.70–9.72 (m, 3 H, β-thiophene) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.66, 123.64, 124.08, 127.49, 128.00, 130.06, 134.72, 135.91, 136.50, 137.75, 138.63, 142.82, 146.32, 147.75, 149.51, 152.82, 154.62 ppm. ES-MS: m/z (%) = 716.2 (100) [M^+]. $C_{48}H_{33}N_3S_2$ (715.9): calcd. C 80.52, H 4.65, N 5.87, S 8.96; found C 80.30, H 4.50, N 5.60, S 8.68. UV/Vis (toluene): λ_{max} (ε) = 438 nm (220 808 $M^{-1}cm^{-1}$), 515 (21 454), 549 (7247), 634 (1597), 697 (4045).

5-(3-Nitrophenyl)-10,15,20-tri(*p*-tolyl)-21,23-dithiaporphyrin (26): Diol **12** (0.50 g, 1.41 mmol) and 16-thiatripyrrane (0.59 g, 1.41 mmol) were condensed in the presence of $BF_3{\cdot}OEt_2$ (0.06 mL of a 2.5 M stock solution) in 140 mL of dichloromethane under nitrogen for 1 h followed by oxidation with DDQ (0.32 g, 1.41 mmol) in air. Column chromatography on silica with petroleum ether/dichloromethane (45:55) as eluent gave pure **26** as a purple lustrous solid (0.10 g, 10%). M.p. > 250 °C. IR (KBr film): $\tilde{\nu}$ = 3074 cm^{-1}, 2962, 2852, 1520, 1454, 1340, 970, 850, 762. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.71 (s, 9 H, CH_3), 7.62 (d, J = 7.5 Hz, 6 H, aryl), 7.78–7.80 (m, 2 H, aryl), 8.13 (d, J = 7.5 Hz, 6 H, aryl), 8.54–8.56 (m, 1 H, aryl), 8.60 (d, J = 4.4 Hz, 1 H, β-pyrrole), 8.72–8.75 (m, 3 H, β-pyrrole), 9.81 (s, 1 H, aryl), 9.58 (d, J = 5.1 Hz, 1 H, β-thiophene), 9.74–9.78 (m, 3 H, β-thiophene) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.65, 123.66, 124.08, 127.49, 128.00, 130.05, 134.28, 135.17, 136.02, 137.51, 138.34, 142.22, 146.27, 147.54, 149.15, 152.22, 154.28 ppm. ES-MS: *m*/*z* (%) = 736.17 (100) [M^+]. $C_{47}H_{33}N_3O_2S_2$ (735.92): calcd. C 76.70, H 4.52, N 5.71, S 8.71; found C 76.60, H 4.50, N 5.60, S 8.58. UV/Vis (toluene): λ_{max} (ε) = 437 nm (179 311 $M^{-1}cm^{-1}$), 514 (16 825), 548 (5115), 634 (1167), 697 (3050).

5-(4-Pyridyl)-10,15,20-tri(*p*-tolyl)-21,23-dithiaporphyrin (27):[12] Condensation of diol **7** (0.37 g, 1.18 mmol) with 16-thiatripyrrane (0.50 g, 1.18 mmol) in propionic acid (125 mL) at refluxing temperature for 2 h followed by standard work up and chromatography on silica with dichloromethane/methanol (96:4) as eluent gave the desired porphyrin **27** as a purple solid (0.09 g, 11%). M.p. > 300 °C. IR (KBr film): $\tilde{\nu}$ = 2930 cm^{-1}, 2860, 1455, 982, 798. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.69 (s, 9 H, CH_3), 7.61–7.63 (m, 6 H, aryl), 8.12–8.14 (m, 6 H, aryl), 8.18–8.19 (m, 2 H, pyridyl) 8.60 (d, J = 4.8 Hz, 1 H, β-pyrrole), 8.69 (s, 2 H, β-pyrrole), 8.73 (d, J = 4.8 Hz, 1 H, β-pyrrole), 9.07 (br. s, 2 H, pyridyl), 9.57 (d, J = 5.2 Hz, 1 H, β-thiophene), 9.72–9.74 (m, 3 H, β-thiophene) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.59, 128.03, 129.49, 133.61, 134.71, 134.93, 135.14, 135.73, 136.13, 138.02, 146.90, 147.61, 148.53, 148.68, 149.75, 150.87, 155.11, 156.63, 157.01 ppm. ES-MS: *m*/*z* (%) = 692.3 (100) [M^+]. $C_{46}H_{33}N_3S_2$ (691.9): calcd. C 79.82, H 4.92, N 6.07, S 9.25; found C 79.71, H 4.77, N 6.28, S 9.10. UV/Vis (toluene): λ_{max} (ε) = 437 nm (375 029 $M^{-1}cm^{-1}$), 515 (321 942 $M^{-1}cm^{-1}$), 549 (9637), 634 (2430), 697 (5661).

5-[3-(3-Hydroxy-3-methylbut-1-ynyl)phenyl]-10,15,20-tri(*p*-tolyl)-21,23-dithiaporphyrin (28): Condensation of diol **14** (0.50 mg, 1.28 mmol) with 16-thiatripyrrane (0.54 g, 1.28 mmol) in propionic acid (125 mL) at refluxing temperature for 2 h followed by standard work up and purification on silica gel column chromatography with petroleum ether/dichloromethane (15:85) as eluent gave the desired porphyrin **28** as a purple solid (0.16 g, 16%). M.p. > 300 °C. IR (KBr film): $\tilde{\nu}$ = 3360 cm^{-1}, 3071, 2942, 2860, 1520, 1457, 1050, 972, 792. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.43 (s, 6 H, CH_3), 2.72 (s, 9 H, CH_3), 7.60 (d, J = 7.6 Hz, 6 H, aryl), 7.78–7.80 (m, 1 H, aryl), 7.98–8.00 (m, 2 H, aryl), 8.10 (d, J = 7.6 Hz, 6 H, aryl), 8.11 (s, 1 H, aryl), 8.50 (m, 1 H, β-pyrrole), 8.59–8.61 (m, 3 H, β-pyrrole), 9.79–9.81 (m, 4 H, β-thiophene) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.70, 121.59, 123.26, 125.77, 127.06, 129.25, 129.38, 131.39, 131.56, 132.11, 132.00, 135.16, 137.79, 146.07, 147.00 ppm. ES-MS: *m*/*z* (%) = 773.5 (100) [M^+]. $C_{52}H_{40}N_2OS_2$ (773.0): calcd. C 80.80, H 5.22, N 3.62, S 8.30; found C 80.62, H 5.15, N 3.61, S 8.45. UV/Vis (toluene): λ_{max} (ε) = 437 nm (237 785 $M^{-1}cm^{-1}$), 515 (38 606), 548 (11 698), 634 (2726), 698 (7048).

5-(4-Iodophenyl)-10,15,20-tri(*p*-tolyl)-21-thia-23-oxaporphyrin (29): Diol **9** (0.50 g, 1.15 mmol) and 16-oxatripyrrane (0.47 g, 1.15 mmol) were condensed in 115 mL of dichloromethane under nitrogen in the presence of a catalytic amount of $BF_3{\cdot}OEt_2$ (0.05 mL of a 2.5 M stock solution) for 1 h followed by the oxidation with DDQ (0.26 g, 1.15 mmol). Purification on a silica gel chromatography column with petroleum ether/dichloromethane (65:35) as eluent afforded the required porphyrin **29** as a purple solid (0.07 g, 8%). M.p. > 250 °C. IR (KBr film): $\tilde{\nu}$ = 3070 cm^{-1}, 2940, 2868, 1456, 972, 791, 558. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.72 (s, 9 H, CH_3), 7.53 (d, J = 7.6 Hz, 4 H, aryl), 7.61 (d, J = 7.6 Hz, 2 H, aryl), 7.94 (d, J = 7.6 Hz, 2 H, aryl), 8.10 (d, J = 7.6 Hz, 6 H, aryl), 8.07 (d, J = 7.6 Hz, 2 H, aryl), 8.52 (d, J = 4.6 Hz, 2 H, β-pyrrole), 8.57 (d, J = 4.6 Hz, 2 H, β-pyrrole), 9.19 (s, 2 H, β-furan), 9.65 (d, J = 4.8 Hz, 1 H, β-thiophene), 9.73 (d, J = 4.8 Hz, 1 H, β-thiophene) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.62, 22.00, 122.00, 128.26, 131.32, 132.49, 134.78, 135.73, 138.06, 138.32, 142.03, 147.47, 147.76, 148.00, 148.15, 156.07, 156.58, 156.66, 156.72 ppm. ES-MS: *m*/*z* (%) = 801.2 (100) [M^+]. $C_{47}H_{33}IN_2OS$ (800.8): calcd. C 70.49, H 4.15, N 3.50, S 4.00; found C 70.20, H 4.02, N 3.62, S 4.11. UV/Vis (toluene): λ_{max} (ε) = 432 nm (181 906 $M^{-1}cm^{-1}$), 512 (23 664), 545 (5396), 645 (1584), 710 (5963).

5-(3-Bromophenyl)-10,15,20-tri(*p*-tolyl)-21-thia-23-oxaporphyrin (30): A catalytic amount of $BF_3{\cdot}OEt_2$ (0.05 mL of a 2.5 M stock solution) was added to a solution of diol **8** (0.50 g, 1.29 mmol) and 16-oxatripyrrane (0.52 g, 1.29 mmol) in 130 mL of dichloromethane under nitrogen to initiate the condensation. After 1 h, DDQ (0.29 g, 1.41 mmol) was added and stirred in air for an additional hour. The crude compound was subjected to silica gel column chromatography with petroleum ether/dichloromethane (60:40) as eluent to give the desired compound **30** as a purple lustrous solid (0.07 g, 7%). M.p. > 250 °C. IR (KBr film): $\tilde{\nu}$ = 3069 cm^{-1}, 2930, 2863, 1454, 972, 790, 577. ^1H NMR ($CDCl_3$): δ = 2.72 (s, 9 H, CH_3), 7.56–7.59 (m, 6 H, aryl), 7.94–7.96 (m, 2 H, aryl), 8.06–8.10 (m, 8 H, aryl), 8.52–8.56 (m, 2 H, β-pyrrole), 8.60–8.62 (m, 2 H, β-pyrrole), 9.26 (s, 2 H, β-furan), 9.70 (d, J = 4.8 Hz, 1 H, β-thiophene), 9.80 (d, J = 4.8 Hz, 1 H, β-thiophene) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.10, 22.60, 122.11, 125.44, 129.54, 130.12, 131.99, 132.49, 134.78, 134.85, 135.63, 137.56, 138.22, 140.63, 142.03, 147.47, 148.00, 149.58, 154.72, 156.33, 156.58, 156.66, 156.72 ppm. ES-MS: *m*/*z* (%) = 753.2 (83) [M^+], 755.2 (100%). $C_{47}H_{33}BrN_2OS$ (753.8): calcd. C 74.89, H 4.41, N 3.72, S 4.25; found C 74.70, H 4.42, N 3.62, S 4.11. UV/Vis (toluene): λ_{max} (ε) = 432 nm (166 254 $M^{-1}cm^{-1}$), 512 (21 894), 545 (4709), 645 (1480), 709 (4481).

5-(3-Nitrophenyl)-10,15,20-tri(*p*-tolyl)-21-thia-23-oxaporphyrin (31): Diol **12** (0.50 g, 1.41 mmol) and 16-oxatripyrrane (0.57 g, 1.41 mmol) in 140 mL of dichloromethane were condensed in the presence of $BF_3{\cdot}OEt_2$ (0.06 mL of a 2.5 M stock solution) under nitrogen for 1 h. DDQ (0.32 g, 1.41 mmol) was then added and stirred in air for an additional hour. After standard work up, the crude compound was purified by silica gel column chromatography with petroleum ether/dichloromethane (15:85) as eluent to give pure **31** as a purple lustrous solid (0.06 g, 6%). M.p. > 250 °C. IR (KBr film): $\tilde{\nu}$ = 3069 cm^{-1}, 2930, 2863, 1454, 972, 790, 577. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.72 (s, 9 H, CH_3), 7.58–7.60 (m, 6 H, aryl), 7.78–7.80 (m, 1 H, aryl), 8.00–8.05 (m, 8 H, aryl), 8.20 (s, 1 H, aryl), 8.66–8.68 (m, 2 H, β-pyrrole), 8.71–8.73 (m, 2 H, β-pyrrole), 9.22 (s, 2 H, β-furan), 9.70–9.78 (m, 2 H, β-thiophene) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.64, 22.14, 122.11, 124.87, 126.55, 127.34, 128.36, 130.56, 132.52, 133.78, 135.73, 138.05, 138.32, 142.03, 145.10, 147.47, 147.76, 148.44, 148.15, 150.73, 154.78, 155.20, 156.66, 156.72 ppm. ES-MS: *m*/*z* (%) = 720.3 (100) [M^+]. $C_{47}H_{33}N_3O_3S$ (719.9): calcd. C 78.42, H 4.62, N 6.67, S 4.45; found C 78.50, H 4.42, N 6.62, S 4.11. UV/Vis (tolu-

ene): λ_{max} (ε) = 432 nm (154 973 $M^{-1}cm^{-1}$), 512 (20 722), 545 (4664), 645 (1406), 710 (4638).

5-(4-Iodophenyl)-10,15,20-tri(*p*-tolyl)porphyrinzinc(II) (32): This porphyrin was prepared by a literature method.[4]

5-(4-Iodophenyl)-10,15,20-tri(*p*-tolyl)-21-monothiaporphyrin (33): This porphyrin was prepared as reported previously.[1]

N_2S_2-N_4 Dimer 34: A solution of N_2S_2 porphyrin **21a** (0.02 g, 0.03 mmol) and **32** (0.02 g, 0.03 mmol) in dry toluene/triethylamine (3:1, 30 mL) 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 nitrogen for 15 min, $AsPh_3$ (0.01 g, 0.03 mmol) and $Pd_2(dba)_3$ (0.004 g, 0.01 mmol) were added successively and the reaction was stirred at 35 °C for 12 h. TLC analysis of the reaction mixture indicated the virtual disappearance of spots corresponding to starting materials and the appearance of a new spot corresponding to the dimer. The solvent was removed under vacuum and the crude compound was purified by silica gel chromatography with petroleum ether/dichloromethane (80:20) as eluent to remove the excess $AsPh_3$ and the small amounts of monomeric porphyrins. The desired dimer **34** was then collected with petroleum ether/dichloromethane (65:35) as eluent. The solvent was removed on a rotary evaporator under vacuum to afford dimer **34** as a violet solid (0.02 g, 57%). M.p. > 300 °C. IR (KBr film): $\tilde{\nu}$ = 3069 cm^{-1}, 2930, 2863, 2110, 1453, 980, 750. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.72 (s, 18 H, CH_3), 7.42–7.43 (m, 4 H, aryl), 7.61–7.63 (m, 8 H, aryl), 7.81 (d, J = 8.0 Hz, 4 H, aryl), 8.06–8.16 (m, 12 H, aryl), 8.32 (d, J = 8.0 Hz, 4 H, aryl), 8.69–8.71 (m, 4 H, β-pyrrole), 8.75 (s, 2 H, β-pyrrole), 8.93–8.96 (m, 2 H, β-pyrrole), 9.04–9.07 (m, 4 H, β-pyrrole), 9.73–9.76 (m, 4 H, β-thiophene) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.14, 21.64, 128.32, 128.88, 129.80, 130.98, 132.36, 134.32, 135.0, 137.95, 138.37, 141.92, 144.63, 147.93, 148.60, 148.66, 150.53 ppm. ES-MS: *m*/*z* (%) = 1433.2 (60) [M^+]. $C_{96}H_{66}N_6S_2Zn$ (1433.1): calcd. C 80.46, H 4.64, N 5.86, S 4.47; found C 80.20, H 4.42, N 5.72, S 4.40. UV/Vis (toluene): λ_{max} (ε) = 425 nm (229 043 $M^{-1}cm^{-1}$), 439 (206 668 $M^{-1}cm^{-1}$), 516 (18 962), 551 (13 737), 592 (3125), 636 (1558), 699 (3375).

N_2S_2-N_3S Dimer 35: A solution of N_2S_2 porphyrin **21a** (0.02 g, 0.03 mmol) and **33** (0.02 g, 0.03 mmol) in dry toluene/triethylamine (3:1, 30 mL) was purged with nitrogen for 15 min. The coupling was initiated by adding $AsPh_3$ (0.01 g, 0.03 mmol) and $Pd_2(dba)_3$ (0.004 g, 0.01 mmol) and the reaction mixture was then stirred at 35 °C for 12 h. TLC analysis indicated the appearance of new spot apart from the corresponding monomeric spots. The crude reaction mixture was purified by silica gel chromatography with petroleum ether/dichloromethane as eluent. The excess $AsPh_3$ and small amounts of unreacted monomers were removed with petroleum ether/dichloromethane (80:20) as eluent and the desired dimer was then collected with petroleum ether/dichloromethane (50:50) as eluent. The solvent was removed on a rotary evaporator under vacuum to give dimer **35** as a purple solid (0.02 g, 54%). M.p. > 300 °C. IR (KBr film): $\tilde{\nu}$ = 3072 cm^{-1}, 2930, 2863, 2112, 1450, 990, 752. ^1H NMR (400 MHz, $CDCl_3$): δ = –2.65 (br. s, 1 H, NH), 2.73 (s, 18 H, CH_3), 7.32–7.42 (m, 6 H, aryl), 7.44–7.56 (m, 2 H, aryl), 7.56–7.64 (m, 4 H, aryl), 7.66–7.84 (m, 10 H, aryl), 7.92 (d, J = 7.6 Hz, 2 H, aryl), 8.09 (d, J = 7.6 Hz, 2 H, aryl), 8.16–8.28 (m, 6 H, aryl), 8.58–8.72 (m, 8 H, β-pyrrole), 8.94 (br. s, 4 H, β-pyrrole), 9.48–9.51 (m, 2 H, β-thiophene), 9.68–9.78 (m, 4 H, β-thiophene) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.13, 21.61, 125.23, 125.93, 128.25, 129.16, 134.26, 134.51, 135.39, 136.45, 137.81, 138.44, 139.80, 142.91, 143.02, 144.53, 147.86, 156.50 ppm. ES-MS: *m*/*z* (%) = 1388.4 (50) [M^+ + H]. $C_{96}H_{67}N_5S_3$ (1386.8): calcd. C 83.15, H 4.87, N 5.05, S 6.94; found C 83.10, H 4.62, N 5.12, S 7.01. UV/Vis (toluene): λ_{max} (ε) = 432 nm (387 067 $M^{-1}cm^{-1}$), 514 (33 331), 548 (9652), 619 (2624), 633 (2079), 678 (3596), 697 (3477).

N_2S_2-N_2SO Dimer 36: A solution of N_2S_2 porphyrin **21a** (0.02 g, 0.03 mmol) and **29** (0.02 g, 0.03 mmol) in dry toluene/triethylamine (3:1, 30 mL) was purged with nitrogen for 15 min. $AsPh_3$ (0.01 g, 0.03 mmol) and $Pd_2(dba)_3$ (0.004 g, 0.01 mmol) were added to this solution, and stirred at 35 °C for 15 h. Formation of the dimer was confirmed by the appearance of a new spot in the TLC as well as from the characteristic splitting pattern of bands observed in the UV/Vis spectrum. The crude compound was purified by silica gel column chromatography and the desired dimer **36** was collected with petroleum ether/dichloromethane (25:75) as eluent and obtained as a purple solid (0.02 g, 40%). M.p. > 300 °C. IR (KBr film): $\tilde{\nu}$ = 3065 cm^{-1}, 2920, 2860, 2112, 1454, 990, 750. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.70 (s, 18 H, CH_3), 7.55 (d, J = 8.0 Hz, 4 H, aryl), 7.62 (d, J = 7.2 Hz, 10 H, aryl), 7.95 (d, J = 8.0 Hz, 4 H, aryl), 8.04 (d, J = 7.2 Hz, 4 H, aryl), 8.14–8.18 (m, 10 H, aryl), 8.40–8.43 (m, 2 H, β-pyrrole), 8.51 (d, J = 4.8 Hz, 1 H, β-pyrrole), 8.55 (d, J = 4.8 Hz, 1 H, β-pyrrole), 8.64 (d, J = 4.8 Hz, 1 H, β-pyrrole), 8.70 (s, 2 H, β-pyrrole), 8.73 (d, J = 5.0 Hz, 1 H, β-pyrrole), 9.18 (s, 2 H, β-furan), 9.61–9.64 (m, 2 H, β-thiophene), 9.70–9.73 (m, 4 H, β-thiophene) ppm. ES-MS: *m*/*z* (%) = 1388.5 (50) [M^+]. $C_{96}H_{66}N_4OS_3$ (1387.8): calcd. C 83.09, H 4.79, N 4.04, S 6.93; found C 83.33, H 4.62, N 4.01, S 7.04. UV/Vis (toluene): λ_{max} (ε) = 435 nm (443 457 $M^{-1}cm^{-1}$), 514 (50 982), 547 (13 422), 639 (3115), 696 (6550), 708 (8834).

Supporting Information: The NMR and mass spectra of compounds **1**, **2**, **4**, **8**–**13**, **15**–**17**, **20**–**31**, and **34**–**36** and mass spectra of **18** and **19** (33 pages).

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