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Tetrahedron
Tetrahedron 63 (2007) 2455–2465

Synthesis and fluorescence properties of covalently linked homo- and hetero-porphyrin dyads containing *meso*-tolyl porphyrin and *meso*-furyl porphyrin sub-units

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Received 21 September 2006; revised 29 November 2006; accepted 4 January 2007
Available online 7 January 2007

Abstract—Three porphyrin building blocks with N_4, N_3S and N_2S_2 cores having three *meso*-furyl groups and one *meso*-iodophenyl group were synthesized and characterized. The porphyrin building blocks were used to synthesize six porphyrin dyads such as N_4–N_4, N_3S–N_3S, N_2S_2–N_2S_2, N_4–N_3S, N_4–N_2S_2 and N_3S–N_2S_2 containing *meso*-tolyl and *meso*-furyl porphyrin sub-units under mild Pd(0) mediated coupling conditions. Steady state fluorescence studies indicated an efficient energy transfer from the *meso*-tolyl porphyrin sub-unit to the *meso*-furyl porphyrin sub-unit in all six dyads. This study supported the argument that the *meso*-furyl porphyrins can be used as good energy acceptors when *meso*-aryl porphyrins act as energy donors in their metal free form.

1. Introduction

Porphyrin dyads containing an energy donor and acceptor have been the topic of interesting research because they are very useful to understand the process of photosynthesis. A variety of covalently and non-covalently linked porphyrin dyads with various constraints, such as changing the nature of the spacers, the distance and orientation of donor with respect to acceptor, have been synthesized and their excited state properties have been well documented in the literature.[1] Investigation of the energy transfer mechanism in these dyads would not only yield valuable information on the intrinsic properties of reaction centre proteins but would also be helpful in the construction of solar energy cells, molecular photonic wires and molecular optoelectronic gates.[2] A common feature among the various porphyrin dyads reported in the literature is that they invariably contain similar porphyrin cores (N_4). However, the energy transfer properties of such symmetrical dyads have been studied by creating an energy gradient between the two porphyrin sub-units on insertion of metals such as Zn(II), Mg(II) and Cd(II) in one porphyrin sub-unit and leaving the other porphyrin sub-unit in the free base form. On excitation, the energy from the metallated porphyrin, which is at higher energy is transferred to the free base porphyrin, which is at low energy. However, in these symmetrical porphyrin dyads it is sometimes difficult to achieve the selective excitation of the donor porphyrin unit upon irradiation of one porphyrin sub-unit to study energy transfer properties. Selective excitation of the porphyrin unit can be easily achieved if the porphyrin sub-units in the dyad are not identical (unsymmetrical). In these unsymmetrical porphyrin dyads, the two different types of macrocycles in the metal free form can be connected either covalently or non-covalently to study the energy transfer properties. We[3] and others[4] have synthesized a series of unsymmetrical porphyrin dyads containing two different types of porphyrin macrocycles, such as porphyrin–phthalocyanine, porphyrin–corrole and porphyrin–hetero-atom substituted porphyrin and studied their energy transfer properties. Recently, we synthesized[5] a series of porphyrins with different porphyrin cores such as N_4, N_3S, N_3O, N_2S_2, etc. having five-membered furyl groups in place of six-membered aryl groups, and the studies showed that the electronic properties are greatly altered on the introduction of furyl groups in place of aryl groups at *meso* positions. Our studies indicated that the *meso*-furyl porphyrins have favourable energetics for electronic communication with *meso*-aryl porphyrins. Thus assembling a *meso*-furyl porphyrin and a *meso*-aryl porphyrin in a single unit may be expected to lead to interesting excited state properties. In this paper, we synthesized mono-functionalized *meso*-furyl porphyrin building blocks with N_4, N_3S and N_2S_2 porphyrin cores (Chart 1) and used them for the synthesis of covalently linked diphenyl ethyne bridged three homo- and three hetero-porphyrin dyads (Chart 2). The preliminary fluorescence study indicated the possibility of energy transfer from the *meso*-aryl porphyrin to the *meso*-furyl porphyrin in metal free form.

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doi:10.1016/j.tet.2007.01.005

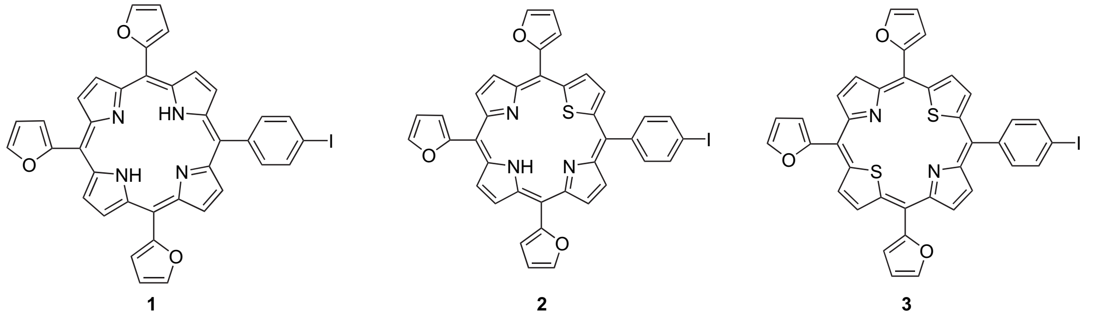


Chart 1. Structures of *meso*-furyl porphyrin building blocks.

2. Results and discussion

2.1. Synthesis of mono-functionalized *meso*-furyl porphyrin building blocks 1–3

The mono-functionalized *meso*-furyl porphyrin building block **1** was synthesized by mixed aldehyde condensation of 1 equiv of 4-iodobenzaldehyde, 3 equiv of furan-2-aldehyde with 4 equiv of pyrrole under standard porphyrin forming conditions.[6] This condensation resulted in the formation of a mixture of six porphyrins as expected, and the desired compound **1** was separated from the mixture by column chromatography. The compound was characterized by NMR, mass, elemental analysis and absorption spectroscopic

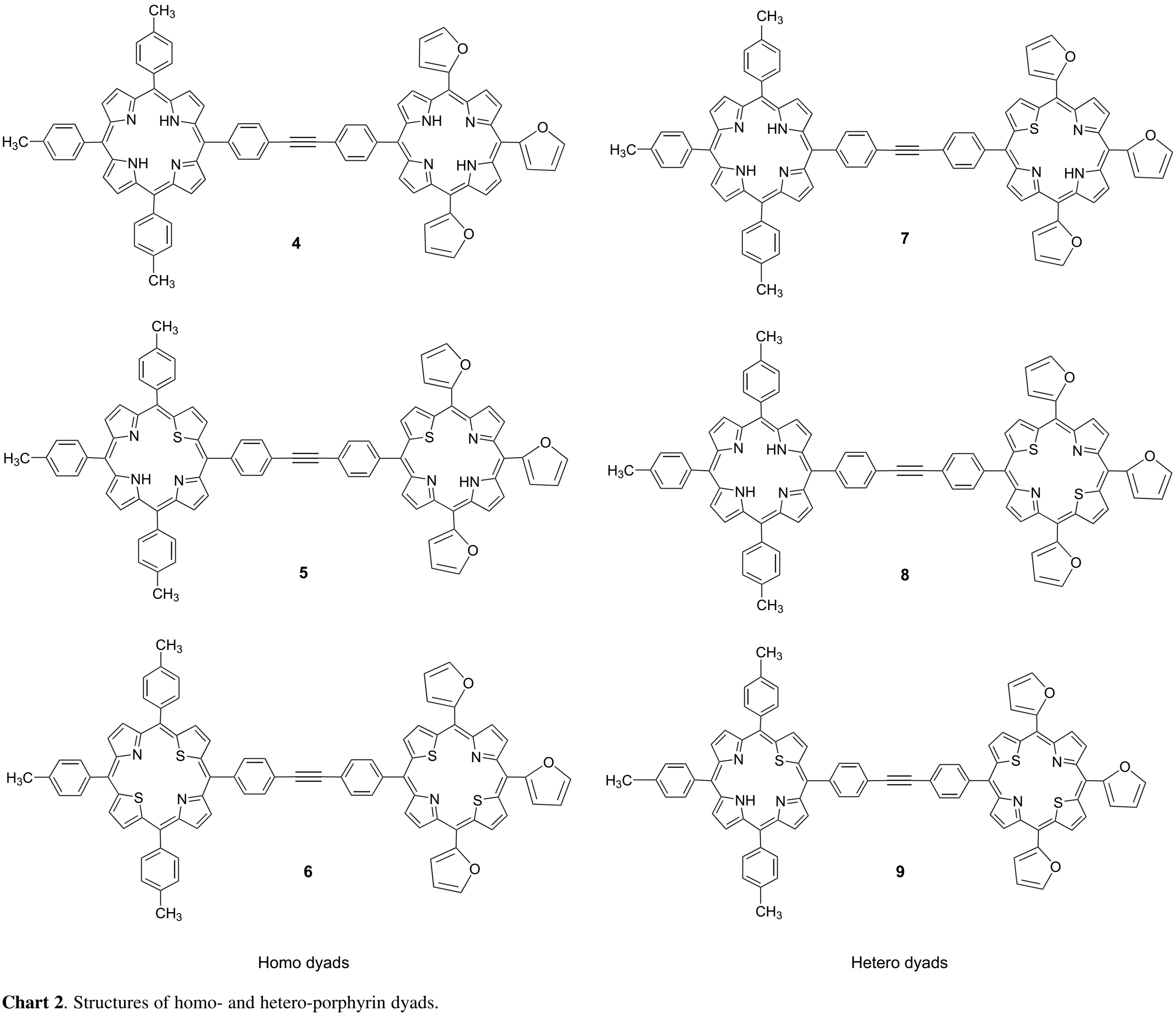


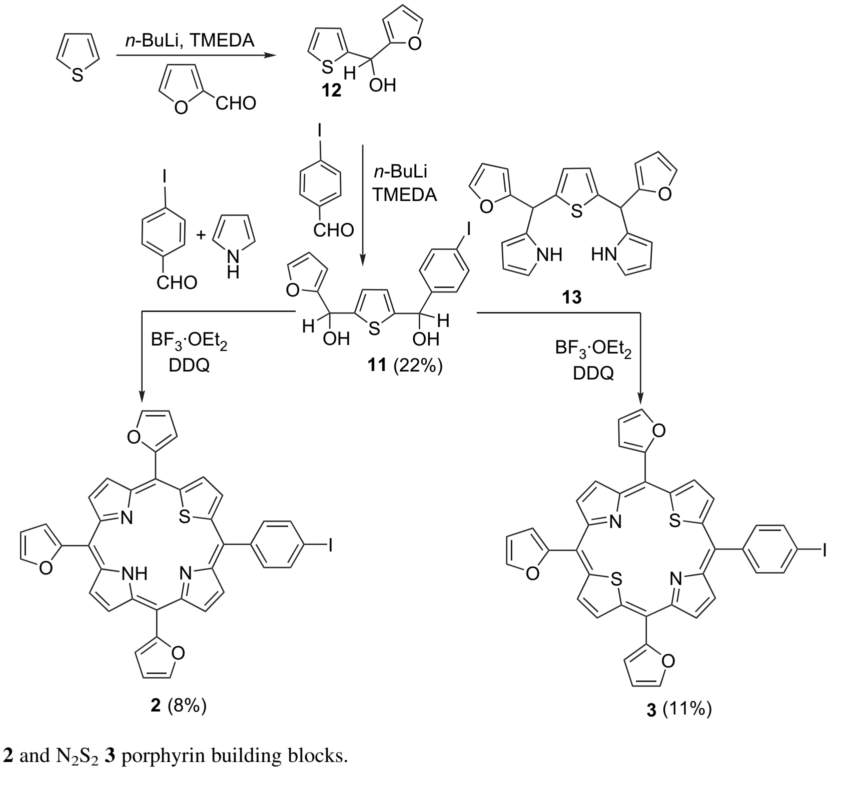
Chart 2. Structures of homo- and hetero-porphyrin dyads.

techniques. The M^+ ion peak in the mass spectrum and matching elemental analysis confirmed compound **1**. In the ^{1}H NMR spectrum, the eight pyrrole protons, which generally appeared as singlet in symmetrically substituted porphyrin such as 5,10,15,20-*meso*-tetrafuryl porphyrin,[5a] appeared in **1** as two sets of signals due to unsymmetric substitution. The absorption spectrum showed three Q-bands and one Soret band with the peak positions closely matched with those of 5,10,15,20-*meso*-tetrafuryl porphyrin.[5]

To synthesize the mono-functionalized *meso*-furyl porphyrins with N_3S (**2**) and N_2S_2 (**3**) cores, we required the symmetrical and unsymmetrical thiophene diols. The symmetrical thiophene diol, 2,5-bis(2-furylhydroxymethyl)thiophene **10** was prepared by following our earlier procedure.[5a] The unknown unsymmetrical thiophene diol, 2-(4-iodophenylhydroxymethyl)-5-(2-furylhydroxymethyl)thiophene **11** was prepared in two steps starting from thiophene (Scheme 1). The required thiophene mono-ol, 2-(2-furylhydroxymethyl)thiophene **12** was prepared in 40% yield by treating thiophene with 1.2 equiv of *n*-BuLi followed by 1.2 equiv of furan-2-aldehyde in THF at 0 °C and purified by column chromatography. The unsymmetrical thiophene diol **11** was prepared by treating the mono-ol **12** with 2 equiv of *n*-BuLi followed by 1.2 equiv of 4-iodobenzaldehyde in THF at 0 °C. The crude diol was purified by silica gel column chromatography to afford pure diol **11** as a yellow oily liquid in 22% yield. The ES MS mass spectrum of **11** showed M^+-OH peak and elemental analysis was in agreement with the composition of diol **11**. In ^{1}H NMR, the thiophene protons appeared as a multiplet due to unsymmetric substitution. Furthermore, the presence of a broad singlet at 2.20 ppm in the ^{1}H NMR spectrum and a very strong broad peak at 3400 cm^{-1} in IR spectrum confirmed the presence of hydroxyl groups.

The mono-functionalized *meso*-furyl-21-thiaporphyrin **2** was synthesized by condensing 1 equiv of thiophene diol **11** with 2 equiv of furan-2-aldehyde and 3 equiv of pyrrole under mild acid catalyzed conditions. The crude porphyrin mixture containing four different porphyrins was separated by column chromatography on silica and the desired mono-functionalized *meso*-furyl-21-thiaporphyrin **2** was afforded as a purple solid in 8% yield. The M^+ ion peak in ES MS spectrum and matching elemental analysis confirmed the compound **2**. In ^{1}H NMR, the two thiophene protons appeared as two sets of well defined doublets at 9.67 and 10.12 ppm due to the unsymmetrical substitution. The six pyrrole protons appeared as four sets of signals. The three sets of chemically non-equivalent furyl protons appeared as three sets of signals, and the inner NH proton appeared as a broad singlet at −2.62 ppm.

The mono-functionalized *meso*-furyl 21,23-dithiaporphyrin building block **3** was prepared by condensing the same thiophene diol **11** with unknown 5,10-bis(2-furyl)-16-thia-15,17-dihydrotripyrrane **13** under mild acid catalyzed conditions. The unknown **13** was prepared by treating diol **10** with excess pyrrole in the presence of an acid, followed by column chromatographic purification. Condensation of 1 equiv of diol **11** and tripyrrane **13** under mild acid catalyzed porphyrin forming conditions followed by column chromatographic purification yielded the mono-functionalized *meso*-furyl-21,23-dithiaporphyrin **3** as single product in 11% yield. The ES MS mass spectrum showed M^+ ion peak and the elemental analysis matched the expected composition of the compound. In ^{1}H NMR spectrum, the four thiophene protons appeared as three sets of signals and the four pyrrole protons appeared as two sets of signals. The chemically non-equivalent furyl protons appeared as complex multiplet in the 7.50–8.05 ppm region.



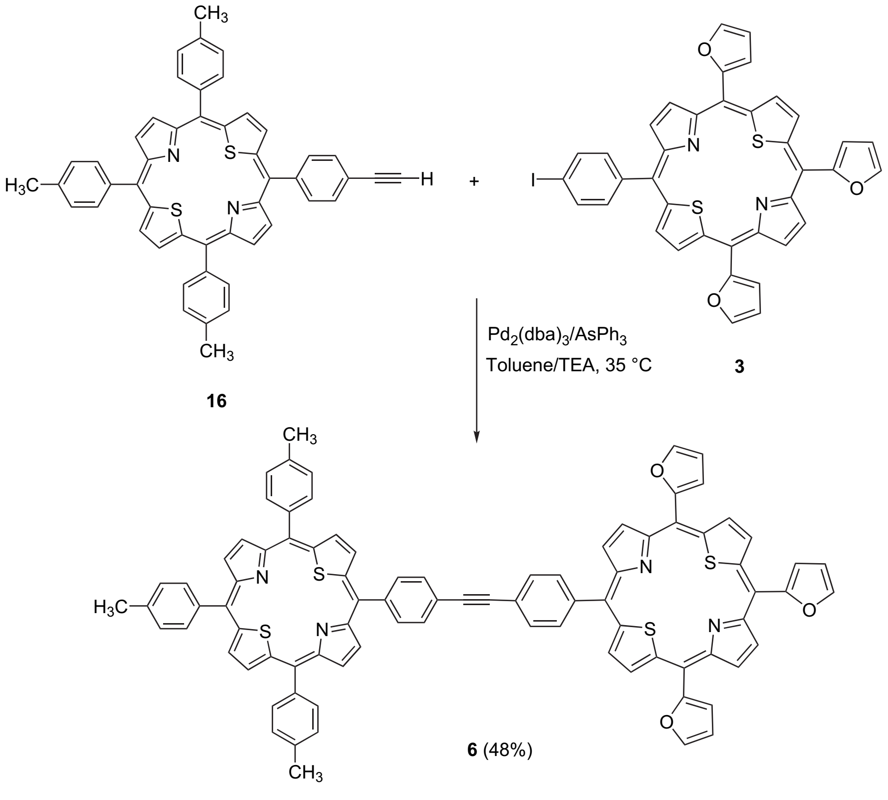
Scheme 1. Synthesis of N_3S **2** and N_2S_2 **3** porphyrin building blocks.

2.2. Synthesis of diphenyl ethyne bridged porphyrin dyads

2.2.1. Synthesis of homo-porphyrin dyads. The porphyrin dyads containing two porphyrin sub-units with the same porphyrin core such as N_4–N_4 (**4**), N_3S–N_3S (**5**) and N_2S_2–N_2S_2 (**6**) were synthesized by adopting Lindsey's mild, copper free, palladium(0) mediated Sonogashira coupling conditions.[7] The three required mono-functionalized *meso*-aryl porphyrins such as 5,10,15-tris(4-tolyl)-20-(4-ethynylphenyl)porphyrin[8] (N_4 core) **14**, 5,10,15-tris(4-tolyl)-20-(4-ethynylphenyl)-21-thiaporphyrin[3d] (N_3S core) **15** and 5,10,15-tris(4-tolyl)-20-(4-ethynylphenyl)-21,23-dithiaporphyrin[3e] (N_2S_2 core) **16** which were synthesized by following reported methods. The porphyrin dyad **4** was synthesized by coupling **1** with **14** in toluene/triethylamine at 35 °C in the presence of a catalytic amount of $Pd_2(dba)_3$ and $AsPh_3$. The progress of the reaction was followed by TLC analysis, which showed the starting materials as minor spots and the required dyad as a major spot, after 12 h.

The crude compound was purified twice by column chromatography on silica and the desired dyad **4** was obtained as a purple solid in 56% yield. Similarly, the N_3S–N_3S dyad **5** was prepared by coupling of **2** and **15** and N_2S_2–N_2S_2 dyad **6** by coupling of **3** and **16** under identical palladium(0) coupling conditions as mentioned for dyad **4** (Scheme 2). The coupling reactions worked smoothly and required two straightforward column chromatographic purifications to afford pure dyads in decent yields. Dyads **4–6** are highly soluble in all common organic solvents and were characterized by all spectroscopic techniques. Dyads **4–6** showed M^+-2, M^+ and M^++1 ion peaks, respectively, in mass spectra confirming the identities of the dyads. The ^1H NMR spectra of dyads **4–6** were clean and the resonances of the dyads were assigned on the basis of the spectra observed for the corresponding two monomers taken independently. In N_4–N_4 dyad **4**, the 16 pyrrole protons appeared as 2 sets of signals: 6 pyrrole protons appeared as a multiplet in 9.10–9.30 ppm region and the 10 pyrrole protons appeared as complex multiplet in 8.89–8.93 ppm region. The *meso*-tolyl, *meso*-furyl and bridging phenyl group protons appeared as overlapping signals in 7.05–8.22 ppm region. The NH protons appeared as two broad singlets at −2.60 and −2.74 ppm. The ^1H NMR spectrum of dyad **5** showed one multiplet at 10.19 ppm and two doublets at 9.74 and 9.82 ppm for the four thiophene protons. The 12 pyrrole protons in **5** appeared as 5 sets of signals in 8.56–9.55 ppm region and the 2 NH protons appeared as broad singlet at −2.62 ppm. Similarly, dyad **6** showed two sets of multiplets for the eight thiophene protons and two sets of multiplets for the eight pyrrole protons. The other aryl and furyl protons appeared in 6.90–8.10 ppm region. A comparison of chemical shifts of the various protons of the dyads **4–6** with those of the corresponding monomeric porphyrin sub-units indicates only minor differences suggesting that the two porphyrinic sub-units in the dyads interact very weakly. This is consistent with the earlier reports on the covalently linked porphyrin dyads.[2]

2.2.2. Synthesis of hetero-porphyrin dyads. The hetero-porphyrin dyads such as N_4–N_3S (**7**), N_4–N_2S_2 (**8**) and N_3S–N_2S_2 (**9**) were synthesized by coupling appropriate porphyrin building blocks under similar palladium(0) coupling conditions. The coupling of **2** and **14** in the presence of $Pd_2(dba)_3$/$AsPh_3$ at 35 °C overnight followed by column



Scheme 2. Synthesis of porphyrin dyad **6**.

chromatographic purification yielded dyad **7** in 45% yield. Dyad **8** was obtained in 48% yield by coupling of **3** and **14** under similar Pd(0) coupling conditions followed by column chromatographic purification. Similarly dyad **9** was obtained in 42% yield by coupling **3** and **15** under same reaction conditions and purification by column chromatography. The three dyads **7–9** have good solubility in most of the common organic solvents. Dyads **7–9** were confirmed by ES MS mass spectra, which showed a strong M^+ ion peak for all three dyads. ^{1}H NMR spectroscopy has been used to characterize the dyads **7–9**. In dyad **7**, which contains N_4 and N_3S porphyrin sub-units, the two thiophene protons of N_3S porphyrin sub-unit appeared as two sets of multiplets at 10.12 and 9.75 ppm regions. The 14 pyrrole protons, 8 belonging to the N_4 porphyrin sub-unit and 6 belonging to N_3S porphyrin sub-unit appeared as 2 sets of multiplets in 8.84–8.95 ppm region. The *meso*-furyl and *meso*-aryl protons also appeared in 7.11–8.18 ppm region. The two inner NH protons of N_4 porphyrin sub-unit were observed as broad singlet at −2.78 ppm and the inner NH proton of N_3S porphyrin sub-unit was observed as broad singlet at −2.38 ppm. Similarly in dyad **8**, which contains N_4 and N_2S_2 porphyrin sub-units, the 4 thiophene protons appeared as 3 sets of signals in the region 9.72–10.13 ppm and 12 pyrrole protons as a complex multiplet in 8.71–9.04 ppm region. The N_2S_2 porphyrin sub-unit did not have any inner NH protons and the two inner NH protons of N_4 porphyrin sub-unit appeared as broad singlet at −2.70 ppm. In dyad **9** containing N_3S and N_2S_2 porphyrin sub-units, the six thiophene protons appeared as two sets of signals in 9.60–10.20 ppm region. The 10 pyrrole protons appeared as 2 sets of multiplets and the inner NH proton of N_3S porphyrin sub-unit appeared as broad singlet at −2.69 ppm. Thus, the proton NMR spectra clearly support the proposed structures of all the dyads **4–9**.

2.3. Absorption properties

The absorption spectra of *meso*-furyl porphyrin building blocks **1–3**, dyads **4–9** and their corresponding 1:1 mixtures of monomers were recorded in toluene and the data are presented in Table 1. The literature data[3d,3e,8] for *meso*-aryl porphyrin building blocks **14–16** are also included in Table 1. The monomeric furyl porphyrin building blocks showed three Q-bands and one strong Soret band and the peak maxima matched closely with their corresponding tetrafuryl porphyrins reported previously.[5] The absorption spectra of dyad **6** along with the corresponding monomers, in both the Q-band and the Soret region are shown in Figure 1. As is clear

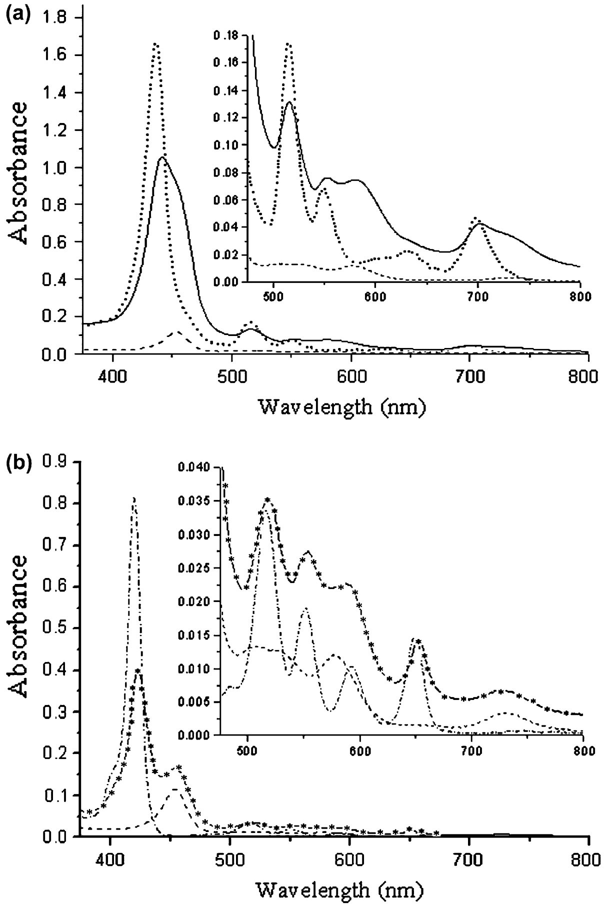


Figure 1. (a) Comparison of absorption spectra of dyad **6** (———) and its corresponding monomers **3** (- - - - -) and **16** (·········) recorded in toluene. (b) Comparison of absorption spectra of dyad **8** (–∗–∗–∗–) and its corresponding monomers **3** (- - - - -) and **14** (–·–·–·–) recorded in toluene.

Table 1. Absorption data of porphyrin monomers, porphyrin dyads and their corresponding 1:1 mixture of monomers recorded in toluene

Porphyrin	Soret band λ (nm) (log ε)	Absorption Q-bands λ (nm) (log ε)			
1	430 (8.83)	523 (6.9)	563 (4.8)	599 (br)	660 (2.5)
2	440 (4.7)	525 (5.1)	566 (18.1)	622 (br)	691 (2.0)
3	454 (2.1)	522 (br)	573 (4.5)	—	717 (2.1)
14	422 (28.9)	517 (13.4)	551 (7.5)	594 (3.9)	652 (5.9)
15	430 (5.4)	514 (4.3)	547 (3.8)	617 (3.4)	676 (3.5)
16	437 (5.3)	514 (4.3)	548 (3.9)	632 (3.2)	697 (3.6)
4	423 (18.9)	518 (10.2)	553 (6.2)	594 (3.9)	653 (4.2), 659 (sh)
1:1 mix of **1** and **14**	422 (38.6)	517 (27.1)	551 (17.9)	594 (11.1)	652 (10.5)
5	433 (4.97)	516 (3.9)	552 (3.5), 574 (sh)	620 (3.0)	681 (3.2), 706 (2.0)
1:1 mix of **2** and **15**	432 (5.01)	515 (3.8)	551 (3.4)	620 (3.0)	679 (3.2)
6	440 (5.08)	517 (4.0)	552 (3.6)	636 (3.0)	699 (3.3), 730 (2.0)
1:1 mix of **3** and **16**	438 (4.76)	516 (3.6)	550 (3.2)	634 (2.7)	698 (3.0)
7	423 (12.1)	517 (6.3)	553 (4.2)	594 (2.2)	653 (2.6), 690 (sh)
1:1 mix of **2** and **14**	422 (18.8)	517 (9.9)	551 (6.0)	593 (3.5)	652 (4.1)
8	422 (13.0), 454 (5.3)	518 (10.2)	553 (7.8)	589 (br)	653 (4.2), 728 (3.2)
1:1 mix of **3** and **14**	422 (18.3)	516 (10.1)	551 (6.4)	593 (4.1)	652 (4.6), 714 (sh)
9	433 (4.96), 459 (4.47)	517 (3.88)	552 (3.61)	619 (3.27)	681 (3.31), 727 (2.90)
1:1 mix of **3** and **15**	432 (5.02)	516 (3.98)	551 (3.69), 578 (sh)	619 (3.41)	679 (3.50), 731 (sh)

from Figure 1 and the data presented in Table 1, the absorption spectra of the dyads resembles, but does not equal, the sum of the spectra of the corresponding monomeric units. The absorption spectrum of dyad **4** was not significantly changed in shape, position and bandwidth compared to its 1:1 mixture of corresponding monomers. However, the extinction coefficients of dyad **4** were significantly reduced as compared to the 1:1 mixture suggesting a weak interaction between the two porphyrin sub-units. Dyad **5** showed six Q-bands at 516, 552, 574, 620, 681 and 706 nm and one strong broad Soret band at 433 nm. The peak at 706 nm is mainly because of *meso*-furyl N_3S porphyrin sub-unit and the peak at 681 nm is due to *meso*-aryl N_3S porphyrin sub-unit. The peak at 706 nm was not observed in the 1:1 mixture of monomers because the extinction coefficients of *meso*-aryl porphyrins are much higher as compared to *meso*-furyl porphyrins. Hence the absorption spectra of the 1:1 mixture show absorption bands, which correspond mainly to *meso*-aryl porphyrin. But in covalently linked dyad **5**, due to weak interaction between the porphyrin sub-units, the extinction coefficients of both the porphyrin sub-units were significantly reduced and the dyad exhibits the spectral features of both the porphyrin sub-units. Similarly, the dyad **6** containing two N_2S_2 porphyrin sub-units showed five Q-bands and one broad Soret band with a reduction in extinction coefficients as compared to the 1:1 mixture of monomers. The hetero-dyads **7–9** containing two different porphyrin cores also showed similar absorption spectral features as observed for homo-dyads **4–6**. In dyad **7** containing N_4 and N_3S porphyrin sub-units, five Q-bands and one broad Soret band with a reduction in extinction coefficients as compared to the 1:1 mixture was observed. Dyads **8** and **9** containing N_4–N_2S_2 and N_3S–N_2S_2 porphyrin sub-units, respectively, showed a split Soret band in addition to five Q-bands unlike their corresponding 1:1 mixture of monomers, which showed one broad Soret band and five Q-bands. Thus, the absorption spectral studies of dyads **4–9** and their corresponding 1:1 porphyrin mixture showed that the two porphyrin sub-units in dyads interact very weakly.

2.4. Fluorescence properties

The fluorescence properties of homo- and hetero-porphyrin dyads **4–9** and their corresponding 1:1 mixture of monomers and the appropriate reference compounds were recorded in toluene at room temperature and the data for fluorescence yields are presented in Table 2. The emission spectra of homo-dyad **6** and hetero-dyad **9** and their 1:1 mixture of corresponding monomers are shown in Figure 2. As is evident from Figure 2a, in homo-dyad **6**, which is composed of *meso*-phenyl N_2S_2 and *meso*-furyl N_2S_2 porphyrin sub-units, excitation at 450 nm where the *meso*-furyl N_2S_2 porphyrin sub-unit absorbs strongly, results in typical *meso*-furyl N_2S_2 porphyrin emission with a quantum yield resembling that of **S_2TFP** (Table 2). Illumination of dyad **6** at 430 nm where *meso*-phenyl N_2S_2 porphyrin sub-unit absorbs strongly, causes the emission of *meso*-phenyl N_2S_2 porphyrin sub-unit to be quenched by 94% and the strong emission from *meso*-furyl N_2S_2 porphyrin sub-unit was observed (Fig. 2a). However, when the 1:1 mixture of *meso*-phenyl N_2S_2 porphyrin **16** and *meso*-furyl N_2S_2 porphyrin **3** was excited at 430 nm, strong emission was mainly observed from the *meso*-phenyl N_2S_2 porphyrin sub-unit (Fig. 2a). These results indicate that the *meso*-furyl N_2S_2 porphyrin can act as an energy acceptor and there is an efficient energy transfer from *meso*-phenyl N_2S_2 porphyrin sub-unit to *meso*-furyl N_2S_2 porphyrin sub-unit in dyad **6**. The excitation spectrum recorded for dyad **6** at 790 nm matches exactly with its absorption spectrum, further confirming the efficient energy transfer between the porphyrin sub-units.

Table 2. Fluorescence data of homo- and hetero-porphyrin dyads and appropriate porphyrin monomers

Compound	λ_{ex}	Φ_f (Donor)	Φ_f (Acceptor)
H_2TPP[a]	415	0.11	—
STPPH[a]	420	0.0168	—
S_2TPP[a]	430	0.0076	—
H_2TFP[a]	430	—	0.0109
STFPH[a]	440	—	0.0021
S_2TFP[a]	450	—	0.0019
1	430	—	0.0102
2	440	—	0.0020
3	450	—	0.0018
4	415	0.00812	—
	430	—	0.00990
5	420	0.00116	—
	440	—	0.00201
6	430	0.00046	—
	450	—	0.00182
7	415	0.00240	—
	440	—	0.00193
8	415	0.00385	—
	450	—	0.00189
9	420	0.00118	—
	450	—	0.00189

[a] Data taken from Ref. 5b.

Similarly, the other two homo-dyads **4** and **5** showed efficient energy transfer from *meso*-phenyl porphyrin to *meso*-furyl porphyrin. These observations are in line with diphenyl ethyne bridged dyads containing *meso*-aryl metallated porphyrin and *meso*-aryl free base porphyrin sub-units.[9] The hetero-dyads containing two different types of porphyrin cores also showed similar energy transfer between the porphyrin sub-units. As shown in Figure 2b, in dyad **9** containing *meso*-phenyl N_3S porphyrin sub-unit and *meso*-furyl N_2S_2 porphyrin sub-unit, on excitation at 420 nm where *meso*-phenyl N_3S porphyrin sub-unit absorbs strongly, the emission of *meso*-phenyl N_3S porphyrin was quenched by 93% and the strong emission from *meso*-furyl N_2S_2 porphyrin sub-unit was observed. It is also clear from Figure 2b that when the 1:1 mixture of *meso*-phenyl N_3S porphyrin **15** and *meso*-furyl N_2S_2 porphyrin **3** was excited at 420 nm, emission was observed mainly from the *meso*-phenyl N_3S porphyrin sub-unit. The excitation spectrum of dyad **9** recorded at 790 nm closely matched with its absorption spectrum. These observations support an efficient energy transfer between the porphyrin sub-units in hetero-dyad **9**. Similar observations were made in dyads **7** and **8** supporting an energy transfer from *meso*-phenyl porphyrin sub-unit to *meso*-furyl porphyrin sub-unit in hetero-dyads as well. Thus, the steady state fluorescence studies clearly indicate that in both homo- and hetero-dyads, an efficient energy transfer occurs from *meso*-phenyl porphyrin sub-unit to *meso*-furyl porphyrin sub-unit. Detailed time-resolved

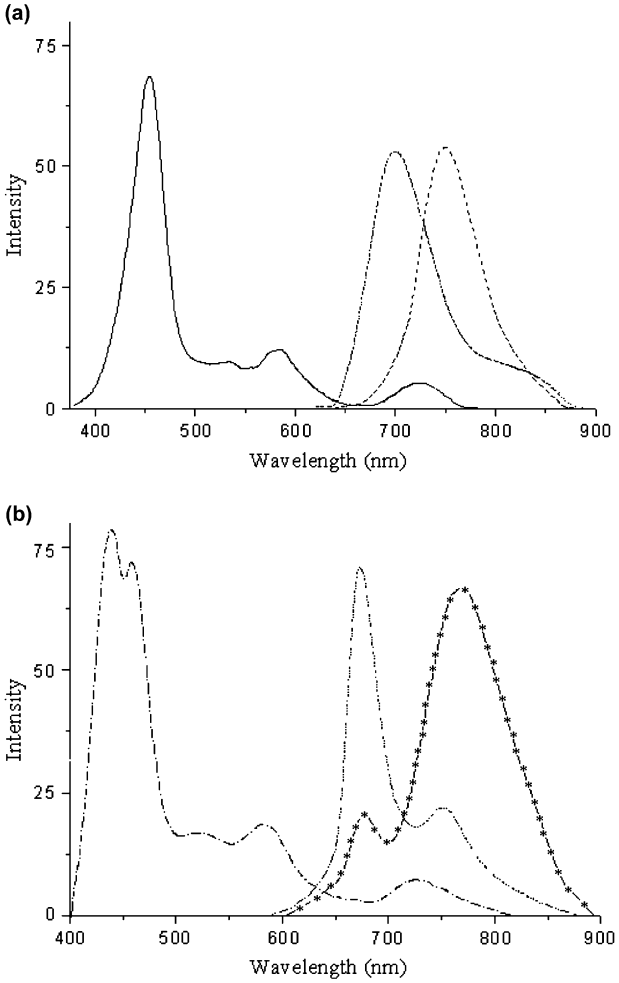


Figure 2. (a) Comparison of emission spectra of dyad **6** (- - - - -) and 1:1 mixture of **3** and **16** (·········) recorded at excitation wavelength 430 nm in toluene. The excitation spectrum of dyad **6** (———) recorded at emission wavelength 790 nm is also shown. (b) Comparison of emission spectra of dyad **9** (-✱-✱-✱-) and 1:1 mixture of **3** and **15** (–··–··–··) recorded at excitation wavelength 420 nm and the excitation spectrum of dyad **9** (–·–·–·–) recorded at emission wavelength 790 nm in toluene.

studies are now required to quantify the energy transfer dynamics.

3. Conclusions

Mono-functionalized *meso*-furyl porphyrin building blocks with N_4, N_3S and N_2S_2 porphyrin cores were synthesized and characterized. The *meso*-furyl porphyrin building blocks were used further to synthesize three homo-dyads containing two similar porphyrin cores and three hetero-dyads containing two dissimilar porphyrin cores. The absorption studies indicated a weak interaction between the two porphyrin sub-units. The steady state fluorescence studies supported an energy transfer from *meso*-aryl porphyrin to *meso*-furyl porphyrin in dyads on selective excitation of *meso*-aryl porphyrin sub-unit. Thus, we have demonstrated that by introducing *meso*-furyl groups in place of *meso*-aryl groups, the energy levels are altered and the *meso*-furyl porphyrins can act as good energy acceptors when these porphyrins are connected to *meso*-aryl porphyrins.

4. Experimental

4.1. Data for compounds

4.1.1. General. ^{1}H and ^{13}C NMR spectra were recorded using a Varian 400 MHz spectrometer using tetramethylsilane as an internal standard and chemical shifts are reported in δ (ppm), referred to ^{1}H (of residual proton; δ 7.26) and ^{13}C (δ 77.0) signals of $CDCl_3$. Absorption and fluorescence spectra were obtained with Perkin–Elmer Lambda 35 and Perkin–Elmer Lambda 55 models, respectively. Infrared spectra were recorded on a Nicolet Impact-400 FT-IR spectrometer and the ES MS mass spectra were recorded with a Q-Tof micro (YA-105) mass spectrometer. Elemental analyses were conducted using Thermo Finnigan Flash EA 1112. Diethyl ether, *n*-hexane, THF and toluene were obtained from S.D. Fine chemicals, India, and dried over 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), *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA), $AsPh_3$ and $Pd_2(dba)_3$ were used as obtained from Sigma–Aldrich Chemical Co. All other chemicals used for the synthesis were of reagent grade unless otherwise specified. Column chromatography was performed on silica (Merck, 60–120 mesh) obtained from Sisco Research Laboratories, India. 2,5-Bis[2-furylhydroxymethyl]thiophene[3a] (symmetrical diol) **10**, 5,10,15-tris(4-tolyl)-20-(4-ethynylphenyl)porphyrin[8] (N_4 core) **14**, 5,10,15-tris(4-tolyl)-20-(4-ethynylphenyl)-21-thiaporphyrin[3d] (N_3S core) **15** and 5,10,15-tris(4-tolyl)-20-(4-ethynylphenyl)-21,23-dithiaporphyrin[3e] (N_2S_2 core) **16** were synthesized by the reported methods.

4.1.2. 2-(2-Furylhydroxymethyl)thiophene (12). Dry, distilled ether (40 mL) was added to a 250 mL three-necked, round-bottomed flask fitted with a rubber septum and gas inlet tube; the flask was flushed with argon for 10 min. Tetramethylethylenediamine (TMEDA) (4.6 mL, 30.42 mmol) and *n*-BuLi (20 mL of ca. 15% solution in hexane) were added to the stirred solution and the reaction temperature maintained at 0 °C in an ice bath. Thiophene (2.0 mL, 25.35 mmol) was added and the solution was stirred for 1 h. As the reaction progressed, a white turbid solution formed indicating the formation of 2-lithiated salt of thiophene. An ice-cold solution of furan-2-aldehyde (2.5 mL, 30.42 mmol) in dry THF (40 mL) was then added and 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 ether and washed several times with water and brine and dried over anhydrous Na_2SO_4. The solvent was removed in a rotary evaporator under reduced pressure to afford the crude compound. TLC analysis showed two spots mainly corresponding to unchanged aldehyde and the desired mono-ol **12**. The crude compound was loaded on silica and eluted with petroleum ether. The unchanged aldehyde was removed with petroleum ether/ethylacetate (98:2) solvent mixture and the desired mono-ol **12** was collected with petroleum ether/ethylacetate (96:4) solvent mixture (R_f 0.60). The solvent was removed in a rotary evaporator to afford **12** as a light yellow solid (2.1 g, 40% yield). Mp 38–40 °C. IR (KBr, cm^{-1}): ν=3280 (OH). ^{1}H NMR

(400 MHz, $CDCl_3$, δ in ppm): 2.86 (1H, br s, OH), 6.03 (1H, s, CHOH), 6.27–6.34 (2H, m, furyl), 6.97–7.00 (2H, m, thiophene), 7.27–7.29 (1H, m, furyl), 7.35–7.40 (1H, m, thiophene). ^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm): 67.60 (CHOH), 104.00, 116.02, 146.93, 148.04 (furyl), 126.24, 126.37, 126.83, 144.26 (thiophene). ES MS: $C_9H_8O_2S$, calcd av mass 180.2, obsd *m/z* 163.2 (M^+-17, 100%). Anal. Calcd: C, 59.98; H, 4.47; S, 17.79. Found: C, 59.70; H, 4.21; S, 17.62.

4.1.3. 2-(4-Iodophenylhydroxymethyl)-5-(2-furylhydroxymethyl)thiophene (11). In a three-necked round-bottomed flask equipped with rubber septum, gas inlet and gas outlet tube, freshly distilled dry diethyl ether (40 mL) was taken and a positive pressure of nitrogen was maintained. Mono-ol **12** (2.00 g, 11.10 mmol) was added to it and the temperature of the reaction flask was maintained at 0 °C. TMEDA (4.17 mL, 27.75 mmol) followed by *n*-BuLi (17.34 mL of ca. 15% solution in hexane) was added dropwise over 10 min into the stirred solution and the reaction mixture was allowed to stir for 30 min at 0 °C. An ice-cold solution of 4-iodobenzaldehyde (3.86 g, 16.6 mmol) in dry THF (40 mL) was added using siphon apparatus from another round-bottomed flask. 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 ether. All the organic layers were combined and washed with water and brine and dried over 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 4-iodobenzaldehyde, unreacted mono-ol and the desired diol **11**. The aldehyde and the mono-ol were removed by silica gel column chromatography using petroleum ether/ethyl acetate (90:10) as an eluent and the major diol fraction **11** was collected using petroleum ether/ethyl acetate (80:20, R_f 0.22). The solvent was removed on a rotary evaporator under reduced pressure to afford the pure diol **11** as a yellow oily compound (500 mg, 22%). IR (neat, cm^{-1}): ν=3400, 2955, 2929, 1965, 1652, 1515, 1483, 1413, 1263, 1006, 884, 814, 735, 597. ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 2.20 (2H, br s, OH), 5.80–5.95 (2H, m, CHOH), 6.25–6.31 (1H, m, furyl), 6.68–6.69 (1H, m, furyl), 6.78–6.80 (1H, m, thiophene), 6.95–6.98 (1H, m, thiophene), 7.12 (2H, d, *J*=8.0 Hz, aryl), 7.32–7.36 (1H, m, furyl), 7.64 (2H, d, *J*=8.0 Hz, aryl). ^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm): 67.72, 73.45 (CHOH), 101.00, 129.33, 134.56, 136.04 (aryl), 105.32, 114.44, 146.00, 146.91 (furyl), 124.57, 128.13, 140.29, 143.71 (thiophene). ES MS: $C_{16}H_{13}O_3SI$, calcd av mass 412.2, obsd *m/z* 394.9 (M^+-17, 100%). Anal. Calcd: C, 46.61; H, 3.17; S, 7.77. Found: C, 46.79; H, 3.09; S, 7.72.

4.1.4. 5,10-Bis(2-furyl)-16-thia-15,17-dihydrotripyrrane (13). A mixture of **10** (500 mg, 1.81 mmol) and pyrrole (5.0 mL, 72.44 mmol) was degassed by bubbling with N_2 for 10 min. $BF_3\cdot OEt_2$ (274 μL, 1.81 mmol) was added and the reaction mixture was stirred for 30 min at room temperature. The mixture was then diluted with CH_2Cl_2 (100 mL), washed with 0.1 M NaOH, followed by water washing. The organic layer was dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the unreacted pyrrole was removed by vacuum distillation at room temperature. The resulting viscous dark yellow liquid was purified by column chromatography (silica gel 60–120 mesh, ethyl acetate/petroleum ether (10:90)). After the initial tailing material, a pale orange band eluted (R_f 0.21), which gave a brown solid identified as **13** in 55% yield (390 mg). Mp 80–82 °C. IR (KBr, cm^{-1}): ν=3402 (NH). ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 5.53 (2H, s, *meso*), 5.99–6.09 (6H, m, pyrrole [4H]+furyl [2H]), 6.25–6.28 (2H, m, furyl), 6.57–6.60 (4H, m, pyrrole [2H]+thiophene [2H]), 7.29 (2H, m, furyl), 8.05 (2H, br s, NH). ^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm): 55.22 (*meso*), 107.01, 110.35, 143.69, 154.68 (furyl), 107.15, 108.02, 117.70, 130.31 (pyrrole), 125.16, 142.06 (thiophene). ES MS: $C_{22}H_{18}N_2O_2S$, calcd av mass 374.4, obsd *m/z* 375.4 (M^++1, 100%). Anal. Calcd: C, 70.57; H, 4.84; N, 7.48; S, 8.56. Found: C, 70.69; H, 4.72; N, 7.43; S, 8.42.

4.1.5. 5-(4-Iodophenyl)-10,15,20-tris(2-furyl)porphyrin (1). In a 500 mL one-necked round-bottomed flask fitted with argon bubbler, furan-2-aldehyde (0.56 mL, 6.81 mmol), pyrrole (0.63 mL, 9.08 mmol) and 4-iodobenzaldehyde (500 mg, 2.27 mmol) were dissolved in 230 mL of CH_2Cl_2. After purging with argon for 10 min, the condensation of furan-2-aldehyde, pyrrole and iodobenzaldehyde was initiated by adding a catalytic amount of $BF_3\cdot OEt_2$ (91 μL of 2.5 M stock solution). The reaction mixture was stirred at room temperature for 1 h. The progress of the reaction was checked by taking aliquots of the reaction mixture at regular intervals and oxidizing with DDQ. Recording the absorption spectra clearly confirmed the formation of porphyrin. After 1 h, DDQ (385 mg, 1.70 mmol) was added and the reaction mixture was stirred in air for an additional 1 h. The solvent was removed under reduced pressure and the crude compound was purified by silica gel column chromatography. TLC analysis indicated the formation of a mixture of six porphyrins: *meso*-tetrafuryl porphyrin **H_2TFP**, the desired mono-functionalized N_4 porphyrin **1**, cis and trans mixture of N_4 porphyrin, tri-functionalized N_4 porphyrin and tetra-functionalized N_4 porphyrin. The crude compound containing a mixture of six porphyrins was subjected to silica gel column chromatography and the desired mono-functionalized N_4 porphyrin **1** with small impurities was obtained as the fifth band using petroleum ether/dichloromethane (75:25). The compound with small impurities was further subjected to second silica gel column chromatography using same solvent mixture and afforded the pure **1** as a purple solid (0.09 g, 8%). Mp >300 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): −2.78 (2H, s, NH), 6.90 (3H, s, furyl), 7.40–7.46 (3H, br m, furyl [1H]+aryl [2H]), 7.60–7.68 (3H, br m, furyl [1H]+aryl [2H]), 7.75–7.77 (1H, br m, furyl), 7.99 (3H, s, furyl), 8.71 (2H, s, β-pyrrole), 9.01–9.06 (6H, br m, β-pyrrole). ^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm): 100.12, 128.15, 134.50, 142.28 (aryl), 110.78, 116.03, 147.22, 157.16, 157.62 (furyl), 129.75, 130.88, 131.55, 131.78, 132.90, 132.99, 133.37, 134.03, 140.07, 140.33, 141.05, 141.50 (pyrrole), 139.46, 154.70 (*meso*). ES MS: $C_{38}H_{23}N_4O_3I$, calcd av mass 710.5, obsd *m/z* 710.8 (M^+, 100%). Anal. Calcd: C, 64.23; H, 3.26; N, 7.89. Found: C, 64.31; H, 3.32; N, 7.95.

4.1.6. 5-(4-Iodophenyl)-10,15,20-tris(2-furyl)-21-monothiaporphyrin (2). Samples of diol **11** (500 mg, 1.21 mmol), furan-2-aldehyde (0.20 mL, 2.42 mmol) and pyrrole (0.25 mL, 3.63 mmol) were dissolved in dichloromethane (121 mL) taken in 250 mL round-bottomed flask and nitrogen was purged for 10 min. $BF_3 \cdot OEt_2$ (50 μL of 2.5 M stock solution) was added to catalyze the reaction and the stirring was continued for 1 h. DDQ (410 mg, 1.81 mmol) was added to oxidize the porphyrinogen to porphyrin and stirring was continued for an additional 1 h in air. TLC analysis indicated the formation of a mixture of four porphyrins: tetrafuryl porphyrin (**H_2TFP**), the desired 21-thiaporphyrin **2** and cis and trans mixture of 21,23-dithiaporphyrins. The crude compound containing a mixture of four porphyrins was subjected to silica gel column chromatography and the desired N_3S porphyrin **2** with small impurities was obtained as the first band using petroleum ether/dichloromethane (80:20). The compound was further subjected to second silica gel column chromatography using same solvent mixture and afforded pure **2** as a purple solid (0.07 g, 8%). Mp >300 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): −2.62 (1H, s, NH), 7.39 (3H, d, J=2.0 Hz, furyl), 7.91 (2H, d, J=8.0 Hz, aryl), 8.01–8.05 (3H, m, furyl), 8.11 (2H, d, J=8.0 Hz, aryl), 8.79–8.81 (3H, m, furyl), 8.60 (1H, d, J=4.4 Hz, β-pyrrole), 8.97 (1H, d, J=4.0 Hz, β-pyrrole), 9.09 (2H, s, β-pyrrole), 9.20 (2H, s, β-pyrrole), 9.67 (1H, d, J=4.8 Hz, β-thiophene), 10.12 (1H, d, J=5.2 Hz, β-thiophene). ^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm): 100.10, 128.05, 134.53, 142.35 (aryl), 110.80, 116.14, 147.21, 157.11, 157.65 (furyl), 126.77, 127.70, 137.74, 138.65 (thiophene), 129.75, 130.88, 132.90, 133.37, 134.03, 140.07, 141.05 (pyrrole), 139.21, 154.66 (*meso*). ES MS: $C_{38}H_{22}N_3O_3SI$, calcd av mass 727.5, obsd *m/z* 727.9 (M^+, 100%). Anal. Calcd: C, 62.73; H, 3.04; N, 5.77; S, 4.40. Found: C, 62.99; H, 3.12; N, 5.63; S, 4.32.

4.1.7. 5-(4-Iodophenyl)-10,15,20-tris(2-furyl)-21,23-dithiaporphyrin (3). A solution of diol **11** (500 mg, 1.21 mmol) and 16-thiatripyrrane **13** (470 mg, 1.21 mmol) in dichloromethane (121 mL) was condensed by the addition of a catalytic amount of $BF_3 \cdot OEt_2$ (60 μL of 2.5 M stock solution) for 1 h. DDQ (275 mg, 1.21 mmol) was then added and the reaction mixture was stirred in air for an additional 1 h. 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 using petroleum ether/dichloromethane (65:35) as eluent to afford the desired porphyrin **3** as a purple solid (0.09 g, 11%). Mp >300 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): 7.50–7.55 (3H, m, furyl), 7.61–7.68 (5H, m, furyl [3H]+aryl [2H]), 7.70–7.75 (2H, m, aryl), 8.02–8.05 (3H, m, furyl), 8.62 (1H, d, J=4.8 Hz, β-pyrrole), 8.99–9.00 (3H, m, β-pyrrole), 9.61 (1H, d, J=4.8 Hz, β-thiophene), 10.04 (1H, d, J=5.2 Hz, β-thiophene), 10.10 (2H, s, β-thiophene). ^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm): 100.00, 124.42, 133.16, 143.30 (aryl), 112.54, 113.05, 144.65, 148.26 (furyl), 124.09, 127.67, 135.09, 136.53 (thiophene), 128.81, 129.04, 138.44, 141.29 (pyrrole), 139.06, 147.65 (*meso*). ES MS: $C_{38}H_{21}N_2O_3S_2I$, calcd av mass 744.6, obsd *m/z* 746.1 (M^+, 100%). Anal. Calcd: C, 61.29; H, 2.84; N, 3.76; S, 8.61. Found: C, 61.20; H, 2.90; N, 3.80; S, 8.52.

4.1.8. 4-[5,10,15-Tris(4-tolyl)-20-porphinyl]-4′-[5,10,15-trifuryl-20-porphinyl]diphenyl-ethyne (4). A solution of **14** (15.0 mg, 0.02 mmol) and **1** (16.0 mg, 0.02 mmol) in dry toluene/triethylamine (3:1, 30 mL) was taken 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 pre-heated to 35 °C. After purging nitrogen for 15 min, $AsPh_3$ (8.0 mg, 0.003 mmol) followed by $Pd_2(dba)_3$ (3.0 mg, 0.003 mmol) was added 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 dyad **4**. The solvent was removed under vacuum and the crude compound was purified by silica gel chromatography using petroleum ether/dichloromethane (80:20) to remove the excess $AsPh_3$ and the small amounts of monomeric porphyrins. The desired dyad **4** was then collected with petroleum ether/dichloromethane (65:35). The solvent was removed on rotary evaporator under vacuo and afforded dyad **4** as a violet solid (11.0 mg, 56%). Mp >300 °C. IR (KBr film, cm^{-1}): ν=3069, 2925, 2853, 1965, 2110, 1648, 1465, 967, 800, 656, 618. ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): −2.74 (2H, br s, NH), −2.60 (2H, br s, NH), 2.80 (9H, s, CH_3), 7.05–7.09 (3H, br m, furyl), 7.42–7.43 (3H, m, furyl), 7.57–7.59 (6H, m, aryl), 8.12–8.14 (13H, m, furyl [3H]+aryl [10H]), 8.18–8.22 (4H, m, aryl), 8.89–8.93 (10H, m, β-pyrrole), 9.10–9.30 (6H, br m, β-pyrrole). ^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm): 21.14, 21.64 (aryl CH_3), 100.10 (ethynyl), 128.14, 129.01, 131.26, 134.72 (aryl), 130.30, 130.39, 130.45, 131.10 (pyrrole), 108.43, 113.70, 144.56, 154.42 (furyl), 135.92, 137.50, 137.58, 139.40, 146.11, 146.24, 145.20, 146.10 (*meso*). ES MS: $C_{87}H_{58}N_8O_3$, calcd av mass 1263.4, obsd *m/z* 1261.2 ($M^+{-}2$, 50%). Anal. Calcd: C, 82.71; H, 4.63; N, 8.87. Found: C, 82.86; H, 4.78; N, 8.92.

4.1.9. 4-[5,10,15-Tris(4-tolyl)-21-monothia-20-porphinyl]-4′-[5,10,15-trifuryl-21-monothia-20-porphinyl]-diphenylethyne (5). A solution of **15** (15.0 mg, 0.02 mmol) and **2** (15.6 mg, 0.02 mmol) in dry toluene/triethylamine (3:1, 30 mL) was coupled by the addition of $AsPh_3$ (8.0 mg, 0.003 mmol) followed by $Pd_2(dba)_3$ (3.0 mg, 0.003 mmol) under the same reaction conditions described for dyad **4**. Purification by silica gel column chromatography using petroleum ether/dichloromethane (65:35) afforded dyad **5** as a violet solid (11.2 mg, 40%). Mp >300 °C. IR (KBr film, cm^{-1}): ν=3070, 2925, 2853, 1965, 2110, 1648, 1460, 970, 800, 656, 615. ^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): −2.62 (2H, br s, NH), 2.70 (9H, s, CH_3), 7.03–7.05 (3H, m, furyl), 7.52–7.64 (9H, m, furyl [3H]+aryl [6H]), 7.97–8.19 (17H, m, furyl [3H]+aryl [14H]), 8.56–8.58 (1H, m, β-pyrrole), 8.62–8.67 (3H, m, β-pyrrole), 8.87–8.89 (4H, m, β-pyrrole), 9.04 (1H, d, J=4.8 Hz, β-pyrrole), 9.55–9.62 (3H, m, β-pyrrole), 9.74 (1H, d, J=5.2 Hz, β-thiophene), 9.82 (1H, d, J=5.2 Hz, β-thiophene), 10.18–10.20 (2H, m, β-thiophene). ^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm): 21.65, 22.86 (aryl CH_3), 128.40, 128.97, 134.31, 135.29 (aryl), 130.31, 130.58, 137.55, 139.28 (thiophene), 131.15, 131.64, 132.73 (pyrrole), 110.42, 113.70, 143.38, 154.54 (furyl), 140.22, 141.63, 144.20, 147.22, 146.01 (*meso*). ES MS: $C_{87}H_{56}N_6S_2O_3$, calcd av mass 1298.2, obsd *m/z* 1298.4 (M^+, 60%). Anal. Calcd: C, 80.49; H, 4.35; N, 6.47; S, 4.94. Found: C, 80.53; H, 4.48; N, 6.52; S, 4.99.

4.1.10. 4-[5,10,15-Tris(4-tolyl)-21,23-dithia-20-porphinyl]-4′-[5,10,15-trifuryl-21,23-dithia-20-porphinyl]-diphenylethyne (6). Coupling of N_2S_2 porphyrin **3** (15.0 mg, 0.02 mmol) and 5-(4-iodophenyl)-10,15,20-tris(2-furyl)-21,23-dithiaporphyrin **16** (16.0 mg, 0.02 mmol) in dry toluene/triethylamine (3:1, 30 mL) in the presence of $AsPh_3$ (8.0 mg, 0.003 mmol) and $Pd_2(dba)_3$ (3.0 mg, 0.003 mmol) at 35 °C overnight followed by silica gel column chromatographic purification using petroleum ether/dichloromethane (60:40) gave dyad **6** as a violet solid (13.4 mg, 48%). Mp >300 °C. IR (KBr film, cm^{-1}): ν=3068, 2923, 2854, 1964, 2110, 1648, 1465, 967, 802, 656, 616. ^1H NMR (400 MHz, $CDCl_3$, δ in ppm): 2.62 (9H, s, CH_3), 6.90 (3H, s, furyl), 7.29–7.31 (6H, m, aryl), 7.52–7.54 (4H, d, J=7.2 Hz, aryl), 7.64–7.80 (6H, m, furyl), 8.04–8.10 (10H, m, aryl), 8.53–8.62 (4H, m, β-pyrrole), 8.88–8.91 (4H, m, β-pyrrole), 9.55–9.62 (4H, m, β-thiophene), 9.95–10.01 (4H, m, β-thiophene). ^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm): 21.50, 22.69 (aryl CH_3), 101.41 (ethynyl), 128.31, 128.98, 134.16, 134.36 (aryl), 130.64, 130.70, 131.73, 131.80, 137.56, 138.55 (thiophene), 131.92, 132.55, 132.90, 133.08, 139.10, 140.09 (pyrrole), 110.21, 114.30, 143.30, 157.89 (furyl), 145.29, 146.01, 146.20, 146.33, 154.33 (*meso*). ES MS: $C_{87}H_{54}N_4S_4O_3$, calcd av mass 1332.1, obsd m/z 1333.1 (M^++1, 30%). Anal. Calcd: C, 78.39; H, 4.08; N, 4.20; S, 9.62. Found: C, 78.48; H, 4.18; N, 4.32; S, 9.69.

4.1.11. 4-[5,10,15-Tris(4-tolyl)-20-porphinyl]-4′-[5,10,15-trifuryl-21-monothia-20-porphinyl]diphenylethyne (7). Samples of **14** (10.0 mg, 0.014 mmol) and 5-(4-iodophenyl)-10,15,20-tris(2-furyl)-21-monothiaporphyrin **2** (10.0 mg, 0.014 mmol) in dry toluene/triethylamine (3:1, 30 mL) were coupled in the presence of $AsPh_3$ (5.35 mg, 0.002 mmol) and $Pd_2(dba)_3$ (1.92 g, 0.002 mmol) at 35 °C for 12 h under nitrogen atmosphere. The crude reaction mixture was purified by column chromatography and the desired dyad **7** was collected using petroleum ether/dichloromethane (50:50). The solvent was removed on rotary evaporator under vacuum and dyad **7** was obtained as a purple solid (8.1 mg, 45%). Mp >300 °C. IR (KBr film, cm^{-1}): ν=3073, 2930, 2862, 2112, 1450, 990, 752. ^1H NMR (400 MHz, $CDCl_3$, δ in ppm): −2.38 (1H, s, NH), −2.78 (2H, s, NH), 2.73 (9H, s, CH_3), 7.11–7.13 (3H, m, furyl), 7.38–7.40 (3H, m, furyl), 7.54–7.56 (8H, m, aryl), 7.74–7.76 (4H, m, aryl), 8.09–8.11 (8H, m, aryl), 8.16–8.18 (3H, m, furyl), 8.84–8.86 (9H, m, β-pyrrole), 8.93–8.95 (5H, m, β-pyrrole), 9.75 (1H, s, β-thiophene), 10.12 (1H, s, β-thiophene). ^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm): 21.13, 21.61 (aryl CH_3), 102.11 (ethynyl), 124.74, 124.99, 128.14, 129.16, 131.33, 134.26 (aryl), 130.32, 130.44, 137.81, 138.44 (thiophene), 131.19, 131.49, 132.45, 132.65 (pyrrole), 109.23, 114.70, 144.53, 156.50 (furyl), 135.39, 136.45, 137.81, 139.80, 146.24, 147.86 (*meso*). HRMS: $C_{87}H_{57}N_7O_3S$, calcd av mass 1280.5210, obsd m/z 1280.5215 (M^+, 45%). Anal. Calcd: C, 81.60; H, 4.49; N, 7.66; S, 2.50. Found: C, 81.65; H, 4.54; N, 7.72; S, 2.59.

4.1.12. 4-[5,10,15-Tris(4-tolyl)-20-porphinyl]-4′-[5,10,15-trifuryl-21,23-dithia-20-porphinyl]diphenylethyne (8). Samples of **14** (20.0 mg, 0.03 mmol) and **3** (22.0 mg, 0.03 mmol) in dry toluene/triethylamine (3:1, 30 mL) were coupled in the presence of $AsPh_3$ (9.79 mg, 0.004 mmol) and $Pd_2(dba)_3$ (4.11 mg, 0.004 mmol) at 35 °C for 15 h. Column chromatography on silica using petroleum ether/dichloromethane (60:40) gave dyad **8** as purple solid (18.6 mg, 48%). Mp >300 °C. IR (KBr film, cm^{-1}): ν=3055, 2922, 2850, 2112, 1454, 990, 750. ^1H NMR (400 MHz, $CDCl_3$, δ in ppm): −2.70 (2H, br s, NH), 2.70 (9H, s, Me), 7.05–7.09 (3H, m, furyl), 7.42–7.46 (3H, m, furyl), 7.50–7.59 (10H, m, aryl), 8.04–8.14 (10H, m, aryl), 8.18–8.22 (3H, m, furyl), 8.71–9.04 (12H, m, β-pyrrole), 9.72–9.74 (1H, m, β-thiophene), 10.04 (1H, s, β-thiophene), 10.09–10.13 (2H, m, β-thiophene). ^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm): 21.11, 21.58 (aryl CH_3), 102.05 (ethynyl), 124.62, 124.79, 128.52, 130.06, 131.24, 134.11 (aryl), 130.32, 130.41, 137.81, 138.00 (thiophene), 131.15, 131.39, 132.60, 132.71, 133.28, 133.88 (pyrrole), 110.20, 114.82, 144.26, 156.25 (furyl), 135.41, 136.16, 137.70, 139.81, 146.20, 147.89 (*meso*). ES MS: $C_{87}H_{56}N_6O_3S_2$, calcd av mass 1297.4, obsd m/z 1296.7 (M^+, 50%). Anal. Calcd: C, 80.54; H, 4.35; N, 6.48; S, 4.94. Found: C, 80.61; H, 4.38; N, 6.42; S, 4.99.

4.1.13. 4-[5,10,15-Tris(4-tolyl)-21-monothia-20-porphinyl]-4′-[5,10,15-trifuryl-21,23-dithia-20-porphinyl]-diphenylethyne (9). A solution of **15** (15.0 mg, 0.02 mmol) and **3** (14.0 mg, 0.02 mmol) in dry toluene/triethylamine (3:1, 30 mL) was coupled in the presence of $AsPh_3$ (8.0 mg, 0.003 mmol) and $Pd_2(dba)_3$ (3.0 mg, 0.003 mmol) at 35 °C for 12 h. Column chromatography purification on silica gel using petroleum ether/dichloromethane (50:50) gave dyad **9** as a violet solid in 42% yield (12.0 mg). Mp >300 °C. IR (KBr film, cm^{-1}): ν=3065, 2925, 2853, 1965, 2110, 1648, 1465, 967, 800, 656, 620. ^1H NMR (400 MHz, $CDCl_3$, δ in ppm): −2.69 (1H, br s, NH), 2.68 (9H, s, CH_3), 7.04–7.06 (3H, m, furyl), 7.34–7.41 (8H, m, aryl), 7.50–7.54 (3H, m, furyl), 7.58–7.63 (4H, m, aryl), 7.90–7.98 (4H, m, aryl), 8.04–8.12 (4H, m, aryl), 8.16–8.22 (3H, m, furyl), 8.51–8.52 (6H, m, β-pyrrole), 8.92–9.01 (4H, m, β-pyrrole), 9.60–9.70 (4H, m, β-thiophene), 10.13–10.20 (2H, m, β-thiophene). ^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm): 21.69, 22.09 (aryl CH_3), 100.24 (ethynyl), 128.49, 129.06, 133.25, 134.29 (aryl), 130.01, 131.23, 131.47, 137.72, 138.55 (thiophene), 132.80, 132.55, 132.90, 134.54, 136.87, 139.26, 140.09 (pyrrole), 110.21, 114.30, 142.01, 157.72 (furyl), 145.29, 146.01, 146.20, 150.62, 154.67 (*meso*). ES MS: $C_{87}H_{55}N_5S_3O_3$, calcd av mass 1315.3, obsd m/z 1315.2 (M^+, 60%). Anal. Calcd: C, 79.45; H, 4.21; N, 5.32; S, 7.31. Found: C, 79.53; H, 4.28; N, 5.39; S, 7.39.

Acknowledgements

This research was supported by Department of Science and Technology and Department of Atomic Energy, Govt. of India, New Delhi. NMR and mass spectra were obtained at Department of Chemistry, IIT-Bombay.

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