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Synthesis and Anion-Binding Studies of Thiaphlorins and Covalently Linked Thiaphlorin–Porphyrin Dyads

Iti Gupta,[a] Roland Fröhlich,[b] and Mangalampalli Ravikanth*[c]

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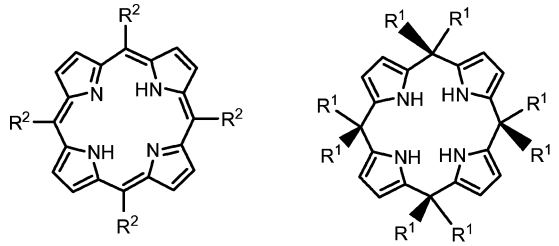
A series of thiaphlorins with N_2S_2 and N_3S cores have been prepared in decent yields from readily available precursors. The thiaphlorins were characterized by all spectroscopic techniques and the structures of two thiaphlorins were solved by X-ray crystallography. The spectral studies indicated that the properties of thiaphlorins were quite different from those of thiaporphyrins. The methodology used for the synthesis of thiaphlorins has been extended to synthesize a series of monofunctionalized thiaphlorins. We also performed functional group transformation of thiaphlorins without decomposition, supporting the conjecture of the stable natures of thiaphlorins. The crystal structure analysis of two thiaphlorins indicated that the macrocycles are not planar and that they each show a marked kink at sp^3-hybridised *meso* carbon. The functionalized thiaphlorins have been used to synthesize several novel porphyrin–thiaphlorin dyads as well as a bis-(thiaphlorin) dyad under mild palladium(0) coupling conditions. Preliminary anion-binding studies carried out on thiaphlorins and porphyrin–thiaphlorin dyads indicated that they can bind anions effectively in their protonated forms and that these systems can also be used as optical sensors.

Introduction

Porphyrins are macrocycles that contain only sp^2-hybridised bridging *meso* carbon atoms (**1.1.1.1**- four sp^2 hybridized carbon atoms) within their frameworks and are well known for their versatile metal coordination chemistry.[1] On the other hand, calix(4)pyrroles,[2] the porphyrin analogues containing pyrroles bridged exclusively by sp^3 *meso* carbon centres (***1.1.1.1***) have attracted attention recently for their anion-binding chemistry (Scheme 1). Calix-(4)phyrins[3] are a class of hybrid molecules containing a mixture of sp^2- and sp^3-hybridized *meso* carbon bridges that lie at the structural crossroads between porphyrins and calix(4)pyrroles and have been shown to be good receptors for cations and, more importantly, for anions. The different classes of calix(4)phyrins are shown in Scheme 2.

These classes are porphomonomethenes (**1.*1.1.1*** – one sp^2- and three sp^3-hybridized *meso* carbon atoms), porphodimethenes (**1.1.*1.1*** and **1.*1*.1.*1*** – two sp^2- and two sp^3-hybridized *meso* carbon atoms) and porphotrimethenes (**1.1.1.*1*** – three sp^2- and one sp^3-hybridized *meso* carbon atoms). Phlorins are a class of porphotrimethenes containing three sp^2 *meso* carbon atoms and one sp^3 one and were first identified by R. B. Woodward during his landmark studies directed towards the synthesis of chlorophyll a.[4] Phlorins have also been proposed as intermediates in the catalytic cycle of the haem p460 of hydroxylamine oxidoreductase[5] and also during some syntheses of porphyrins[6] and chlorines.[7] Phlorins have been found to be good anion sensors and have been obtained on reduction of porphyrins and metalloporphyrins by photochemical,[8] radiolytic,[9] electrochemical[10] and chemical[11] methods. However, phlorins in general are very unstable for exploration of their complete potential for various applications. Recently, several methods to obtain stable phlorins in metallated and metal-free forms have become available. Setsune et al.,[12] Callot et al.,[13] Lee et al.,[14] Furuta et al.[15] and others[16] have independently developed some novel routes by which to synthesize phlorins starting from porphyrins or oligopyr-



Scheme 1. Structures of porphyrins and calix(4)pyrroles.

[a] BITS-Pilani, Goa Campus,
Near NH-17B, Bye Pass Road, Zuarinagar, Goa 403726, India
[b] Organisch-Chemisches Institut, Universität Münster,
Corrensstraße 40, 48149 Münster, Germany
[c] Department of Chemistry, Indian Institute of Technology, Bomay, Powai,
Mumbai 400076, India
E-mail: ravikanth@chem.iitb.ac.in

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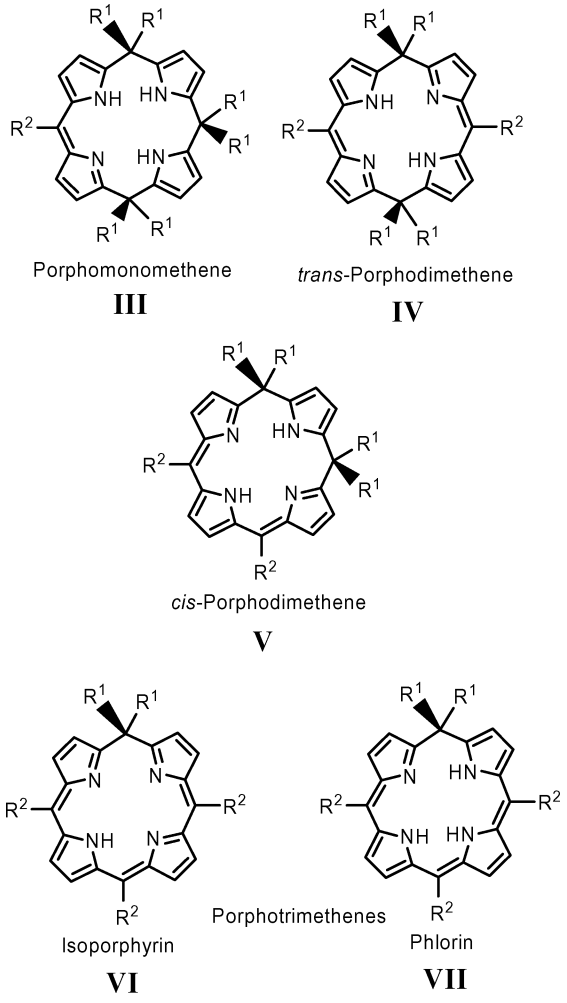
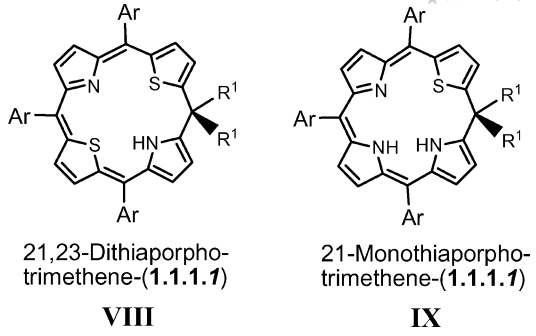


Scheme 2. Structures of calix(4)phyrins.

roles as precursors. Modification of the phlorin core by replacement of one or two nitrogen atoms with heteroatoms such as sulfur (Scheme 3) and oxygen may lead to core-modified phlorins that may possess interesting metal- and anion-binding properties. With this in mind, we recently reported the synthesis of a series of monofunctionalized thia analogues of phlorins and their use in the synthesis of phlorin–porphyrin dyads in a communication.[17]



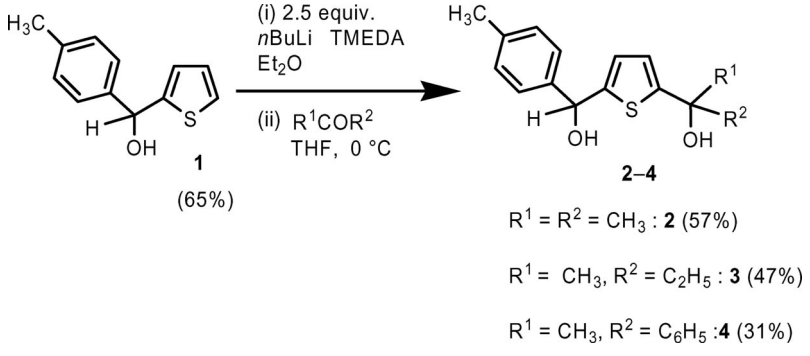
Scheme 3. Structures of 21,23-dithia- and 21-thiaphlorins.

Except for our own report, there are to the best of our knowledge no reports on core-modified calix(4)phyrins to test their potential for various applications. Our group has been involved in developing methods to synthesize core-modified porphyrin building blocks and to use them for the synthesis of porphyrin dyads, triads, tetrads and pentads containing two or more different porphyrin subunits.[18] In this paper we describe the synthesis of N_2S_2 and N_3S phlorins in decent yields from very simple precursors in detail. The methodology adopted here has been extended to synthesize several monofunctionalized thiaphlorins containing *p*-iodophenyl, *p*-ethynylphenyl, *p*-bromophenyl, *p*-cyanophenyl and *m*-nitrophenyl groups etc., and these have been used further for the synthesis of several novel thiaphlorin–porphyrin and thiaphlorin–thiaphlorin dyads. Preliminary anion-binding studies of some of these thiaphlorins and thiaphlorin–porphyrin dyads and their suitability as optical sensors is also presented.

Results and Discussion

Synthesis of Unsymmetrically Substituted 2,5-Thiophenedimethanols 2–4

The desired diols **2**–**4** (Scheme 4) were synthesized in two steps starting from thiophene. The 2-thiophenemethanol derivative **1** was synthesized in 65% yield by treatment of the thiophene with *n*BuLi (1.2 equiv.) followed by *p*-tolylaldehyde (1.2 equiv.) in THF at 0 °C and purified by silica gel column chromatography.[18f] After treatment with *n*BuLi



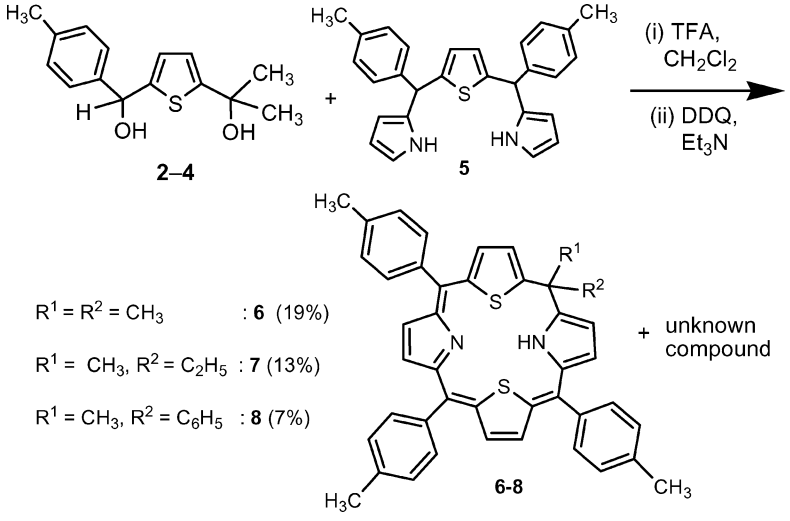
Scheme 4. Synthesis of unsymmetrically substituted 2,5-thiophenedimethanols **2**–**4**.

(2.5 equiv.), compound **1** was allowed to react with ketones like acetone, butan-2-one or acetophenone (1.2 equiv.) in THF at 0 °C (Scheme 4). After workup, TLC analysis of the crude mixtures showed four spots: two fast-moving minor spots corresponding to the unreacted ketone and **1**, respectively, and one unknown minor spot, closely followed by one major spot corresponding to the required unsymmetrical diol. The crude mixture was subjected to silica gel column chromatography, and unreacted ketone and **1** were collected with petroleum ether/ethyl acetate 5–7%. The third unknown minor spot was then collected with petroleum ether/ethyl acetate 25–30%, followed by the desired unsymmetrical diol eluted with petroleum ether/ethyl acetate 30–40%. Removal of solvent in vacuo afforded unsymmetrical diols **2**–**4** in 31–57% yields. Since the unsymmetrical 2,5-thiophenedimethanols **2**–**4** each have two chiral centres, the additional minor spots observed just above the desired major spots could be due to their diastereomers.[19] However, we collected the major product in each case and used it for condensation reactions. Although the yields of diols are moderate, the ready availability of **1** allows the easy preparation of the desired unsymmetrical thiophenedimethanols in about 5 g batches. The diols **2**–**4** were characterized by spectrometric and routine spectroscopic techniques. The $[M - 17]^+$ ion peak in the mass spectra and the matching elemental analysis confirmed the formation of diols.

Synthesis of 21,23-Dithiaphlorins 6–8 and 21-Thiaphlorin 9

The 21,23-dithiaphlorins **6**–**8** were prepared as shown in Scheme 5. The other desired precursor, the symmetrical 16-thiatripyrrane **5**, was synthesized by a literature procedure.[20] An unsymmetrical diol **2**–**4** (1 equiv.) was condensed with 16-thiatripyrrane **5** (1 equiv.) in the presence of a catalytic amount of trifluoroacetic acid at room temperature, and this was followed by oxidation with DDQ. After standard workup, the resulting crude compound was purified in order to remove polymeric materials. TLC analysis after the filtration column showed a fast-moving orange spot corresponding to an unidentified product, followed by a green spot corresponding to the relevant 21,23-dithiaphlorin **6**–**8**. The crude mixture was subjected to a second chromatographic purification. The unidentified orange product of low polarity (<1% yield) was collected and the desired 21,23-dithiaphlorins **6**–**8** were then collected as green compounds in 7–19% yields. Dithiaphlorins **6**–**8** were characterized by spectrometry and spectroscopic techniques and also in the case of **8** by X-ray crystallographic analysis. The presence of strong $[M]^+$ ion peaks in the mass spectra and matching elemental analyses confirmed the identities of the 21,23-dithiaphlorins **6**–**8**.

The ^{1}H NMR spectra of 21,23-dithiaphlorins **6**–**8** were recorded in $CDCl_3$ both at room temperature and at –50 °C. In the ^{1}H NMR spectrum, the four β-pyrrole protons gave rise to a sets of four signals, either doublets or broad singlets, shifted significantly upfield to the 6.2–7.2 ppm region, indicating the non-aromatic natures of the compounds. The four β-thiophene protons appeared as sets of two signals: a doublet at ca. 7.2 ppm due to one proton and a multiplet at ca. 7.3 ppm due to three protons. The inner NH proton appeared as two broad signals at ca. 11.3 and ca. 12.7 ppm, indicating the presence of two tautomers in solution. However, when the spectra were recorded in [D_5]pyridine, only one broad signal at δ = 10.1 ppm was observed for the NH proton, disappearing on the addition of a drop of D_2O due to exchange of the NH proton for a deuterium atom, confirming the NH signal (see Supporting Information). The absorption spectra of **6**–**8** each showed a broad band at ca. 680 nm, together with broad and sometimes split moderately intense absorption at ca. 420 nm (Figure 1). The protonated species of **6**–**8** generated by addition of few drops of dilute trifluoroacetic acid to **6**–**8** in dichloromethane each showed a significantly red-shifted



Scheme 5. Synthesis of 21,23-dithiaphlorins **6**–**8**.

strong absorption band at ca. 825 nm, together with two or three moderately intense broad peaks in the 300–500 nm region (Figure 1).

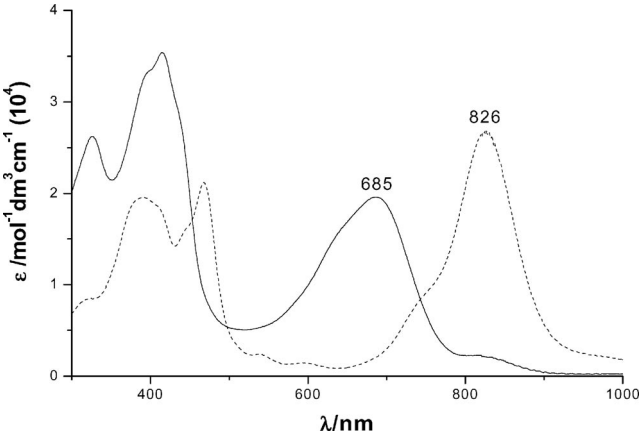


Figure 1. Absorption spectra of 21,23-dithiaphlorin **6** (—) and **6**·H^+ (------) recorded in dichloromethane. The concentration of **6** used was 2.34×10^{-5} M.

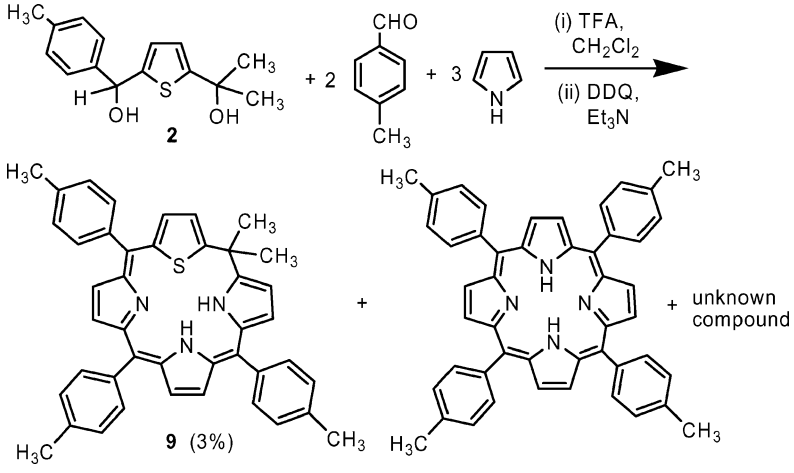
The 21-thiaphlorin **9** was synthesized by condensing the diol **2** (1 equiv.) with *p*-tolylaldehyde (2 equiv.) and pyrrole (3 equiv.) under acid catalysis conditions (Scheme 6).

The crude mixture containing the desired compound **9** together with 5,10,15,20-tetratolylporphyrin and some unidentified compound was separated by silica gel column chromatography and afforded **9** in 3% yield. Compound **9** was characterized by all spectroscopic techniques. Its mass spectra showed the $[M]^+$ ion peak, and its elemental analysis was in agreement with the proposed composition of **9**. In the ^{1}H NMR, a set of three signals corresponding to six β-pyrrole protons can be seen, further two multiplets and one broad singlet, shifted significantly upfield to the 6.5–6.9 ppm region. The broad singlet at $\delta \approx 7.2$ ppm was assigned to the two β-thiophene protons. The two inner NH protons were assigned to either two or three signals in 9.8–12.2 ppm region. The ^{1}H NMR spectrum of 21-thiaphlorin **9** was very similar to those of the 21,23-dithiaphlorins. The absorption spectrum of **9** showed a very broad band at ca. 672 nm and two bands in the 300–500 nm region. The protonated species of **9** also showed similar absorption features. The absorption bands of the protonated species of **9** were bathochromically shifted in relation to its neutral analogue. The absorption bands of **9** and its protonated species were blue-shifted in relation to the neutral and protonated species of the 21,23-dithiaphlorins.

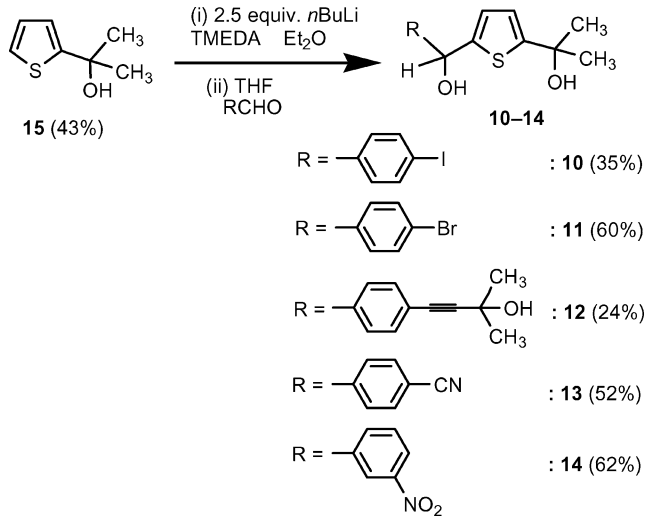
Synthesis of Unsymmetrically Substituted 2,5-Thiophenedimethanols 10–14

The synthetic methodology discussed above for the preparation of thia analogues of phlorins has been extended further to synthesize monofunctionalized thiaphlorins in order to use them as building blocks for the synthesis of covalently linked porphyrin–thiaphlorin and thiaphlorin–thiaphlorin dyads. To synthesize the monofunctionalized thiaphlorins, the functionalized unsymmetrically substituted 2,5-thiophenedimethanols **10**–**14** are needed, and these were synthesized as shown in Scheme 7. The 2-thiophenemethanol derivative **15** was synthesized in 43% yield by treatment of thiophene with *n*BuLi (1.2 equiv.) followed by reaction with acetone (1.2 equiv.) in THF and was purified. Compound **15** was first treated with *n*BuLi (2.5 equiv.) then with an appropriate functionalized aromatic aldehyde (1.2 equiv.) (see Scheme 7).

Purification of the crude reaction mixtures by silica gel column chromatography afforded the pure functionalized diols **10**–**14** in 24–62% yields. The functionalized diols **10**–**14** were characterized by common techniques. The diols **10**–**14** each showed two signals for OH protons in their infrared spectra, due to their unsymmetrical natures. The $[M]^+$ (10%) and $[M - 17]^+$ (90%) ion peaks in the mass spectra confirmed the identities of the diols **10**–**14**.



Scheme 6. Synthesis of 21-thiaphlorin **9**.



Scheme 7. Synthesis of functionalized unsymmetrically substituted 2,5-thiophenedimethanols **10**–**14**.

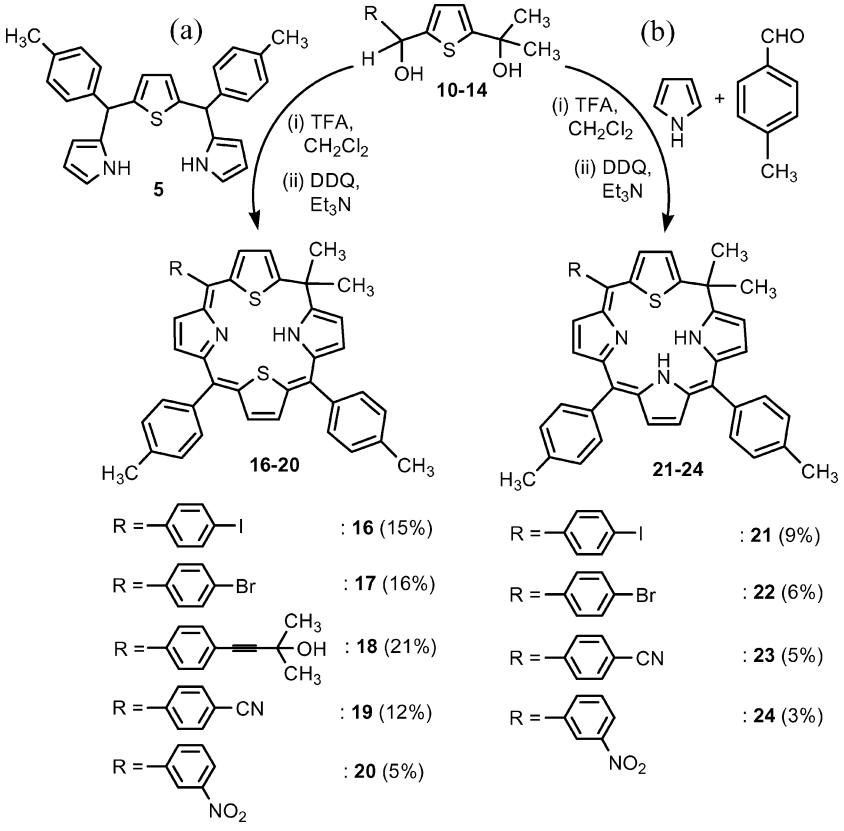
Monofunctionalized 21,23-Dithiaphlorins 16–20

The monofunctionalized 21,23-dithiaphlorins **16**–**20** were synthesized by condensing each of the appropriate diols **10**–**14** (1 equiv.) with 16-thiatripyrrane **5**[20] under mild acid catalysis conditions (Scheme 8, a). Purification by silica gel column chromatography with petroleum ether/ethyl acetate 5–15% afforded the desired monofunctionalized 21,23-dithiaphlorins **16**–**20** as the second bands in 12–20% yields. Compounds **16**–**20** were characterized by NMR, mass, absorption and elemental analysis. The monofunctionalized 21,23-dithiaphlorins **16**–**20** each showed a strong $[M]^+$ ion peak in the mass spectrum, and the elemental analyses were in agreement with the proposed compositions of the compounds. The β-pyrrole protons cause ^{1}H NMR signals in the 6.3–7.1 ppm region as sets of three or four peaks. Sets of two multiplets in the 7.1–7.3 ppm region were assigned to the four β-thiophene protons.

Monofunctionalized 21-Thiaphlorins 21–24

The monofunctionalized 21-thiaphlorins **21**–**24**, containing functional groups such as iodophenyl, bromophenyl, cyanophenyl and nitrophenyl at their *meso*-positions were synthesized by using the appropriate diols (Scheme 8, b). Condensation of the appropriate functionalized 2,5-thiophenedimethanol (1 equiv.) with *p*-tolylaldehyde (2 equiv.) and pyrrole (3 equiv.) in dichloromethane under nitrogen in the presence of catalytic amounts of trifluoroacetic acid at room temperature, followed by oxidation with DDQ, gave a crude mixture of the desired compound along with 5,10,15,20-tetratolylporphyrin and some unidentified macrocycles (Scheme 8, b). Column chromatographic purification on silica with petroleum ether/ethyl acetate 5–10% afforded pure **21**–**24** as green solids in 3–5% yields.

The functionalized 21-thiaphlorins **21**–**24** were characterized by spectrometric and spectroscopic techniques. The



Scheme 8. Synthesis of monofunctionalized 21,23-dithiaphlorins **16**–**20** and 21-thiaphlorins **21**–**24**.

mass spectra of **21**–**24** each showed a molecular ion peak at the expected molecular weight, and the elemental analyses were in agreement with the compositions of the compounds. In the ^{1}H NMR, the signals of the six β-pyrrole and the two β-thiophene protons were found in the 6.4–7.3 ppm region (see Supporting Information). The two inner NH protons produced sets of two or three broad singlets in the 9.9–12.0 ppm region. In [D_5]pyridine, two broad signals were observed for the inner NH protons at low temperature, and these disappeared on addition of a drop of D_2O, due to exchange of NH protons for deuterium atoms, confirming the identities of the NH protons (see Supporting Information). The absorption spectra of **21**–**24** and their protonated species showed features similar to those of **9** and its protonated species, respectively.

X-ray Diffraction Analysis

The X-ray structures of **8**[21] and the protonated form of **17**[21] were solved. The crystal structures are shown in Figure 2 and the crystal data are presented in Table 1.

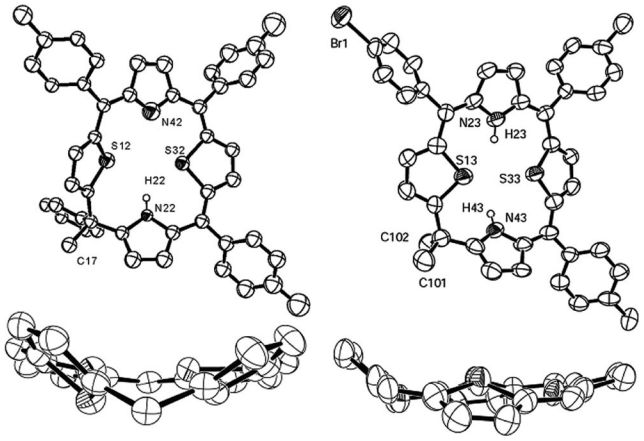


Figure 2. X-ray crystal structures of a) **8** and b) **17**·H$^+$ Thermal ellipsoids are shown at the 50% probability level. In the bottom view, *meso* aryl groups have been removed for clarity.

It is clear from the figure that both **8** and **17**·H$^+$ are nonplanar and possess marked kinks at their sp^3-hybridized *meso* carbons. In dithiaphlorin **8**, the nonbonding N···N (4.69 Å) and S···S (3.43 Å) distances are slightly larger than those in *meso*-tetraphenyl-21,23-dithiaporphyrin (S_2TPP) [N···N (4.65 Å) and S···S (3.07 Å)], indicating that **8** is less planar than S_2TPP.[22] Similarly the nonbonding N···N (4.84 Å) and S···S (3.39 Å) distances in the protonated dithiaphlorin **17**·H$^+$ were found to be greater than those in S_2TPP, showing that **17**·H$^+$ is not planar, due to the presence of one *meso* sp^3 carbon.

The nonplanarity of **8** and **17**·H$^+$ was clearly reflected in their dihedral angels between their mean core planes consisting of 24 atoms and the planes of the individual pyrrole or thiophene. In each macrocycle, the mean core plane of 24 atoms was highly distorted, with a mean deviation of 4.41 Å for **8** and 4.58 Å for **17**·H$^+$. The thiophene and pyrrole rings in thiaphlorins **8** and **17**·H$^+$ can be categorised into two types: a) thiophene I and pyrrole I (lying between the two sp^2 *meso* carbon atoms), and b) thiophene II and pyrrole II (lying between sp^3 and sp^2 *meso* carbon atoms). The dihedral angels between the mean core planes and the thiophene I, II and pyrrole I, II units of **8** and **17**·H$^+$ are tabulated in Table 2. It is very clear from Table 2 that in thiaphlorin **8** the thiophene II and pyrrole II units are much more deviated from the mean plane than the thiophene I and pyrrole I units. The presence of one sp^3 *meso* carbon forces the thiophene II and pyrrole II units to tilt away from the mean core plane in the macrocycles **8** and **17**·H$^+$. Furthermore, the pyrrole II unit is more deviated from the mean core plane than the thiophene II unit in both macrocycles.

Table 1. Crystal data and data collection parameters for **8** and **17**·H$^+$.

Parameters	**8**	**17**·H$^+$
Empirical formula	$C_{48}H_{38}N_2S_2$	$C_{42}H_{34}N_2S_2BrI_3{\cdot}0.5\,C_6H_6$
Formula weight	706.92	1130.50
Dimensions [mm]	0.35 × 0.15 × 0.05	0.25 × 0.20 × 0.05
Crystal system	monoclinic	monoclinic
a [Å]	8.990 (1)	13.440 (1)
b [Å]	16.034 (1)	15.667 (1)
c [Å]	25.816 (1)	20.937 (1)
α [°]	90	90
β [°]	98.78 (1)	103.82 (1)
γ [°]	90	90
V [Å^3]	3677.7 (5)	4283.5 (12)
space group	$P2_1/n$	$P2_1/c$
Z	4	4
μ(Mo-K_α) [cm^{-1}]	1.83	32.53
Residuals: R_1	0.064	0.085
Reflections measured	19039	12124
T [K]	198 (2)	198 (2)

Table 2. Selected bond lengths and dihedral angles in **8** and **17**·H$^+$, together with free thiophene and free pyrrole units.

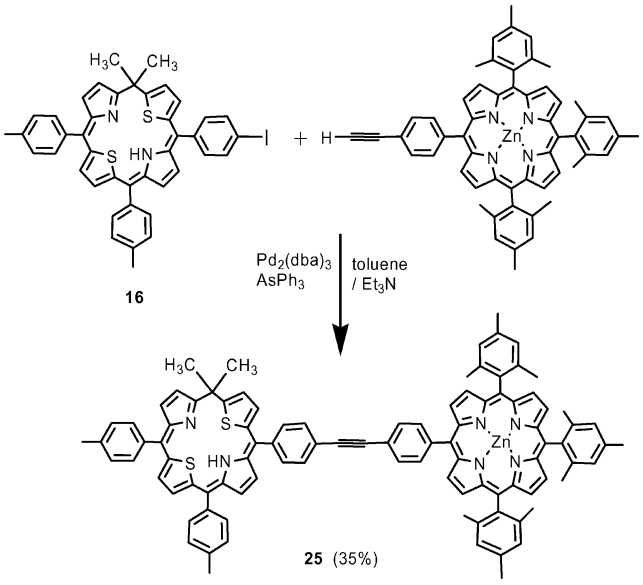
Ring	C_α–X [Å]	C_α–C_β [Å]	C_β–C_β [Å]	∠ [°]
Free thiophene	1.714	1.370	1.423	–
Free pyrrole	1.370	1.382	1.417	–
8				
Thiophene I	1.783(3), 1.780(2)	1.427(5), 1.417(5)	1.365(5)	34.1
Thiophene II	1.725(3), 1.736(3)	1.365(5), 1.380(5)	1.406(5)	67.9
Pyrrole I	1.314(3), 1.317(3)	1.440(5), 1.462(5)	1.357(5)	22.4
Pyrrole II	1.433(4), 1.447(4)	1.369(5), 1.374(5)	1.400(5)	74.6
17				
Thiophene I	1.733(11), 1.770(11)	1.415(14), 1.402(16)	1.354(14)	12.2
Thiophene II	1.740(12), 1.736(12)	1.351(16), 1.365(16)	1.390(16)	7.8
Pyrrole I	1.372(13), 1.401(13)	1.428(16), 1.426(14)	1.353(15)	9.0
Pyrrole II	1.377(14), 1.386(14)	1.392(15), 1.381(16)	1.381(16)	25.9

The relevant bond lengths in the heterocyclic rings in thiaphlorins **8** and **17**·H$^+$, together with those in free thiophene and free pyrrole, are also listed in Table 2. Closer inspection of Table 2 shows that significant changes in C_α–X, C_α–C_β and C_β–C_β bond lengths are observed in **8** and **17**·H$^+$ in relation to those in free thiophene and free pyr-

role.[23] The inner NH atom in **8** is present on the pyrrole N (pyrrole II), which is adjacent to the *meso* sp^3 carbon. The macrocycles **8** and **17**·H^+ each adopt a ruffled conformation, due to the nonplanarity induced by the presence of one *meso* sp^3 carbon. To accommodate the deformation caused by the *meso* sp^3 carbon atom, the pyrrole and the thiophene units in **8** and **17** each adopt an alternate conformation.

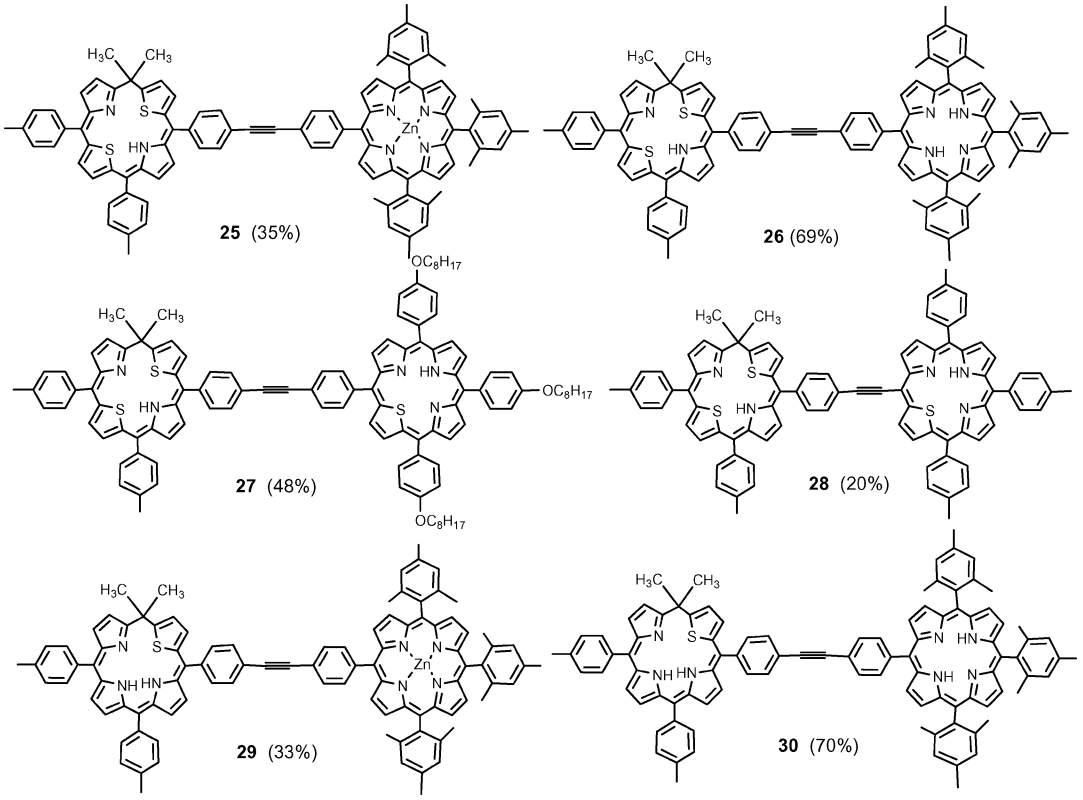
Synthesis of Covalently Linked 21,23-Dithiaphlorin–Porphyrin Dyads 25–28 and 21-Thiaphlorin–Porphyrin Dyads 29, 30

To show the applicability of the monofunctionalized thiaphlorins, we synthesized a series of covalently linked unsymmetrical dyads **25**–**28** (Scheme 9). The diarylethyne-bridged covalently linked unsymmetrical dyad **25** containing 21,23-dithiaphlorin and ZnN_4 porphyrin subunits was synthesized by coupling of **16** with the zinc(II) complex of 5,10,15-tri(mesityl)-20-(*p*-ethynylphenyl)porphyrin[24] in toluene/triethylamine at 50 °C in the presence of catalytic amounts of $AsPh_3/Pd_2(dba)_3$ under inert atmosphere[25] (Scheme 10). The crude compound was purified by column chromatography on neutral alumina with petroleum ether/ethyl acetate 3–5% and afforded dyad **25** in 35% yield. The dyad **26** was synthesized in 69% yield by demetallation of **25** with trifluoroacetic acid at room temperature.



Scheme 10. Synthesis of covalently linked 21,23-dithiaphlorin–porphyrin dyad **25**.

The diarylethyne-bridged dyad **27** containing 21,23-dithiaphlorin and N_3S porphyrin subunits was synthesized in 48% yield by coupling of **16** with 5-(*p*-ethynylphenyl)-10,15,20-tris(*p*-octyloxyphenyl)-21-thiaporphyrin[18f] under similar palladium coupling conditions.[25] The phenylethyne-bridged dyad **28** containing 21,23-dithiaphlorin and



Scheme 9. Covalently linked thiaphlorin–porphyrin dyads **25**–**30**.

N_3S porphyrin subunits was synthesized in 20% yield under the same mild palladium(0)-assisted coupling conditions through the coupling of **16** with 5-ethynyl-10,15,20-tri(*p*-tolyl)-21-thiaporphyrin[18g].

To synthesize dyad **29**, the 21-thiaphlorin building block **21** was coupled with 5-ethynylphenyl-10,15,20-trimesitylzinc(II)porphyrin[24] in toluene/triethylamine at 50 °C in the presence of $AsPh_3/Pd_2(dba)_3$ as catalyst, followed by standard workup and chromatography on neutral alumina with petroleum ether/ethyl acetate to give dyad **29** in 33% yield. The dyad **29** was treated with trifluoroacetic acid in dichloromethane for 12 h to give after purification the free base dyad **30** as a green–violet solid in 70% yield.

The dyads **25**–**30** are highly soluble in all common organic solvents and were characterized by NMR, mass and absorption spectroscopic techniques. In the ^1H NMR, the dyads **25**–**27** each showed peaks corresponding to both monomeric units. For dyad **25**, the four β-pyrrole protons of the 21,23-dithiaphlorin subunit gave signals upfield in the 6.4–6.9 ppm region as a set of four signals whereas the signals of the eight β-pyrrole protons of the ZnN_4 porphyrin subunit appeared downfield as a set of three signals in the 8.7–8.9 ppm region (see Supporting Information). The signals of the two β-thiophene protons of the 21,23-dithiaphlorin subunit also appeared upfield as two multiplets in the 6.9–7.2 ppm region. The inner NH signal of the 21,23-dithiaphlorin subunit of dyad **25** was detected downfield.

The dyad **26**, containing 21,23-dithiaphlorin and N_4 porphyrin subunits, and the dyad **27**, containing 21,23-dithiaphlorin and 21-thiaporphyrin subunits, both showed ^1H NMR spectral features similar to those of dyad **25**. Comparison of the chemical shifts of the various protons of the dyads **25**–**27** with those of the corresponding individual monomeric units indicates only minor differences, suggesting that the 21,23-dithiaphlorin and porphyrin subunits in dyads **25**–**27** interact very weakly.

The phenylethyne-bridged dyad **28** showed peaks corresponding to its constituent monomeric units. The chemical shifts of the protons corresponding to the N_3S porphyrin subunit with the ethyne group directly at the *meso* position were affected, whereas the protons of the 21,23-dithiaphlorin subunit with the phenyl group at the *meso* position remained unaffected. The β-thiophene and β-pyrrole protons of the N_3S-porphyrin subunit in dyad **28** were shifted downfield in relation to 5-ethynyl-10,15,20-tri(*p*-tolyl)-21-thiaporphyrin,[18g] indicating a strong interaction between the two subunits.

The absorption spectra of dyads **25**–**28** are each essentially a linear combination of the spectra of the corresponding monomers with only minor differences in wavelength maxima and band shapes, indicating that the monomeric subunits essentially retain their individual identities in the dyads **25**–**28**. In the visible region, the dyad **25** showed a broad absorption at 700 nm corresponding to the 21,23-dithiaphlorin subunit and two absorption bands at 550 and 590 nm corresponding to the ZnN_4 porphyrin subunit (Figure 3). In addition to the visible bands, the dyad **25** also showed a strong Soret band at 422 nm, corresponding mainly to the ZnN_4 porphyrin subunit, completely masking the absorption of the 21,23-dithiaphlorin subunit in that region. Interestingly, it is possible to protonate the 21,23-dithiaphlorin subunit with trifluoroacetic acid without causing any demetallation of the ZnN_4 porphyrin subunit. Comparison of the absorption spectra of dyad **25** and of its protonated species as shown in Figure 3 clearly indicated that the protonation had occurred at the 21,23-dithiaphlorin subunit site without causing any demetallation of the porphyrin subunit.

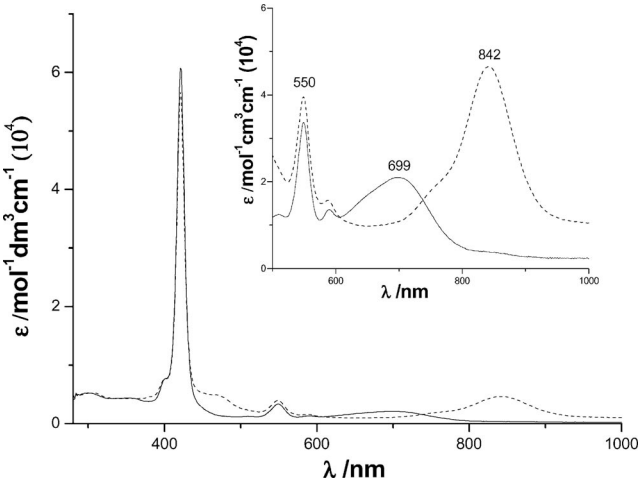


Figure 3. Absorption spectra of dyad **25** (—) and **25**·H^+ (-----) recorded in dichloromethane (concentration of **25** used was 1.97×10^{-6} M). The inset shows expansion of 500–1000 nm region.

The dyad **26** showed a broad absorption band of the 21,23-dithiaphlorin subunit at 699 nm and four Q-bands of the N_4 porphyrin subunit in the visible region, together with one strong Soret band, mainly of the N_4 porphyrin subunit, at 420 nm. In dyad **27**, the absorption bands of the 21,23-dithiaphlorin subunit and the N_3S porphyrin subunit overlapped and showed a broad band at 685 nm along with three other Q-bands at 627, 556 and 518 nm mainly corresponding to the N_3S porphyrin subunit. The dyad **27** also showed a single strong Soret band at 435 nm, corresponding mainly to the N_3S porphyrin subunit. The dyad **28** showed ill-defined Q-bands and one strong Soret band, which were bathochromically shifted in relation to 5-ethynyl-10,15,20-tri(*p*-toyl)-21-thiaporphyrin[18g] because of the strong interaction between the two subunits. In all these dyads, it is possible to protonate the 21,23-dithiaphlorin subunit selectively without protonation of the porphyrin subunit.

The dyads **29** and **30** were identified by clear NMR spectra and by $[M]^+$ ion peaks in their mass spectra. In the ^1H NMR of dyad **29**, the six β-pyrrole H signals of the 21-thiaphlorin subunit appeared upfield as a set of three signals in the 6.5–7.0 ppm region, while the signals of the eight β-pyrrole protons of the ZnN_4 porphyrin subunit appeared downfield as a set of three broad signals in the 8.7–8.9 ppm region. The two β-thiophene H signals of the 21-thiaphlorin subunit appeared as a multiplet at 7.3 ppm. Dyad **30** showed similar ^1H NMR features. The visible absorption

spectra of dyad **29** showed a broad absorption at 681 nm corresponding to the 21-thiaphlorin subunit and two bands at 550 and 590 nm corresponding to the ZnN_4 porphyrin subunit. In addition, the dyad **29** also showed a strong Soret band at 432 nm, corresponding mainly to the ZnN_4 porphyrin subunit. The visible absorption spectrum of dyad **30** showed a broad absorption at 679 nm for the 21-thiaphlorin subunit and four Q-bands in the 500–650 nm region corresponding to the N_4 porphyrin subunit. The dyad **30** also showed a strong Soret band at 419 nm, corresponding mainly to the N_4 porphyrin subunit. In dyads **29** and **30**, it is possible to protonate the 21-thiaphlorin subunit selectively.

Bis(21,23-dithiaphlorin) Dyad 33

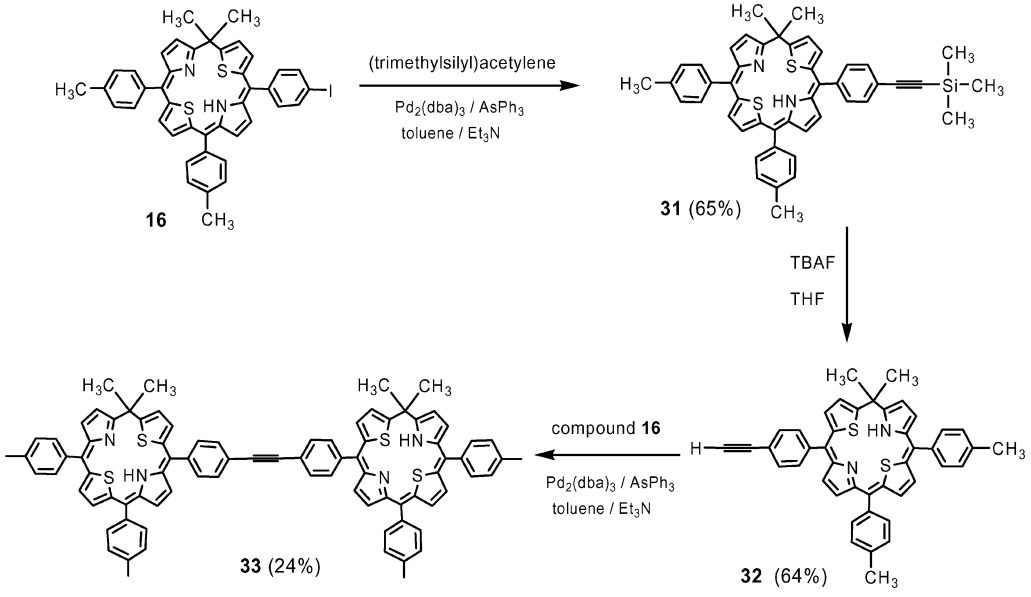
To synthesize bis(21,23-dithiaphlorin) dyad **33**, the other required 21,23-dithiaphlorin building block **31**, with a *p*-ethynylphenyl group at the *meso* position, was synthesized as shown in Scheme 11. The 21,23-dithiaphlorin **16**, with a *meso p*-iodophenyl group, was treated with (trimethylsilyl)-acetylene in toluene/triethylamine in the presence of $AsPh_3$ and $Pd_2(dba)_3$ at 50 °C under inert atmosphere[25] for 24 h. After purification **31** was obtained in 65% yield. Deprotection of **31** with tetrabutylammonium fluoride (TBAF) at room temperature in dry THF gave **32** in 64% yield. Compound **32** showed a singlet at 3.2 ppm in the ^1H NMR, corresponding to the CCH proton and a molecular ion peak in its mass spectrum, confirming the identity of the compound.

The diarylethyne-bridged bis(dithiaphlorin) dyad **33** containing two 21,23-dithiaphlorin subunits was synthesized in 24% yield by coupling of **16** with **32** under mild palladium(0) coupling conditions as used for the preparation of other dyads, followed by purification by column chromatography on neutral alumina (Scheme 11). The ^1H NMR spectra of dyad **33** showed a set of four signals for the eight β-pyrrole protons and two sets of signals for the β-thiophene protons of both the 21,23-dithiaphlorin subunits. The dyad **33** also showed two broad singlets for inner NH protons at $\delta = 11.9$ and 13.1 ppm. The absorption spectrum of dyad **33** showed a broad absorption at 706 nm and multiple absorption bands in the 300–450 nm region.

Anion-Binding Studies

The calix(4)pyrroles, calix(4)phyrins and their expanded analogues are well known for their strong abilities to coordinate anions.[26] The driving force for anion coordination in these macrocycles is mainly through electrostatic interactions and hydrogen bonds. The thiaphlorins synthesized here have been found to have less affinity for anion coordination in neutral form, due to smaller numbers of inner hydrogen atoms, which would be expected to be involved in anion binding through hydrogen-bonding interactions. Similar observations were made earlier with calix(4)phyrins with N_4 cores[26] and expanded heteroporphyrins.[27] However, these macrocycles were found to be effective in anion coordination in their protonated forms. It should be noted that the protonated forms of thiaphlorins absorb very strongly in the visible region relative to their neutral species, which helps in carrying out anion-binding experiments using optical spectroscopic techniques. Preliminary binding studies of the protonated forms of 21,23-dithiaphlorin **6** and the covalent thiaphlorin–porphyrin dyads **25** and **27** with various tetrabutylammonium salts were carried out in order to test their abilities to coordinate anions.

The protonated forms of thiaphlorin **6** and thiaphlorin–porphyrin dyad **25** show strong absorptions in their 800–860 nm regions, so the changes in the electronic spectra on



Scheme 11. Synthesis of bis(21,23-dithiaphlorin) dyad **33**.

addition of anions were used to study anion complexation. In the case of dyad **27**, the calix(4)phyrin subunit can be selectively protonated without protonating the thiaporphyrin subunit, and the changes in the strong fluorescence of the thiaporphyrin subunit on addition of increasing amounts of anions were used to study the anion complexation. In a typical experiment, an aliquot (3 mL) of the protonated solution of thiaphlorin **6** or thiaphlorin–porphyrin dyad **25** or **27** in dichloromethane was placed in the spectrometric cell and increasing amounts of the tetrabutylammonium halide salt dissolved in dichloromethane were added by Hamilton Micro syringe. The addition of the salt solution changed the colour of the host solution from greenish yellow to brown. Immediately the absorption spectra of the solutions in the desired region for **6**·H^+ and **25**·H^+ and the emission spectral changes for **27**·H^+ were recorded in the overlay mode. The addition of increasing amounts of the salt resulted in the gradual decrease in the absorbance of the protonated host **6**·H or **25**·H^+ with no shift in the absorption peak maxima or gradual increase in the emission intensity of the 21-thiaporphyrin subunit in case of dyad **27**·H^+. In these experiments, the concentration of the host (**6**·H^+, **25**·H^+ or **27**·H^+) was kept constant and the change in absorbance (ΔA) or in emission intensity (ΔI) was calculated at a particular λ value where the spectral change was maximum. The ΔA or ΔI was plotted against the concentration of the added anion guest (C). The data were fitted with the aid of the Origin (version 6.0) software package. The binding constants were calculated with a 1:1 anion binding model according to the formula shown in Equation (1).[28]

$$A = \frac{[K_aC + K_aR + 1) - \sqrt{(K_aC + K_aR + 1)^2 - 4K_a^2CR]A_c}}{2K_aR} \quad (1)$$

A represents the absorbance of host solution (thiaphlorin or thiaphlorin–porphyrin dyad), R is the initial fixed concentration of the host, C is the concentration of the added guest (tetrabutylammonium salt), A_c is the difference in absorbance of host–guest complex and the free host (thiaphlorin or thiaphlorin–porphyrin dyad), and K_a represents the association constant. We used the same equation to calculate the binding constant for dyad **27**·H^+, using the changes in the fluorescence intensity in place of absorbance changes. The shape of the observed titration curves and good fit to 1:1 binding profiles indicated the formation of 1:1 complex in solution.

The effect of addition of increasing amounts of tetrabutylammonium bromide salt on the absorption spectra of the protonated form of **6** is shown in Figure 4 (a). It is clear from the Figure that **6**·H^+ showed a strong peak at 825 nm, which decreased in its intensity when it was titrated with increasing amounts of anion salts, confirming the binding of anion. Figure 4 (b) shows the plot of ΔA vs. concentration of tetrabutylammonium bromide salt. The binding constant was calculated using the above formula, and a good fit to a 1:1 binding profile indicated the formation of a 1:1 thiaphlorin–anion complex.

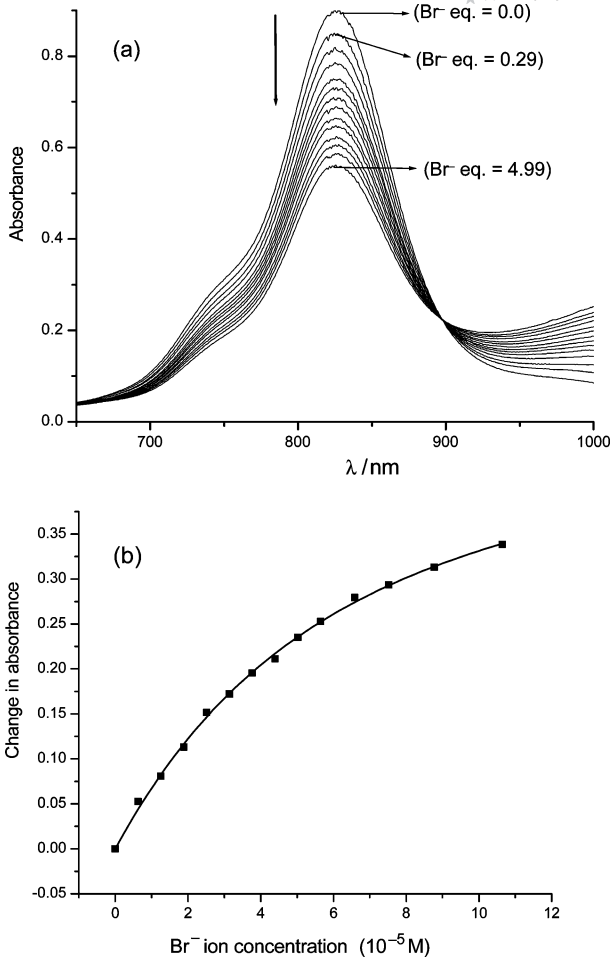


Figure 4. a) UV/Vis titration curve for protonated dithiaphlorin **6**·H^+ with increasing amounts of tetrabutylammonium bromide salt in dichloromethane. b) The curve-fitting plot of the change in absorbance (ΔA) vs. the concentration of Br^- anion. The concentration of the dithiaphlorin used was 2.13×10^{-5} M and the concentration range of the Br^- used was 6.29×10^{-6} M to 1.06×10^{-4} M. The spectra were measured at 825 nm at 22 °C.

Similar anion-binding titrations were carried out for **6**·H^+ with tetrabutylammonium iodide, chloride, thiocyanide and hydrogen sulfate salts (see Supporting Information), and the calculated binding constants are presented in Table 3. The data indicated that the protonated **6** showed higher affinities for bromide and iodide than for other anions, as evident in their binding constants K_a.

Preliminary anion-binding studies by the absorption spectroscopic technique were also carried out with the protonated form of dyad **25**, containing 21,23-dithiaphlorin and ZnN_4 porphyrin subunits. Dyad **25** with the zinc(II) ion in the porphyrin subunit was selectively protonated at the 21,23-dithiaphlorin subunit by careful addition of dilute trifluoroacetic acid without inducing the demetallation of the porphyrin subunit. When the dyad **25**·H^+ was titrated with tetrabutylammonium iodide, the decrease in the intensity of the absorption band at 840 nm, with a clean fit to a 1:1 binding profile, suggested the binding of the anion at the 21,23-dithiaphlorin site in 1:1 stoichiometry. Similar ob-

Table 3. Binding constant (K_a) data for **6**·H^+, **25**·H^+ and **27**·H^+ in dichloromethane at 22 °C determined by absorption and fluorescence spectroscopic techniques.

Compound	Anion[a]	K_a (M^{-1})
6·H^+	Cl^-	$4.8\ (9) \times 10^3$ [b]
6·H^+	Br^-	$2.1\ (1) \times 10^4$ [b]
6·H^+	I^-	$1.5\ (4) \times 10^4$ [b]
6·H^+	HSO_4^-	$3.3\ (7) \times 10^3$ [b]
6·H^+	SCN^-	$1.8\ (2) \times 10^3$ [b]
25·H^+	Br^-	$4.6\ (4) \times 10^4$ [b]
25·H^+	I^-	$2.3\ (2) \times 10^4$ [b]
27·H^+	I^-	$6.2\ (8) \times 10^3$ [c]

[a] Anions used were in the form of their Bu_4N^+ (TBA) salts. The errors in all fits are $< \pm 15\%$. [b] Absorption spectroscopy. [c] Fluorescence spectroscopy; λ_{ex} = 520 nm.

servations were made for tetrabutylammonium bromide ion as well (see Supporting Information). Thus, the dyad **25** is a novel system that binds anions *and* cations.

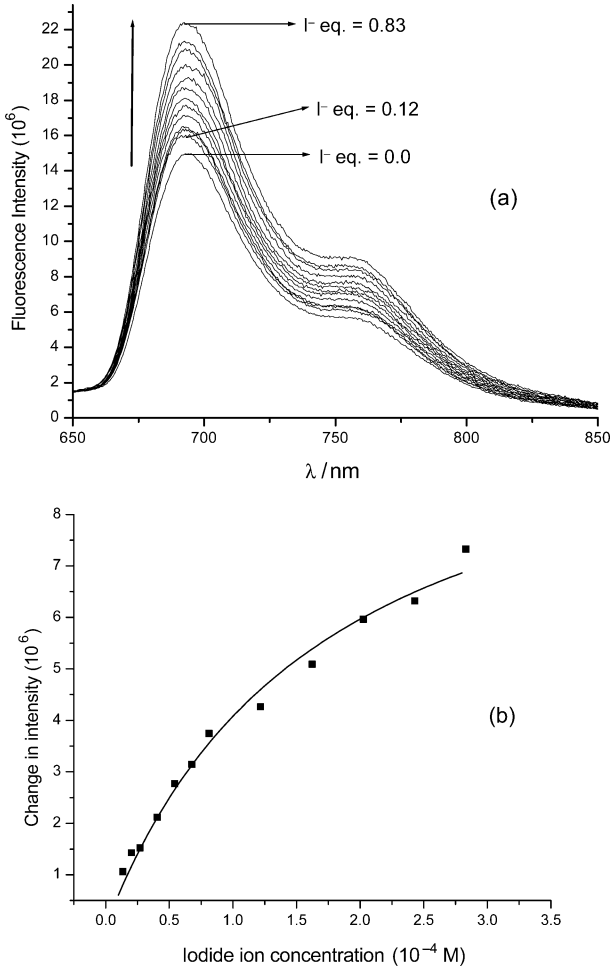


Figure 5. a) Fluorescence titration of thiaphlorin–porphyrin dyad **27**·H^+ with increasing amounts of tetrabutylammonium iodide in dichloromethane. b) The curve fitting plot of the change in fluorescene intensity (ΔI) vs. the concentration of I^- anion. The 8.82×10^{-6} M dichloromethane solution of dyad **27** was selectively protonated by addition of 1.5 μL of 2×10^{-3} M trifluoroacetic acid in dichloromethane (the TFA concentration was 9.67×10^{-7} M). The dyad 27·H^+ was excited at 520 nm and the concentration range of iodide salt used was 1.06×10^{-6} M to 7.32×10^{-6} M.

The dyad **27**, which contains free base N_3S porphyrin and 21,23-dithiaphlorin subunits, was tested for binding of iodide ion by fluorescence.[29] Since the N_3S porphyrin subunit is a good fluorophore, we assumed that it should be usable to sense the anion binding that occurs at the protonated 21,23-dithiaphlorin site by showing changes in its emission band. Increasing amounts of tetrabutylammonium iodide salt solution in dichloromethane were therefore added to the selectively protonated dyad **27**·H^+, and the fluorescence of the 21-thiaporphyrin subunit was monitored by excitation at 520 nm (Figure 5, a). Addition of increasing amounts of iodide ion resulted in the gradual enhancement of the intensity of the 21-thiaporphyrin fluorescent band (λ_{em} = 692 nm), suggesting that the iodide ion was bound at the protonated 21,23-dithiaphlorin site in dyad **27**·H^+. Thus, in dyad **27**, the binding of iodide ion at the 21,23-dithiaphlorin site was sensed by observing the changes in the fluorescence intensity of the 21-thiaporphyrin subunit, suggesting that the dyad **27** should be usable as a fluorescence sensor. The binding stoichiometry is 1:1 as indicated by a good fit to 1:1 binding profile (Figure 5, b). Thus, while a detailed study is needed, these preliminary investigations have indicated that the thiaphlorins and thiaphlorin–porphyrin dyads bind anions effectively, as judged from optical studies.

Conclusions

In conclusion, we have described the synthesis of 21,23-dithia- and 21-thiaphlorins, each containing one sp^3 *meso* carbon, from easily available precursors. The method adopted to synthesize the thiaphlorins is simple and versatile and allows the synthesis of any desired 21,23-dithia and 21-thia analogues of phlorins in metal-free form. The synthetic strategy has been used further to synthesize the monofunctionalized 21,23-dithia- and 21-thiaphlorins. The monofunctionalized 21,23-dithia- and 21-thiaphlorins have been used to synthesize a series of covalently linked thiaphlorin–porphyrin dyads. We have also carried out functional group transformation on thiaphlorin to show that they are quite stable and have synthesized a bis(thiaphlorin) dyad for future use.

Preliminary anion-binding studies indicated that the thiaphlorins and thiaphlorin–porphyrin dyads exhibits very interesting anion binding properties, so the thiaphlorins and the thiaphlorin–porphyrin dyads represent a new class of anion sensors. It is anticipated that more attention will be given in future to the synthesis of various hetero analogues of calix(*n*)phyrins to test their potential for cation- and, more importantly, anion-binding studies. Although the preliminary studies showed that the thiaphlorins and thiaphlorin–porphyrin dyads are good anion-complexing agents, a detailed study is needed to understand the complete potential of these systems to act as anion-binding agents/anion sensors. The synthesis of various hetero analogues of different classes of calix(*n*)phyrins and detailed anion-binding studies will be carried out in these laboratories in the near future.

Experimental Section

2-(Thiophen-2-yl)propan-2-ol (15): Dry, distilled ether (40 mL) was placed in a 250 mL three-necked, round-bottomed flask fitted with a rubber septum and gas inlet tube, and the flask was flushed with argon for 10 min. Tetramethylethylenediamine (TMEDA, 3.5 g, 4.6 mL, 30.457 mmol) and *n*-butyllithium (20 mL of ca. 15% solution in hexane) were added to the stirred solution, and the reaction temperature was maintained at 0 °C (ice bath). Thiophene (2.1 g, 2.0 mL, 25.381 mmol) was added, and the solution was stirred for 1 h at 0 °C. As the reaction progressed, a white turbid solution formed, indicating the formation of the 2-lithiated salt of thiophene. An ice-cold solution of dry acetone (3.6 g, 4.5 mL, 63.453 mmol) in dry THF (20 mL) was then added and the system was stirred for an additional 15 min at 0 °C. The reaction mixture was 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 diluted with diethyl ether and washed several times with water and brine and dried with anhydrous Na_2SO_4. The solvent was removed in a rotary evaporator under reduced pressure to afford the crude compound. TLC analysis mainly showed two spots corresponding to the unreacted thiophene and the desired alcohol. The crude compound was loaded onto silica and eluted with petroleum ether. The unchanged thiophene was removed with a petroleum ether/ethyl acetate (98:2) solvent mixture, and the desired mono-ol **15** was then collected with a petroleum ether/ethyl acetate (94:6) solvent mixture. The solvent was removed in a rotary evaporator to afford **15** as a yellow oil (1.6 g, 44% yield). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.66 (s, 6 H), 2.15 (br. s, 1 H), 6.94 (m, 2 H), 7.18 (m, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 32.04, 71.10, 121.87, 123.61, 126.46, 128.29, 154.32 ppm. IR (neat): $\tilde{\nu}$ = 3389 (OH) cm^{-1}. ES-MS: $C_7H_{10}SO$, calcd. av. mass 142.2; obsd. *m*/*z*: 125.2 [M – 17]$^+$, 90%. $C_7H_{10}OS$ (142.2): calcd. C 59.12, H 7.09, S 22.55; found C 59.01, H 7.03, S 22.49.

2-{[5-Hydroxy(*p*-tolyl)methyl]thiophen-2-yl}propan-2-ol (2): Dry, distilled ether (35 mL) was placed in a 250 mL three-necked, round-bottomed flask fitted with a rubber septum and gas inlet tube, and the flask was flushed with argon for 10 min. Tetramethylethylenediamine (TMEDA, 1.9 g, 2.4 mL, 16.152 mmol) and *n*-butyllithium (12 mL of a ca. 15% solution in hexane) were added to the stirred solution, and the reaction temperature was maintained at 0 °C in an ice bath. Compound **1** (1.5 g, 7.342 mmol) was added, and the solution was stirred for 1 h. An ice-cold solution of dry acetone (1.0 g, 1.3 mL, 18.355 mmol) in dry THF (30 mL) was then added to the turbid solution and the system was stirred for additional 15 min at 0 °C. The reaction mixture was brought to room temperature. An ice-cold NH_4Cl solution (50 mL, ca. 1 M) was added to quench the reaction. The organic layer was washed several times with water and brine and dried with anhydrous Na_2SO_4. The solvent was removed in a rotary evaporator under reduced pressure to afford the crude compound, which was loaded onto silica and eluted with petroleum ether. The unchanged mono-ol was removed with a petroleum ether/ethyl acetate (95:5) solvent mixture, the two other unidentified minor spots were removed in petroleum ether/ethyl acetate (90:10), and the desired diol **2** was then collected with a petroleum ether/ethyl acetate (70:30) solvent mixture. The solvent was removed in a rotary evaporator to afford **2** as a brown oil in 57% yield (1.1 g). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.57 (s, 6 H), 2.32 (s, 3 H), 3.11 (br. s, 2 H) 5.85 (s, 1 H), 6.63 (d, *J* = 3.3 Hz, 1 H), 6.70 (d, *J* = 3.9 Hz, 1 H), 7.12 (d, *J* = 7.5 Hz, 2 H), 7.28 (d, *J* = 8.1 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.11, 29.11, 31.91, 53.71, 72.11, 101.97, 121.35, 123.09, 124.19, 124.81, 126.21, 129.04, 137.49, 140.32, 146.77, 154.08 ppm. IR (neat): $\tilde{\nu}$ = 3394 (OH), 3271 (OH) cm^{-1}. ES-MS: $C_{15}H_{18}SO_2$, calcd. av. mass 262.4; obsd. *m*/*z*: 245.1 [M – 17]$^+$ (90%). $C_{15}H_{18}O_2S$ (262.4): calcd. C 68.67, H 6.92, S 12.22; found C 68.48, H 6.73, S 12.46.

2-{(5-[Hydroxy(*p*-tolyl)methyl]thiophen-2-yl}butan-2-ol (3): The lithiated derivative of **1**, generated as described above, was treated with an ice-cold solution of but-3-en-2-one (1.8 g, 2.2 mL, 24.473 mmol) in THF (25 mL), followed by standard workup and column chromatographic purification on silica with petroleum ether/ethyl acetate (65:35) to give the desired diol **3** as a brown oil in 47% yield (1.3 g). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 0.88 (m, 3 H), 1.55 (s, 3 H), 1.83 (m, 2 H), 1.97 (br. s, 1 H), 2.35 (s, 3 H), 2.48 (br. s, 1 H), 5.94 (s, 1 H), 6.70 (m, 2 H), 7.17 (d, *J* = 8.1 Hz, 2 H), 7.33 (d, *J* = 8.1 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 8.66, 21.23, 29.38, 29.46, 37.26, 72.40, 74.18, 121.98, 124.44, 129.22, 137.70, 140.22, 146.60, 153.12 ppm. IR (neat): $\tilde{\nu}$ = 3384 (OH), 3272 (OH) cm^{-1}. ES-MS: $C_{16}H_{20}SO_2$, calcd. av. mass 276.4; obsd. *m*/*z*: 273.1 [M – 17]$^+$ (90%). $C_{16}H_{20}O_2S$ (276.4): calcd. C 69.53, H 7.29, S 11.60; found C 69.39, H 7.23, S 11.24.

1-{5-[Hydroxy(*p*-tolyl)methyl]thiophen-2-yl}-1-phenylethanol (4): The lithiated derivative of **1** was treated with an ice cold solution of acetophenone (2.2 g, 2.1 mL, 18.355 mmol) in THF (25 mL). Workup and silica gel column chromatographic purification using petroleum ether/ethyl acetate (70:30) gave diol **4** in 31% yield (0.8 g). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.94 (s, 3 H), 2.33 (s, 3 H), 2.49 (br. s, 2 H), 5.89 (s, 1 H), 6.66 (m, 2 H), 7.15 (d, *J* = 6 Hz, 2 H), 7.28 (m, 5 H), 7.46 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.25, 31.99, 72.39, 74.85, 123.78, 123.83, 124.27, 124.32, 125.45, 126.38, 126.42, 127.27, 128.19, 129.26, 137.71, 137.74, 140.18, 147.12, 147.88, 153.28 ppm. IR (neat): $\tilde{\nu}$ = 3409 (OH), 3277 (OH) cm^{-1}. ES-MS: $C_{20}H_{20}SO_2$, calcd. av. mass 324.4; obsd. *m*/*z*: 307.4 [M – 17]$^+$ (90%). $C_{20}H_{20}O_2S$ (324.4): calcd. C 74.04, H 6.21, S 9.88; found C 74.44, H 6.51, S 9.68.

5,5-Dimethyl-10,15,20-tri(*p*-tolyl)-21,23-dithiaphlorin (6): Compound **2** (0.4 g, 1.524 mmol) and 16-thiatripyrrane **5** (0.6 g, 1.524 mmol) were condensed in CH_2Cl_2 (40 mL) under nitrogen at room temperature in the presence of trifluoroacetic acid (0.1 g, 0.1 mL, 1.524 mmol). The reaction mixture was stirred under nitrogen for 1 h. DDQ (0.3 g, 1.524 mmol) was added and stirring was continued in air for an extra 1 h. The crude mixture was purified by silica gel column chromatography, and the desired N_2S_2-phlorin **6** was collected with petroleum ether/ethyl acetate (94:6). The solvent was removed in a rotary evaporator, to afford the N_2S_2-phlorin **6** as a green solid in 19% yield (0.2 g); m.p. >250 °C. ^{1}H NMR (300 MHz, $CDCl_3$, –50 °C, TMS): δ = 1.86 (s, 6 H), 2.45 (s, 9 H), 6.29 (br. s, 1 H), 6.49 (br. s, 1 H), 6.90 (br. s, 1 H), 7.10 (br. s, 1 H), 7.28 (m, 8 H), 7.43 (m, 4 H), 7.52 (m, 4 H), 11.32 (br. s, 1 H), 12.72 (br. s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.43, 29.62, 39.06, 106.77, 121.37, 128.54, 128.77, 129.49, 131.37, 131.97, 132.55, 134.69, 137.14, 138.24, 140.34 ppm. UV/Vis: λ_{max} ($\varepsilon \times 10^3$ L mol^{-1} cm^{-1}) = 327 (23.86), 415 (32.24), 686 nm (19.37). ES-MS: $C_{43}H_{36}N_2S_2$, calcd. av. mass: 644.8; obsd. *m*/*z*: 645.2 [M]$^+$. $C_{43}H_{36}N_2S_2$ (644.8): calcd. C 80.08, H 5.63, N 4.34, S 9.94; found C 80.28, H 5.71, N 4.38, S 9.86.

5-Ethyl-5-methyl-10,15,20-tri(*p*-tolyl)-21,23-dithiaphlorin (7): Samples of **3** (0.4 g, 1.447 mmol) and 16-thiatripyrrane **5** (0.6 g, 1.447 mmol) were condensed under same reaction conditions as described for compound **6**. The crude product was purified by silica gel column chromatography and afforded the desired compound **7** as a green solid in 13% yield (0.1 g); m.p. >250 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.26 (s, 3 H), 1.73 (m, 2 H), 2.15 (s, 3 H), 2.46 (m, 9 H), 6.29 (d, *J* = 3.6 Hz, 1 H), 6.50 (d, *J* =

4.5 Hz, 1 H), 6.89 (d, J = 4.5 Hz, 1 H), 7.09 (d, J = 4.2 Hz, 1 H), 7.22 (d, J = 4.8 Hz, 1 H), 7.27 (m, 7 H), 7.42 (m, 4 H), 7.52 (m, 4 H), 11.73 (br. s, 1 H), 12.87 (br. s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 8.59, 21.38, 22.54, 29.76, 37.23, 43.21, 108.12, 121.19, 122.34, 123.03, 125.98, 128.53, 128.77, 128.86, 129.48, 130.59, 131.37, 131.98, 132.51, 134.69, 134.95, 135.31, 136.70, 136.96, 137.08, 137.18, 138.24, 138.66, 139.32, 140.19, 140.92, 146.92, 146.19, 146.93, 152.79, 166.38 ppm. UV/Vis: λ_{max} ($\varepsilon \times 10^3$ L mol^{-1} cm^{-1}) = 325 (23.13), 415 (30.87), 689 nm (18.28). ES-MS: $C_{44}H_{38}N_2S_2$, calcd. av. mass: 658.9; obsd. m/z: 659.4 $[M]^+$. $C_{44}H_{38}N_2S_2$ (658.9): calcd. C 80.20, H 5.81, N 4.25, S 9.73; found C 80.31, H 5.86, N 4.34, S 9.93.

5-Methyl-5-phenyl-10,15,20-tri(*p*-tolyl)-21,23-dithiaphlorin (8): Condensation of **4** (0.4 g, 1.223 mmol) and 16-thiatripyrrane **5** (0.6 g, 1.223 mmol) under similar reaction conditions and purification by silica gel column chromatography with petroleum ether/ethyl acetate (95:5) afforded pure N_2S_2-phlorin **8** as a green solid in 7% yield (0.07 g); m.p. >250 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 2.47 (m, 9 H, CH_3), 2.56 (s, 3 H), 6.54 (d, J = 3.6 Hz, 1 H), 6.63 (d, J = 3.6 Hz, 1 H), 6.83 (d, J = 7.6 Hz, 2 H), 6.89 (d, J = 4.8 Hz, 1 H), 7.03 (d, J = 7.2 Hz, 1 H), 7.09 (m, 2 H), 7.22 (d, J = 4.4 Hz, 1 H), 7.30 (m, 8 H), 7.41 (d, J = 3.6 Hz, 2 H), 7.48 (d, J = 5.6 Hz, 1 H), 7.56 (m, 5 H), 8.67 (s, 1 H), 9.69 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.35, 21.45, 29.37, 48.53, 109.57, 121.08, 123.25, 124.05, 126.51, 126.96, 128.15, 128.54, 128.84, 129.65, 130.64, 131.42, 132.11, 132.40, 134.54, 135.43, 136.04, 136.79, 136.98, 137.28, 138.32, 138.56, 140.79, 141.37, 145.82, 148.72, 152.83 ppm. UV/Vis: λ_{max} ($\varepsilon \times 10^3$ L mol^{-1} cm^{-1}) = 325 (26.82), 417 (37.70), 686 nm (21.81). ES-MS: $C_{48}H_{38}N_2S_2$, calcd. av. mass: 706.9; obsd. m/z: 706.9 $[M]^+$. $C_{48}H_{38}N_2S_2$ (706.9): calcd. C 81.55, H 5.42, N 3.96, S 9.07; found C 81.83, H 5.71, N 3.48, S 9.46.

5,5-Dimethyl-10,15,20-tri(*p*-tolyl)-21-thiaphlorin (9): Samples of **2** (0.7 g, 2.477 mmol), *p*-tolylaldehyde (0.6 g, 0.6 mL, 4.954 mmol) and pyrrole (0.5 g, 0.5 mL, 7.431 mmol) were condensed in CH_2Cl_2 (70 mL) under the mild acid catalysis conditions used for compound **6**. The crude compound was subjected to silica gel column chromatography and the desired N_3S phlorin **9** was obtained with petroleum ether/ethyl acetate (99:1) as a green solid in 3% yield (0.04 g); m.p. >150 °C. ^{1}H NMR (500 MHz, $CDCl_3$, –50 °C, TMS): δ = 1.79 (s, 6 H), 2.46 (m, 9 H), 6.45 (br. s, 1 H), 6.58 (s, 1 H), 6.98 (m, 4 H), 7.18 (br. s, 2 H), 7.31 (br. s, 5 H), 7.39 (s, 1 H), 7.43 (br. s, 1 H), 7.53 (br. s, 3 H), 7.62 (br. s, 2 H) ppm. UV/Vis: λ_{max} ($\varepsilon \times 10^3$ L mol^{-1} cm^{-1}) = 323 (15.012), 413 (25.67), 672 nm (14.26). ES-MS: $C_{43}H_{37}N_3S$, calcd. av. mass: 627.8; obsd. m/z: 627.9 $[M]^+$. $C_{43}H_{37}N_3S$ (627.8): calcd. C 82.26, H 5.94, N 6.69, S 5.11; found C 82.29, H 5.73, N 6.38, S 5.23.

Diol 10: The lithiated derivative of **15** (1.9 g, 13.359 mmol) was treated with an ice-cold solution of *p*-iodobenzaldehyde (3.7 g, 16.031 mmol) in THF (35 mL), and the crude compound was purified by silica gel column chromatography with petroleum ether/ethyl acetate (65:35). The solvent was removed in a rotary evaporator to afford **10** as a white solid in 36% yield (1.8 g); m.p. 59–61 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.56 (s, 6 H), 2.76 (br. s, 2 H), 5.83 (s, 1 H), 6.43 (d, J = 3.6 Hz, 1 H), 6.71 (d, J = 3.6 Hz, 1 H), 7.13 (m, 2 H), 7.64 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.71, 32.15, 71.42, 71.84, 93.47, 121.45, 124.62, 128.12, 137.41, 142.55, 145.64, 154.46 ppm. IR (KBr, film): $\tilde{\nu}$ = 3445 (OH), 3272 (OH) cm^{-1}. ES-MS: $C_{14}H_{15}IO_2S$, calcd. av. mass 374.2; obsd. m/z: 358.0 $[M + 1 - 17]^+$ (90%). $C_{14}H_{15}IO_2S$ (374.2): calcd. C 44.93, H 4.04, S 8.57; found C 44.59, H 4.25, S 8.19.

Diol 11: Treatment of the lithiated derivative of **15** (1.5 g, 10.547 mmol) with an ice-cold solution of *p*-bromobenzaldehyde (2.3 g, 12.656 mmol) in THF (30 mL) followed by silica gel column chromatographic purification with petroleum ether/ethyl acetate (65:35) yielded diol **11** as a brown oil in 60% yield (2.1 g). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.61 (s, 6 H), 2.09 (s, 2 H) 5.92 (s, 1 H), 6.69 (m, 1 H), 6.75 (m, 1 H), 7.31 (m, 2 H), 7.48 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.19, 21.54, 31.94, 71.38, 71.71, 111.48, 121.54, 123.19, 125.32, 128.01, 131.56, 137.09, 141.94, 145.86, 154.57 ppm. IR (neat): $\tilde{\nu}$ = 3409 (OH), 3277 (OH) cm^{-1}. ES-MS: $C_{14}H_{15}BrO_2S$, calcd. av. mass 327.2; obsd. m/z: 311 $[M + 1 - 17]^+$ (90%). $C_{14}H_{15}BrO_2S$ (327.2): calcd. C 51.38, H 4.62, S 9.80; found C 50.96, H 4.28, S 9.74.

Diol 12: An ice-cold solution of *p*-(3-hydroxy-3-methylbut-1-ynyl)-benzaldehyde (2.3 g, 12.180 mmol) in THF (30 mL) was treated with the lithiated derivative of **15** (1.4 g, 10.125 mmol) followed by silica gel column chromatographic purification with petroleum ether/ethyl acetate (60:40) to afford pure diol **12** as a brown oil in 24% yield (0.8 g). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.57 (m, 12 H, CH_3), 3.06 (br. s, 2 H), 5.88 (s, 1 H), 6.61 (d, J = 3.3 Hz, 1 H), 6.70 (d, J = 3.6 Hz, 1 H), 7.35 (m, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.16, 21.04, 21.51, 30.92, 31.42, 31.94, 60.53, 65.55, 71.28, 71.86, 81.88, 94.08, 111.28, 121.47, 123.17, 124.59, 125.23, 126.21, 126.53, 131.72, 137.11, 143.12, 145.84, 146.03, 146.55, 154.47 ppm. IR (neat): $\tilde{\nu}$ = 3386 (OH), 3277 (OH) cm^{-1}. ES-MS: $C_{19}H_{22}SO_3$, calcd. av. mass 330.5; obsd. m/z: 313.2 $[M - 17]^+$ (90%) 330.2 $[M]^+$ (10%). $C_{19}H_{22}O_3S$ (330.5): calcd. C 69.06, H 6.71, S 9.70; found C 69.42, H 6.37, S 9.42.

Diol 13: The lithiated derivative of **15** (0.8 g, 5.626 mmol) was treated with an ice-cold solution of *p*-cyanobenzaldehyde (0.7 g, 6.751 mmol) in THF (25 mL), and purification of the crude compound by silica gel column chromatography with petroleum ether/ethyl acetate (65:35) afforded the desired diol **13** as a yellow solid in 52% yield (0.9 g); m.p. 78–80 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.59 (s, 6 H, CH_3), 2.08 (s, 1 H), 3.03 (s, 1 H), 6.01 (s, 1 H), 6.73 (d, J = 3.6 Hz, 1 H), 6.76 (d, J = 3.6 Hz, 1 H), 7.55 (d, J = 8.4 Hz, 2 H), 7.63 (d, J = 8.4 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.47, 31.94, 71.39, 71.45, 111.28, 111.72, 118.77, 121.58, 123.21, 124.99, 125.65, 126.87, 132.29, 136.95, 144.99, 145.435, 146.48, 148.14, 155.06 ppm. IR (KBr, film): $\tilde{\nu}$ = 3414 (OH), 3272 (OH) cm^{-1}. ES-MS: $C_{15}H_{15}NO_2S$, calcd. av. mass 273.4; obsd. m/z: 273.2 $[M]^+$ (10%), 256.1 $[M - 17]^+$ (90%). $C_{15}H_{15}NO_2S$ (273.4): calcd. C 65.91, H 5.53, N 5.12, S 11.73; found C 65.46, H 5.23, N 4.96, S 11.39.

Diol 14: The lithiated derivative of **15** was treated with an ice-cold solution of *m*-nitrobenzaldehyde (2.6 g, 16.876 mmol) in THF (40 mL) and the resulting crude compound was purified by silica gel column chromatography with petroleum ether/ethyl acetate (65:35) to give **14** as a brown oil in 62% yield (2.3 g). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.59 (s, 6 H, CH_3), 2.35 (br. s, 1 H), 3.27 (br. s, 1 H), 6.05 (s, 1 H), 6.75 (m, 2 H), 7.52 (m, 1 H), 7.78 (d, J = 7.6 Hz, 1 H), 8.14 (d, J = 7.2 Hz, 1 H), 8.30 (s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.40, 31.81, 60.56, 71.01, 71.31, 111.59, 121.11, 121.57, 124.93, 129.35, 132.42, 145.05, 145.32, 148.10, 154.91 ppm. IR (neat): $\tilde{\nu}$ = 3399 (OH), 3272 (OH) cm^{-1}. ES-MS: $C_{14}H_{15}NO_4S$, calcd. av. mass 293.3; obsd. m/z: 276.1 $[M - 17]^+$ (90%). $C_{14}H_{15}NO_4S$ (293.3): calcd. C 57.32, H 5.15, N 4.77, S 10.93; found C 56.91, H 4.98, N 4.49, S 10.86.

10-(*p*-Iodophenyl)-5,5-dimethyl-15,20-di(*p*-tolyl)-21,23-dithiaphlorin (16): Compound **10** (0.7 g, 1.871 mmol) and 16-thiatripyrrane **5** (0.8 g, 1.871 mmol) were condensed in CH_2Cl_2 under mild acidic catalysis conditions and the resulting crude compound was purified

by silica gel column chromatography with petroleum ether/ethyl acetate (95:5) to afford the pure 21,23-dithiaphlorin **16** as a green solid in 15% yield (0.2 g); m.p. >250 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.84 (s, 6 H), 2.44 (s, 6 H), 6.29 (br. s, 1 H), 6.52 (br. s, 1 H), 6.92 (d, J = 4.5 Hz, 1 H), 7.09 (br. s, 1 H), 7.18 (br. s, 1 H), 7.29 (m, 8 H), 7.47 (m, 5 H), 7.82 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.44, 21.48, 29.71, 29.84, 39.25, 95.01, 107.36, 121.56, 128.88, 128.99, 130.27, 131.47, 132.08, 134.18, 134.86, 135.10, 136.33, 136.33, 136.74, 137.13, 138.45, 139.59, 139.93, 140.47, 147.13, 147.89, 152.87 ppm. UV/Vis: λ_{max} ($\varepsilon \times 10^3$ L mol^{-1} cm^{-1}) = 329 (31.17), 417 (37.23), 696 nm (24.07). ES-MS: $C_{42}H_{33}IN_2S_2$, calcd. av. mass: 756.8; obsd. *m*/*z*: 757.2 [M]$^+$. $C_{42}H_{33}IN_2S_2$ (756.8): calcd. C 66.66, H 4.40, N 3.70, S 8.47; found C 65.98, H 4.71, N 3.68, S 8.56.

10-(*p*-Bromophenyl)-5,5-dimethyl-15,20-di(*p*-tolyl)-21,23-dithiaphlorin (17): Samples of **11** (0.4 g, 1.222 mmol) and 16-thiatripyrrane **5** (0.5 g, 1.222 mmol) were condensed in CH_2Cl_2 (40 mL) under porphyrin forming conditions. The crude compound was purified by silica gel column chromatography with petroleum ether/ethyl acetate (94:6) and afforded **17** as green solid in 16% yield (0.14 g); m.p. >250 °C. ^{1}H NMR (300 MHz, $CDCl_3$, –50 °C, TMS): δ = 1.87 (s, 6 H), 2.50 (s, 6 H), 6.34 (br. s, 1 H), 6.62 (br. s, 1 H), 6.79 (br. s, 1 H), 7.07 (d, J = 4.5 Hz, 1 H), 7.19 (d, J = 4.5 Hz, 2 H), 7.29 (m, 5 H), 7.49 (m, 3 H), 7.59 (m, 3 H), 7.67 (m, 3 H), 11.89 (s, 1 H), 13.17 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.44, 21.71, 29.84, 39.25, 107.30, 121.56, 123.20, 128.89, 129.00, 130.26, 131.16, 131.47, 132.08, 133.16, 133.97, 134.88, 135.10,136.33, 136.74, 137.16, 137.19, 138.46, 138.98, 139.99, 140.48 ppm. UV/Vis: λ_{max} ($\varepsilon \times 10^3$ L mol^{-1} cm^{-1}) = 327 (30.50), 416 (39.84), 694 nm (23.95). ES-MS: $C_{42}H_{33}BrN_2S_2$, calcd. av. mass: 709.8; obsd. *m*/*z*: 709.2 [M]$^+$. $C_{42}H_{33}BrN_2S_2$ (709.8): calcd. C 71.07, H 4.69, N 3.95, S 9.04; found C 71.41, H 4.91, N 3.88, S 9.16.

10-[*p*-(3-Hydroxy-2-methylbut-1-ynyl)phenyl]-5,5-dimethyl-15,20-di(*p*-tolyl)-21,23-dithiaphlorin (18): Samples of **12** (0.3 g, 0.908 mmol) and 16-thiatripyrrane **5** (0.4 g, 0.908 mmol) were condensed in CH_2Cl_2 under similar porphyrin forming conditions. The resulting crude product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (70:30) and afforded pure **18** as a green solid in 21% yield (0.14 g); m.p. >250 °C. ^{1}H NMR (300 MHz, $CDCl_3$, –50 °C, TMS): δ = 1.66 (s, 6 H), 1.87 (s, 6 H), 2.49 (br. s, 6 H), 6.34 (br. s, 1 H), 6.62 (br. s, 1 H), 6.85 (br. s, 1 H), 7.07 (d, J = 4.5 Hz, 1 H), 7.18 (br. s, 1 H), 7.32 (m, 5 H), 7.46 (m, 3 H), 7.59 (m, 7 H), 11.82 (br. s, 1 H), 13.07 (br. s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.43, 21.47, 29.71, 29.83, 31.47, 31.66, 39.25, 65.84, 76.86, 77.18, 77.49, 82.09, 95.47, 107.33, 121.55, 121.71, 123.05, 123.13, 128.88, 128.99, 129.61, 130.16, 131.16, 131.47, 132.07, 132.12, 132.47, 134.94, 135.07, 135.40, 136.37, 136.76, 137.15, 137.19, 138.43, 140.05, 140.46 ppm. UV/Vis: λ_{max} ($\varepsilon \times 10^3$ L mol^{-1} cm^{-1}) = 342 (29.23), 412 (31.81), 697 nm (21.29). ES-MS: $C_{47}H_{40}N_2S_2$, calcd. av. mass: 713.1; obsd. *m*/*z*: 713.4 [M]$^+$. $C_{47}H_{40}N_2S_2$ (713.1): calcd. C 79.18, H 5.65, N 3.93, S 9.00; found C 79.38, H 5.71, N 4.38, S 9.06.

10-(*p*-Cyanophenyl)-5,5-dimethyl-15,20-di(*p*-tolyl)-21,23-dithiaphlorin (19): Condensation of **13** (0.33 g, 1.222 mmol) and 16-thiatripyrrane **5** (0.5 g, 1.222 mmol) in CH_2Cl_2 under acid catalysis conditions and purification of the resulting crude product by silica gel column chromatography afforded **19** as a green solid in 12% yield (0.09 g); m.p. >250 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 1.85 (s, 6 H), 2.46 (s, 6 H), 6.34 (d, J = 3.6 Hz, 1 H), 6.72 (d, J = 3.6 Hz, 1 H), 6.96 (d, J = 4.2 Hz, 1 H), 7.11 (m, 2 H), 7.29 (m, 6 H), 7.43 (d, J = 7.5 Hz, 2 H), 7.51 (m, 3 H), 7.76 (m, 4 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.38, 29.59, 29.75, 39.243, 112.01, 118.82, 121.58, 128.83, 128.95, 130.92, 131.39, 131.61, 132.06, 132.88, 135.41, 136.44, 136.91, 137.21, 138.60, 140.30, 144.67 ppm. UV/Vis: λ_{max} ($\varepsilon \times 10^3$ L mol^{-1} cm^{-1}) = 314 (26.79), 415 (34.36), 708 nm (23.69). ES-MS: $C_{43}H_{33}N_3S_2$, calcd. av. mass: 655.9; obsd. *m*/*z*: 655.8 [M]$^+$. $C_{43}H_{33}N_3S_2$ (655.9): calcd. C 78.74, H 5.07, N 6.41, S 9.78; found C 78.82, H 5.27, N 6.38, S 9.84.

5,5-Dimethyl-10-(*m*-nitrophenyl)-15,20-di(*p*-tolyl)-21,23-dithiaphlorin (20): Samples of thiophenedimethanol **14** (0.4 g, 1.531 mmol) and 16-thiatripyrrane **5** (0.6 g, 1.531 mmol) in CH_2Cl_2 were condensed in the presence of catalytic amounts of trifluoroacetic acid (0.2 g, 0.1 mL, 1.531 mmol). The crude mixture was purified by silica gel column chromatography with petroleum ether/ethyl acetate (90:10) and afforded pure **20** as a green solid in 5% yield (0.05 g); m.p. >150 °C. ^{1}H NMR (300 MHz, $CDCl_3$, –50 °C, TMS): δ = 1.89 (s, 6 H), 2.51 (s, 6 H), 6.38 (s, 1 H), 6.68 (br. s, 2 H), 7.12 (d, J = 4.2 Hz, 1 H), 7.29 (m, 6 H), 7.51 (m, 3 H), 7.62 (d, J = 7.5 Hz, 2 H), 7.73 (m, 2 H), 7.99 (d, J = 7.2 Hz, 1 H), 8.42 (d, J = 7.5 Hz, 1 H), 7.64 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.16, 21.37, 21.42, 22.75, 29.61, 29.76, 31.99, 39.28, 121.69, 123.19, 126.71, 128.85, 128.97, 129.35, 129.64, 131.05, 131.42, 132.07, 134.17, 135.42, 135.78, 136.49, 136.98, 137.58, 138.12, 137.20, 138.12, 138.58, 139.53, 140.37, 141.68, 146.78, 148.07, 148.79 ppm. UV/Vis: λ_{max} ($\varepsilon \times 10^3$ L mol^{-1} cm^{-1}) = 314 (27.77), 407 (36.71), 705 nm (24.19). ES-MS: $C_{42}H_{33}N_3O_2S_2$, calcd. av. mass: 675.9; obsd. *m*/*z*: 676.3 [M]$^+$. $C_{42}H_{33}N_3O_2S_2$ (675.9): calcd. C 74.64, H 4.92, N 6.22, S 9.49; found C 784.71, H 4.83, N 6.34, S 9.72.

10-(*p*-Iodophenyl)-5,5-dimethyl-15,20-di(*p*-tolyl)-21-thiaphlorin (21): Condensation of **10** (0.5 g, 1.344 mmol), *p*-tolylaldehyde (0.3 g, 0.3 mL, 2.688 mmol) and pyrrole (0.3 g, 0.3 mL, 4.032 mmol) in CH_2Cl_2 (50 mL) under mild acid catalysis conditions gave a crude mixture of compounds. The crude mixture was purified by silica gel column chromatography with petroleum ether/ethyl acetate (99:1) and afforded pure **21** as a green solid (0.09 g, 9%); m.p. >250 °C. ^{1}H NMR (300 MHz, $CDCl_3$, –50 °C, TMS): δ = 1.81 (s, 6 H), 2.49 (s, 6 H), 6.49 (m, 1 H), 6.62 (m, 1 H), 6.87 (m, 1 H), 6.97 (br. s, 3 H), 7.25 (m, 6 H), 7.54 (m, 6 H), 7.79 (m, 2 H), 9.85 (s, 1 H), 11.77 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.34, 21.38, 28.63, 29.76, 38.56, 93.02, 106.95, 114.69, 121.20, 126.42, 127.65, 127.86, 128.48, 129.06, 129.17, 132.50, 132.54, 133.25, 133.50, 134.23, 134.84, 135.49, 135.71, 136.59, 137.55, 137.69, 137.81, 138.25, 140.06, 142.03, 142.95, 144.99, 150.65, 165.18 ppm. UV/Vis: λ_{max} ($\varepsilon \times 10^3$ L mol^{-1} cm^{-1}) = 337 (41.03), 416 (78.70), 671 nm (50.77). ES-MS: $C_{42}H_{34}IN_3S$, calcd. av. mass: 739.7; obsd. *m*/*z*: 740.2 [M]$^+$. $C_{42}H_{34}IN_3S$ (739.7): calcd. C 68.20, H 4.63, N 5.68, S 4.33; found C 68.41, H 4.71, N 5.38, S 4.83.

10-(*p*-Bromophenyl)-5,5-dimethyl-15,20-di(*p*-tolyl)-21-thiaphlorin (22): Samples of **11** (0.8 g, 2.445 mmol), *p*-tolylaldehyde (0.6 g, 0.6 mL, 4.889 mmol) and pyrrole (0.5 g, 0.5 mL, 7.335 mmol) were condensed in CH_2Cl_2 (80 mL) under acid catalysis conditions. After standard workup, the crude mixture was subjected to silica gel column chromatography with ether/ethyl acetate (98:2) and afforded pure **22** as a green solid in 6% yield (0.09 g); m.p. >250 °C. ^{1}H NMR (300 MHz, $CDCl_3$, –50 °C, TMS): δ = 1.82 (s, 6 H), 2.46 (s, 6 H), 6.48 (br. s, 1 H), 6.62 (br. s, 1 H), 6.83 (m, 1 H), 6.98 (m, 3 H), 7.30 (m, 6 H), 7.56 (m, 8 H), 9.86 (s, 1 H), 11.81 (s, 1 H), 12.04 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.18, 21.38, 28.63, 29.77, 38.57, 106.96, 109.77, 114.64, 121.21, 121.52, 126.43, 127.68, 127.87, 128.48, 129.14, 131.59, 132.51, 133.19, 133.27, 134.24, 134.87, 135.40, 135.73, 136.59, 137.71, 137.82, 138.26, 139.48, 142.14, 142.94, 145.06, 150.64, 165.19 ppm. UV/Vis: λ_{max} ($\varepsilon \times 10^3$ L mol^{-1} cm^{-1}) = 334 (30.03), 416 (56.12), 669 nm (33.71).

ES-MS: $C_{42}H_{34}BrN_3S$, calcd. av. mass: 692.7; obsd. *m*/*z*: 692.4 $[M]^+$. $C_{42}H_{34}BrN_3S$ (692.7): calcd. C 72.82, H 4.95, N 6.07, S 4.63; found C 72.79, H 4.87, N 6.18, S 4.81.

10-(*p*-Cyanophenyl)-5,5-dimethyl-15,20-di(*p*-tolyl)-21-thiaphlorin (23): Samples of **13** (0.4 g, 1.536 mmol), *p*-tolylaldehyde (0.4 g, 0.4 mL, 3.071 mmol) and pyrrole (0.3 g, 0.3 mL, 4.608 mmol) were condensed in CH_2Cl_2 (40 mL) under acid catalysis conditions and the resulting crude mixture was purified by silica gel column chromatography with petroleum ether/ethyl acetate (98:2) to afford **23** as a green solid (0.05 g, 5%); m.p. >250 °C. ^{1}H NMR (300 MHz, $CDCl_3$, –50 °C, TMS): δ = 1.82 (s, 6 H), 2.47 (s, 6 H), 6.55 (d, *J* = 3.9 Hz, 1 H), 6.85 (d, *J* = 4.8 Hz, 1 H), 6.89 (d, *J* = 3.9 Hz, 2 H), 7.09 (d, *J* = 3.9 Hz, 1 H), 7.15 (d, *J* = 5.7 Hz, 1 H), 7.26 (m, 6 H), 7.46 (m, 4 H), 7.71 (d, *J* = 8.1 Hz, 2 H), 7.79 (d, *J* = 5.7 Hz, 2 H), 9.96 (s, 1 H), 11.32 (s, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.39, 26.98, 28.59, 29.76, 38.56, 107.18, 109.83, 111.28, 112.93, 119.27, 121.27, 127.02, 127.90, 128.52, 129.12, 129.90, 129.99, 131.89, 132.11, 132.38, 132.50, 134.17, 134.45, 134.66, 135.93, 136.67, 136.82, 137.38, 137.98, 138.03, 141.02, 144.12, 145.07, 150.70, 165.23 ppm. UV/Vis: λ_{max} ($\varepsilon \times 10^3$ L mol^{-1} cm^{-1}) = 340 (24.06), 424 (57.75), 671 nm (41.37). ES-MS: $C_{43}H_{34}N_4S$, calcd. av. mass: 638.8; obsd. *m*/*z*: 639.2 $[M]^+$. $C_{43}H_{34}N_4S$ (638.8): calcd. C 80.85, H 5.36, N 8.77, S 5.02; found C 80.94, H 5.72, N 8.38, S 5.16.

5,5-Dimethyl-10-(*m*-nitrophenyl)-15,20-di(*p*-tolyl)-21-thiaphlorin (24): Condensation of **14** (1 g, 3.827 mmol), *p*-tolylaldehyde (0.9 g, 0.9 mL, 7.654 mmol) and pyrrole (0.8 g, 0.8 mL, 11.481 mmol) in CH_2Cl_2 (100 mL) under acid catalysis conditions and purification of the resulting crude mixture by silica gel column chromatography with petroleum ether/ethyl acetate (97:3) afforded **24** as a green solid (0.07 g, 3%); m.p. >250 °C. ^{1}H NMR (500 MHz, $CDCl_3$, –50 °C, TMS): δ = 1.80 (s, 6 H), 2.47 (m, 6 H), 6.54 (s, 1 H), 6.60 (s, 1 H), 6.94 (m, 2 H), 6.99 (s, 1 H), 7.18 (d, *J* = 3.9 Hz, 1 H), 7.25 (m, 2 H), 7.31 (d, *J* = 7.4 Hz, 1 H), 7.36 (m, 2 H), 7.48 (br. s, 3 H), 7.57 (br. s, 1 H), 7.65 (m, 1 H), 7.73 (br. s, 1 H), 8.04 (d, *J* = 7.4 Hz, 1 H), 8.22 (d, *J* = 8 Hz, 1 H), 8.61 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.22, 21.38, 27.78, 28.62, 38.57, 71.85, 107.18, 110.87, 112.23, 121.58, 125.97, 126.82, 127.89, 128.51, 128.90, 129.27, 130.09, 130.97, 132.53, 134.21, 134.56, 135.91, 136.78, 137.32, 138.03, 141.39, 142.32, 144.39, 148.69, 150.65, 165.26, 167.73 ppm. UV/Vis: λ_{max} ($\varepsilon \times 10^3$ L mol^{-1} cm^{-1}) = 342 (24.58), 419 (58.54), 664 nm (31.59). ES-MS: $C_{42}H_{34}N_4SO_2$, calcd. av. mass: 658.8; obsd. *m*/*z*: 659.4 $[M]^+$. $C_{42}H_{34}N_4O_2S$ (658.8): calcd. C 76.57, H 5.20, N 8.50, S 4.87; found C 76.49, H 5.61, N 8.38, S 4.91.

21,23-Dithiaphlorin-ZnN$_4$ Porphyrin Dyad 25: A solution of 21,23-dithiaphlorin **16** (30.0 mg, 39.6 μmol) and 5,10,15-tri(mesityl)-20-(ethynylphenyl)porphyrinzinc(II) (39.0 mg, 47.5 μmol) were dissolved in dry toluene/triethylamine (5:1, 30 mL) in a 50 mL round-bottomed flask. The flask was fitted with a reflux condenser, and a gas inlet tube was inserted through the top of the condenser into the solution for nitrogen purging. The reaction vessel was placed in an oil bath preheated to 50 °C. Nitrogen purging was carried out for 15 min. $AsPh_3$ (14.3 mg, 46.8 μmol) and $Pd_2(dba)_3$ (5.4 mg, 5.9 μmol) were added to this solution and the reaction mixture was stirred under nitrogen at 50 °C for 24 h. TLC analysis of the reaction mixture showed the disappearance of spots corresponding to starting materials and the appearance of a new spot corresponding to dimer. The solvents were removed in vacuo, the crude compound was passed through a small silica column with petroleum ether/dichloromethane (80:20) to remove the excess of $AsPh_3$, and the crude mixture of small amounts of monomeric porphyrins along with desired dimer was collected by elution with petroleum ether/dichloromethane (60:40). The solution was concentrated in vacuo, the resulting crude mixture dimer with small amounts of unchanged monomers was dissolved in dichloromethane (3 mL), and a dry slurry was prepared by adding neutral alumina powder. The slurry was loaded onto a neutral alumina column packed with petroleum ether. The small amounts of porphyrin and phlorin monomers were removed first with petroleum ether/ethyl acetate (98:2) and the desired dyad **25** was then collected with petroleum ether/dichloromethane (96:4). Concentration of the solution gave **25** as a violet solid in 35% yield (20 mg). ^{1}H NMR (300 MHz, $CDCl_3$, –50 °C, TMS): δ = 1.87 (m, 24 H), 2.47 (s, 6 H), 2.65 (s, 9 H), 6.37 (br. s, 1 H), 6.65 (br. s, 1 H), 6.73 (br. s, 1 H), 6.89 (m, 2 H), 7.17 (m, 3 H), 7.28–7.65 (m, 14 H), 7.83 (m, 4 H), 7.99 (d, *J* = 7.5 Hz, 2 H), 8.25 (d, *J* = 7.2 Hz, 2 H), 8.71 (s, 4 H), 8.77 (m, 2 H), 8.88 (br. s, 2 H), 11.47 (br. s, 1 H), 13.05 (br. s, 1 H) ppm. UV/Vis: λ_{max} ($\varepsilon \times 10^4$ L mol^{-1} cm^{-1}) = 422 (59.82), 513 (7.22), 551 (2.53), 592 (0.98), 698 nm (1.81). ES-MS: $C_{97}H_{78}N_6S_2Zn$, calcd. av. mass: 1457.2; obsd. *m*/*z*: 1457.5 $[M]^+$.

21,23-Dithiaphlorin-N$_4$ Porphyrin Dyad 26: Dyad **25** (18.0 mg, 12.8 μmol) was dissolved in dichloromethane (30 mL) in a 100 mL round-bottomed flask. Trifluoroacetic acid (1 mL) was added to this solution, and the reaction mixture was allowed to stir at room temperature for 12 h. The demetallation was confirmed by TLC analysis and absorption spectroscopy. The solution was diluted with CH_2Cl_2, washed thoroughly with sodium hydrogen carbonate and dried with sodium sulfate. The solvent was removed in a rotary evaporator to afford **26** as a violet solid in 69% yield (12 mg). ^{1}H NMR (300 MHz, $CDCl_3$, –50 °C, TMS): δ = –2.74 (s, 2 H), 1.87 (m, 24 H), 2.51 (s, 6 H), 2.66 (s, 9 H), 6.38 (br. s, 1 H), 6.65 (br. s, 1 H), 6.84 (br. s, 1 H), 7.14 (d, *J* = 3.9 Hz, 1 H), 7.24–7.46 or 7.35 (m, 14 H), 7.53 (m, 3 H), 7.66 (m, 5 H), 7.83 (m, 4 H), 8.01 (d, *J* = 7.8 Hz, 2 H), 8.46 (d, *J* = 7.8 Hz, 2 H), 8.78 (m, 8 H), 9.84 (br. s, 1 H), 11.64 (br. s, 1 H) ppm. UV/Vis: λ_{max} ($\varepsilon \times 10^4$ L mol^{-1} cm^{-1}) = 419 (42.18), 516 (2.15), 550 (1.16), 594 (1.08), 649 (1.53), 698 nm (1.61). ES-MS: $C_{97}H_{80}N_6S_2$, calcd. av. mass: 1393.9; obsd. *m*/*z*: 1394.8 $[M]^+$.

4-[5,10,15-Tri(*p*-octyloxyphenyl)-21-thia-20-porphinyl]-4′-[5,5-dimethyl-10,15-di(*p*-tolyl)-21,23-dithia-20-phlorinyl]diphenylethyne (27): Samples of 21,23-dithiaphlorin **16** (30.0 mg, 39.6 μmol) and 5,10,15-tris(*p*-octyloxyphenyl)-20-(*p*-ethynylphenyl)-21-thiaporphyrin (49.4 mg, 47.5 μmol) were dissolved in dry toluene/triethylamine (5:1, 40 mL) in a 100 mL round-bottomed flask, and nitrogen purging was carried out for 15 min. The coupling was initiated by adding $AsPh_3$ (14.3 mg, 46.8 μmol) and $Pd_2(dba)_3$ (5.4 mg, 5.9 μmol) and the reaction mixture was stirred at 50 °C for 24 h. After standard workup, the crude reaction mixture was passed through two neutral alumina columns and the desired dyad **27** was collected with petroleum ether/ethyl acetate (90:10). Concentration of the solution in a rotary evaporator under reduced pressure gave N_2S_2 phlorin-N_3S porphyrin dyad **27** as a violet solid in 48% yield (32 mg). ^{1}H NMR (300 MHz, $CDCl_3$, –50 °C, TMS): δ = –2.76 (s, 1 H), 0.97 (br. s, 9 H), 1.23–1.57 (m, 30 H), 1.93 (br. s, 12 H), 2.48 (m, 6 H), 4.13 (br. s, 6 H), 6.14 (br. s, 1 H), 6.35 (br. s, 1 H), 6.63 (br. s, 1), 6.84 (br. s, 1 H), 6.99 (br. s, 1 H), 7.29 (m, 13 H), 7.69 (m, 10 H, Ar), 8.12 (m, 6 H), 8.31 (br. s, 2 H), 8.68 (m, 4 H), 8.98 (br. s, 2 H), 9.86 (s, 2 H), 11.83 (s, 1 H), 13.09 (s, 1 H) ppm. UV/Vis: λ_{max} ($\varepsilon \times 10^4$ L mol^{-1} cm^{-1}) = 435 (35.14), 520 (2.42), 557 (1.77), 628 (1.59), 864 nm (2.75). ES-MS: $C_{112}H_{109}N_5O_3S_3$, calcd. av. mass: 1669.3; obsd. *m*/*z*: 1669.8 $[M]^+$.

[5,10,15-Tri(*p*-tolyl)-21-thia-20-porphinyl]-4′-[5,5-dimethyl-10,15-di(*p*-tolyl)-21,23-dithia-20-phlorinyl]phenylethyne (28): $AsPh_3$

(14.6 mg, 47.5 μmol) and $Pd_2(dba)_3$ (5.4 mg, 5.9 μmol) were added under nitrogen, to initiate coupling, to a solution of N_2S_2 phlorin **16** (30.0 mg, 39.6 μmol) and 5,10,15-tritolyl-20-ethynyl-21-thiaporphyrin (27.1 mg, 43.6 μmol) in dry toluene/triethylamine (5:1, 30 mL) in a 50 mL round-bottomed flask. The reaction mixture was stirred at 50 °C for 24 h. Column chromatographic purification on neutral alumina with petroleum ether/ethyl acetate (94:6) gave the pure dyad **28** as a green solid in 20% yield (10 mg). ^{1}H NMR (300 MHz, $CDCl_3$, –50 °C, TMS): δ = –2.32 (s, 1 H), 1.81 (m, 6 H), 2.53 (m, 9 H), 2.75 (s, 6 H), 6.19 (br. s, 1 H), 6.45 (br. s, 1 H), 6.70 (br. s, 2 H), 6.94–7.29 (m, 8 H), 7.59–7.70 (m, 14 H), 8.14 (m, 8 H), 8.65 (m, 3 H), 8.91 (br. s, 1 H), 9.41 (br. s, 1 H), 9.93 (br. s, 1 H), 10.40 (br. s, 1 H), 12.01 (br. s, 1 H), 13.14 (br. s, 1 H) ppm. UV/Vis: λ_{max} ($\varepsilon \times 10^3$ L mol^{-1} cm^{-1}) = 445 (86.54), 517 (2.23), 553 (1.98), 698 nm (7.47). ES-MS: $C_{85}H_{63}N_5S_3$, calcd. av. mass: 1250.6; obsd. *m*/*z*: 1250.6 [M]$^+$.

Dyad 29: Coupling of 21-thiaphlorin **21** (40.0 mg, 54.1 μmol) and 5,10,15-tri(mesityl)-20-(4-ethynylphenyl)porphyrinzinc(II) (54.0 mg, 64.9 μmol) in dry toluene/triethylamine (5:1, 40 mL) was carried out under nitrogen in the presence of $AsPh_3$ (19.9 mg, 64.9 μmol) and $Pd_2(dba)_3$ (7.4 mg, 8.1 μmol) at 50 °C for 24 h. After workup, the crude compound was subjected twice to alumina column chromatographic purification, and the pure dyad **29** was collected with petroleum ether/ethyl acetate (98:2). Removal of solvent by rotary evaporation under reduced pressure afforded dyad **29** as a violet solid in 33% yield (26 mg). ^{1}H NMR (500 MHz, $CDCl_3$, –50 °C, TMS): δ = 1.82 (m, 24 H), 2.48 (m, 6 H), 2.63 (s, 9 H), 6.59 (m, 3 H), 6.99 (s, 3 H), 7.27 (m, 10 H), 7.51 (m, 6 H), 7.79 (m, 4 H), 7.96 (s, 2 H), 8.24 (s, 2 H), 8.70 (s, 4 H), 8.77 (s, 2 H), 8.89 (s, 2 H), 9.83 (s, 1 H), 11.73 (s, 1 H), 11.94 (s, 1 H) ppm. UV/Vis: λ_{max} ($\varepsilon \times 10^4$ L mol^{-1} cm^{-1}) = 422 (78.24), 515 (1.49), 552 (4.17), 593 (sh), 681 nm (4.81). ES-MS: $C_{97}H_{79}N_7SZn$, calcd. av. mass: 1440.2; obsd. *m*/*z*: 1440.6 [M]$^+$.

4-[5,10,15-Trimesityl-20-porphinyl]-4′-[5,5-dimethyl-10,15-di(*p*-tolyl)-21-thia-20-phlorinyl]diphenylethyne (30): Trifluoroacetic acid (1 mL) was added to a solution of dyad **29** (30.0 mg, 20.8 μmol) dissolved in dichloromethane (30 mL) in a 50 mL round-bottomed flask, and the reaction mixture was allowed to stir at room temperature for 12 h. The solution was poured into water and washed thoroughly with sodium hydrogen carbonate. The solution was dried with anhydrous sodium sulfate and evaporated in a rotary evaporator to afford dyad **30** as a violet solid in 70% yield (20 mg). ^{1}H NMR (500 MHz, $CDCl_3$, –50 °C, TMS): δ = –2.73 (s, 2 H), 1.88 (m, 24 H), 2.53 (m, 6 H), 2.68 (s, 9 H), 6.67 (br. s, 2 H), 7.04 (br. s, 4 H), 7.32 (m, 10 H), 7.58 (br. s, 6 H), 7.85 (br. s, 4 H), 8.01 (br. s, 2 H), 8.28 (br. s, 2 H), 8.80 (m, 8 H), 9.93 (s, 1 H) ppm. UV/Vis: λ_{max} ($\varepsilon \times 10^4$ L mol^{-1} cm^{-1}) = 419 (52.99), 516 (2.58), 553 (1.59), 598 (2.09), 653 (3.56), 680 nm (4.15). ES-MS: $C_{97}H_{81}N_7S$, calcd. av. mass: 1376.7; obsd. *m*/*z*: 1376.7 [M]$^+$).

5,5-Dimethyl-10-{*p*-[2-(trimethylsilyl)ethynyl]phenyl}-15,20-di(*p*-tolyl)-21,23-dithiaphlorin (31): A solution of N_2S_2 phlorin **16** (90.0 mg, 118.9 μmol) was dissolved in dry toluene/triethylamine (5:1, 30 mL) in a 100 mL round-bottomed flask. The flask was fitted with a reflux condenser and a gas inlet tube was inserted through the top of the condenser into the solution for nitrogen purging. The reaction vessel was placed in an oil bath preheated to 50 °C. Nitrogen purging was carried out for 15 min, and (trimethylsilyl)acetylene (26.9 mg, 31.3 μL, 142.7 μmol) was added slowly by syringe. $AsPh_3$ (43.7 mg, 142.7 μmol) and $Pd_2(dba)_3$ (16.3 mg, 17.8 μmol) were added to initiate the coupling and the reaction mixture was stirred at 50 °C for 24 h. TLC analysis of the reaction mixture showed a new spot corresponding to the desired compound **31** and a very faint spot corresponding to starting phlorin **16**. The solvent was removed in vacuo, the crude compound was dissolved in dichloromethane (3 mL), and a dry slurry was prepared by adding neutral alumina powder followed by removal of traces of solvent under high vacuum. The slurry was loaded onto a neutral alumina column packed with petroleum ether. The small amount of unchanged phlorin **16** was removed first with petroleum ether/ethyl acetate (98:2) and the desired phlorin **31** was collected with petroleum ether/ethyl acetate (96:4). Concentration of the solution gave **31** as a green solid in 65% yield (0.6 g); m.p. >250 °C. ^{1}H NMR (300 MHz, $CDCl_3$, –50 °C, TMS): δ = 0.30 (m, 9 H, CH_3), 1.87 (s, 6 H), 2.49 (s, 6 H), 6.34 (s, 1 H), 6.61 (s, 1 H), 6.82 (s, 1 H), 7.07 (br. s, 1 H), 7.19 (s, 1 H), 7.34 (m, 3 H), 7.48 (m, 4 H), 7.61 (m, 8 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.47, 21.51, 29.75, 32.01, 39.28, 96.11, 104.99, 121.60, 123.51, 128.90, 129.02, 130.19, 131.51, 132.10, 132.47, 134.96, 135.09, 136.42, 136.79, 137.17, 137.23, 138.45, 140.08, 140.29, 146.07, 146.90, 147.81, 153.06 ppm. UV/Vis: λ_{max} ($\varepsilon \times 10^3$ L mol^{-1} cm^{-1}) = 345 (31.22), 436 (35.68), 550 (sh), 696 nm (21.35). ES-MS: $C_{47}H_{42}N_2S_2Si$, calcd. av. mass: 727.1; obsd. *m*/*z*: 727.3 [M]$^+$. $C_{47}H_{42}N_2S_2Si$ (727.1): calcd. C 77.64, H 5.82, N 3.85, S 8.82; found C 77.32, H 5.71, N 3.68, S 8.56.

10-(*p*-Ethynylphenyl)-5,5-dimethyl-15,20-di(*p*-tolyl)-21,23-dithiaphlorin (32): A sample of 21,23-dithiaphlorin **31** (90 mg, 0.124 mmol) in dry and distilled THF (30 mL) was placed in a 100 mL round-bottomed flask fitted with a reflux condenser, and a calcium chloride guard tube was placed on top of the condenser. Tetrabutylammonium fluoride (53.8 μL of a ca. 1 M solution in THF) was added, and the reaction mixture was allowed to stir at room temperature for 12 h. After this period, TLC analysis of the crude reaction mixture showed the formation of a new green spot along with the trace amount of starting compound **31**. The solvents were removed in vacuo and the crude compound was subjected to neutral alumina column with elution with petroleum ether. The small amount of unchanged phlorin **31** was removed first with petroleum ether/ethyl acetate (96:4) and the desired 21,23-dithiaphlorin **32** was then collected with petroleum ether/ethyl acetate (94:6). Concentration of the solution gave **32** as green solid in 64% yield (0.5 g); m.p. >250 °C. ^{1}H NMR (300 MHz, $CDCl_3$, –50 °C, TMS): δ = 1.87 (s, 6 H), 2.49 (s, 6 H), 3.27 (s, 1 H), 6.34 (s, 1 H), 6.61 (s, 1 H), 6.89 (br. s, 1 H), 7.06 (s, 1 H), 7.18 (s, 1 H), 7.31 (m, 3 H), 7.49–7.66 or 7.58 (m, 12 H) ppm. UV/Vis: λ_{max} ($\varepsilon \times 10^3$ L mol^{-1} cm^{-1}) = 334 (32.33), 418 (36.49), 697 nm (20.89). ES-MS: $C_{44}H_{34}N_2S_2$, calcd. av. mass: 654.9; obsd. *m*/*z*: 655.3 [M]$^+$. $C_{44}H_{34}N_2S_2$ (654.9): calcd. C 80.70, H 5.23, N 4.28, S 9.79; found C 80.43, H 4.98, N 4.62, S 9.56.

4,4′-Bis[5,5-dimethyl-10,15-di(*p*-tolyl)-21,23-dithia-20-phlorinyl]diphenylethyne (33): Coupling of 21.23-dithiaphlorin **16** (34.0 mg, 44.9 μmol) with 21,23-dithiaphlorin **32** (35.3 mg, 53.9 μmol) in dry toluene/triethylamine (5:1, 50 mL) in the presence of $AsPh_3$ (16.5 mg, 53.8 μmol) and $Pd_2(dba)_3$ (6.2 mg, 6.7 μmol) at 50 °C under nitrogen for 30 h, followed by standard workup, gave a crude mixture of the desired compound along with unreacted monomers. Column chromatographic purification of the crude mixture on neutral alumina with petroleum ether/ethyl acetate 92:8) afforded pure **33** as a green solid in 24% yield (14 mg). ^{1}H NMR (300 MHz, $CDCl_3$, –50 °C, TMS): δ = 1.88 (br. s, 12 H), 2.49 (m, 12 H), 6.35 (br. s, 2 H), 6.63 (br. s, 2 H), 6.81 (br. s, 2 H), 7.09 (br. s, 2 H), 7.20 (br. s, 2 H), 7.34 (m, 6 H), 7.44–7.64 (m, 16 H), 7.75 (br. s, 8 H), 11.89 (s, 1 H), 13.09 (s, 1 H) ppm. UV/Vis: λ_{max} ($\varepsilon \times 10^3$ L mol^{-1} cm^{-1}) = 394 (8.72), 435 (10.18), 517 (sh), 552 (1.42), 704 nm (5.61). ES-MS: $C_{86}H_{66}N_4S_4$, calcd. av. mass: 1283.7; obsd. *m*/*z*: 1284.9 [M]$^+$.

Supporting Information (see also the footnote on the first page of this article): The characterization data including ES-MS, ^{1}H NMR, ^{13}C NMR, UV/Vis anion-binding titration curves of selected compounds.

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