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Synthesis of mono *meso*-pyridyl 21,23-dithiaporphyrins and unsymmetrical non-covalent porphyrin dimers

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Abstract—A new method has been developed to synthesize 21,23-dithiaporphyrins having one pyridyl group at the *meso* position. The method required easily available unknown precursors and the condensation resulted in mono *meso*-pyridyl 21,23-dithiaporphyrins as single products in 8–11% yield. Two of the three mono *meso*-pyridyl N_2S_2 porphyrins were used to synthesize non-covalent unsymmetrical porphyrin dimers containing one N_2S_2 and one N_4 porphyrin cores.

1. Introduction

Porphyrins and metalloporphyrins provide an advantageous class of building blocks for the construction of large multi-component architectures because of their relatively facile synthesis, stability and diversity of properties. Several synthetic strategies are employed for the assembly of multiporphyrin systems. A wide variety of porphyrin arrays of ever-increasing size have been constructed by the traditional methodology of covalently linking porphyrins.[1] More recently, the incorporation of porphyrins into porphyrin assemblies via non-covalent interactions has proven to be an attractive method for array formation.[2] By controlling the choice of materials, the supramolecular structure of the array can be engineered. To a large extent, the majority of the self-assembling porphyrin arrays are based on metal–ligand interactions and *meso*-pyridyl porphyrins play a key role in this kind of array. There are several reports available on non-covalent porphyrin assemblies connected via pyridyl groups which are mostly concerned with normal porphyrin (N_4 core) systems.[3] The core-modified porphyrins with cores such as N_3S, N_3O, N_2S_2, N_2O_2, N_2SO exhibit unique chemistry and different properties from N_4 porphyrin systems.[4] Core-modified porphyrins with functional groups such as iodophenyl, ethynyl phenyl, pyridyl etc at *meso* positions are suitable building blocks to synthesize unsymmetrical porphyrin arrays.[5] We recently prepared heteroporphyrins building blocks having two iodophenyl and ethynyl phenyl groups at *meso* positions in a *cis* fashion and used them to construct covalently linked energy donor appended systems.[6] We also prepared *cis*-pyridyl porphyrin building blocks with N_3S and N_3O porphyrin cores and synthesized non-covalent unsymmetrical trimers containing one N_3S and two N_4 porphyrin cores.[7] The porphyrins with one functional group are more desirable and available synthetic reports in the literature are useful only to synthesize mono-functionalized N_3S and N_3O porphyrins.[8] To the best of our knowledge, there are no reports available on mono-functionalized 21,23-dithiaporphyrins (N_2S_2 core). In this paper, we report the synthesis of three N_2S_2 porphyrins with one pyridyl group at the *meso* position (Chart 1) and its use to further construct two novel unsymmetrical non-covalent dimers having two different porphyrin cores. These are the first examples of non-covalent porphyrin dimers with N_2S_2 and N_4 porphyrin cores.

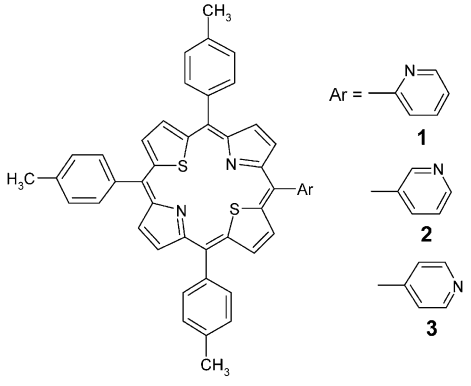

Chart 1. Mono *meso*-pyridyl 21,23-dithiaporphyrins.

Keywords: *meso*-Pyridyl porphyrins; Core-modified porphyrins; Non-covalent; Unsymmetrical array.
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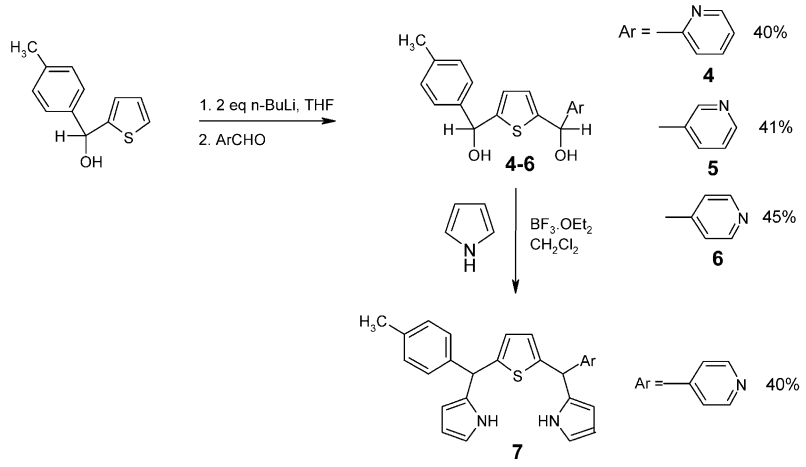


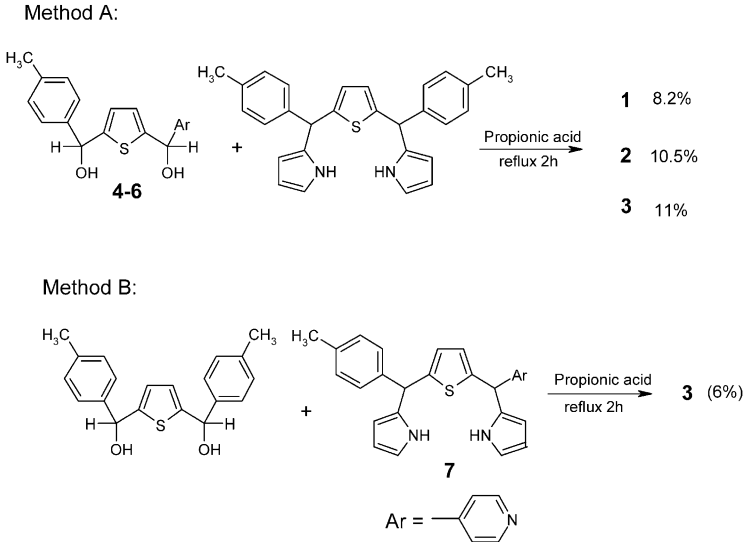
Scheme 1. General synthetic scheme of unsymmetrical diols **4–6** and unsymmetrical tripyrrin **7**.

2. Results and discussion

2.1. Unsymmetrical thiophene diols 4–6 and unsymmetrical tripyrrin 7

To synthesize mono *meso*-pyridyl 21,23-dithiaporphyrins, the unknown key precursors such as unsymmetrical thiophene diols and unsymmetrical 16-thiatripyrrins were required. The unsymmetrical thiophene diols **4–6** were synthesized in two steps starting with thiophene (Scheme 1). The desired thiophene mono-ol, 2-(*p*-tolylhydroxymethyl) thiophene[8b] was prepared by treating thiophene with 1 equiv. of *n*-BuLi followed by addition of 1.2 equiv. of *p*-tolualdehyde in THF at 0 °C. The TLC analysis of the crude mixture indicated the formation of desired mono-ol along with symmetrical diol and unreacted aldehyde. The mono-ol was separated from the mixture by column chromatography and afforded mono-ol in 65% yield. The thiophene mono-ol was then treated with 2 equiv. of *n*-BuLi followed by addition of pyridine 2- or 3- or 4-carboxaldehyde in THF at 0 °C. After work-up, the crude mixture containing the desired unsymmetrical diol along with some unreacted mono-ol and aldehyde was subjected to silica gel column chromatography. Since the unsymmetrical diols have two chiral centres, the TLC analysis showed the presence of an additional minor spot close to the major diol spot, which might be due to its diastereomer. However, we collected the major spot and used it for porphyrin reactions. Because the chirality is lost on porphyrin formation, no attempts were made to characterize the minor spot. The diols **4** and **5** were obtained in 40% yields and diol **6** was afforded as semi-solid in 45% yield. The unsymmetric nature of diols was clearly evident in their ^{1}H NMR spectra. The thiophene and CH protons which appear as singlets in the symmetrical diol[9] appeared as multiplets in diols **4–6** due to unsymmetrical substitution.

The unsymmetrical 16-thiatripyrrin **7** was prepared by treating 1 equiv. of unsymmetrical diol **6** with 40 equiv. of pyrrole in CH_2Cl_2 in the presence of a catalytic amount of $BF_3 \cdot OEt_2$ (Scheme 1). The excess pyrrole was removed under vacuum and the TLC analysis showed only one major spot along with polymeric material at the bottom of the TLC plate. The crude compound was subjected to silica gel column chromatography and afforded **7** in 40% yield. The unsymmetric nature of **7** was clearly established by the



Scheme 2. Two general synthetic schemes for the preparation of mono *meso*-pyridyl 21,23-dithiaporphyrins **1–3**.

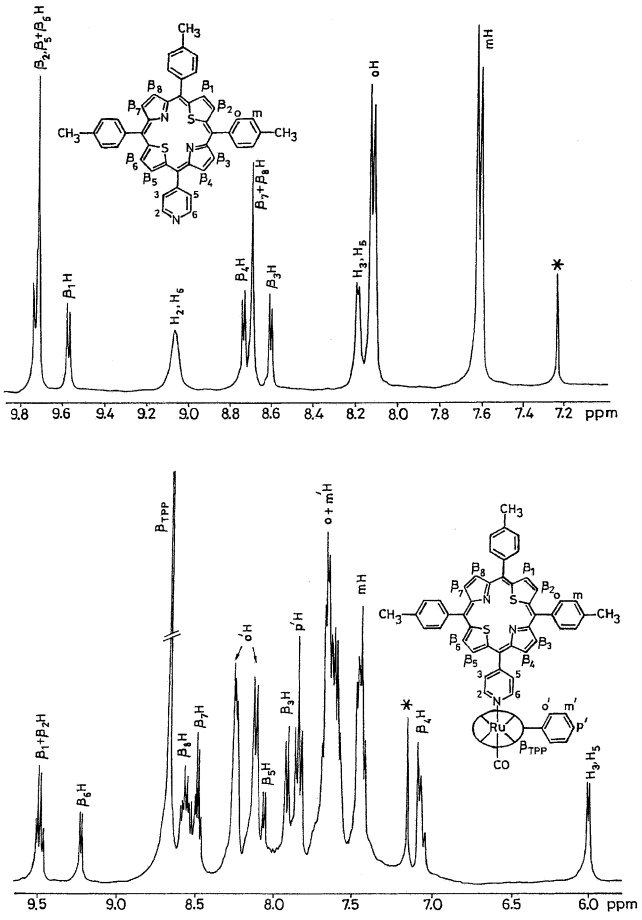


Figure 1. ^{1}H NMR spectra of **3** (top) and dimer **9** (bottom) recorded in $CDCl_3$.

splitting of thiophene and CH signals in the ^{1}H NMR spectra which appears as a singlet in symmetrical 16-thiatripyrrin.[10] The M^+ ion peak in the mass spectrum also confirmed the product.

2.2. Mono *meso*-pyridyl 21,23-dithiaporphyrins 1–3

To synthesize 21,23-dithiaporphyrins **1–3** with one 2- or 3- or 4-pyridyl functional group at the *meso* position (Chart 1), we followed any one of the two methods (Method A and B) shown in Scheme 2. Porphyrins **1–3** were synthesized by condensing 1 equiv. of unsymmetric thiophene diols **4–6**, respectively with 1 equiv. of the symmetrical 16-thiatripyrrin (5,10-ditolyl-16-thia-15,17-dihydrotripyrrin)[10] in propionic acid at refluxing temperature for 2 h (Method A). The propionic acid was removed under vacuum and washed thoroughly with slight warm water and dried in an oven at 100 °C. The crude black compounds of **1–3** were passed through silica gel column eluting with CH_2Cl_2/2%CH_3OH to remove the non-porphyrinic materials. The TLC analysis after the first column indicated the formation of the desired compound as the sole product. The crude compounds were subjected to second silica gel column chromatography using CH_2Cl_2 and the pure porphyrins were afforded as purple solids in 8–11% yields. Alternately porphyrin **3** was also prepared using unsymmetrical 16-thiatripyrrin **7**. One equivalent of unsymmetrical 16-thiatripyrrin **7** was condensed with 1 equiv. of symmetrical thiophene diol (2,5-(*p*-tolylhydroxymethyl) thiophene)[9] in propionic acid at refluxing temperature for 2 h (Method B). The crude compound obtained after usual work-up was purified by column chromatography and afforded **3** in 6% yield. Thus by following the method B, the porphyrin **3** was afforded in much lower yield than method A. Hence the synthesis of porphyrins **1** and **2** were not attempted using method B. However, both the methods are clean and the desired compounds were obtained as the single product. No scrambling was observed in these reactions.

The porphyrins **1–3** were characterized by ^{1}H and ^{13}C NMR spectroscopy, mass spectrometry, elemental analysis, infrared and absorption spectroscopies. The ^{1}H NMR spectrum of porphyrin **3** is presented in Figure 1(top) and the data of selected protons are presented in Table 1. In the ^{1}H NMR spectra, the thiophene and pyrrole protons of **1–3** appeared as two or three signals unlike S_2TPP[4] in which they appear as singlets. This is due to the unsymmetric substitution of porphyrins **1–3**. The presence of strong *m*/*z* peak at 692 confirmed the product. The absorption spectra of **1–3** showed four Q-bands (Fig. 2) and one Soret band and the extinction coefficients were almost comparable to that of S_2TPP (Table 2).

2.3. Non-covalent unsymmetrical dimers 8 and 9

Porphyrins with pyridyl groups at *meso* positions are ideal building blocks to synthesize non-covalent porphyrin arrays.[2,3] Since the heteroporphyrins with pyridyl groups at *meso*-positions are very few,[7,11] the chemistry remained unexplored. In general, *meso*-pyridyl N_4 porphyrins form non-covalent porphyrin arrays by co-ordinating with different metalloporphyrins (M=Zn, Mg, Ru, Rh etc.). However, our earlier study[7] with *cis*-pyridyl heteroporphyrins with N_3S cores showed that the N_3S porphyrins prefers to form non-covalent trimers with RuTPP(CO)(EtOH) but not with ZnTPP. Furthermore, *cis*-pyridyl N_3O porphyrins did not form non-covalent arrays with any metalloporphyrin. Thus, the chemistry of *meso*-pyridyl heteroporphyrins are core dependent and quite different from N_4 porphyrins.

The mono *meso*-pyridyl N_2S_2 porphyrins **1–3** were explored to construct non-covalent unsymmetrical dimers containing one N_2S_2 and one N_4 porphyrin cores. To synthesize unsymmetrical dimer **8**, we treated 1 equiv. of **2** with

Table 1. ^{1}H NMR Spectroscopy chemical shifts (δ in ppm) of selected protons in $CDCl_3$

Porphyrin	β-Pyrrole	β-Thiophene	2,6-Pyridyl	3,5/3,4-Pyridyl
2	8.61(d), 8.69(s), 8.75(d)	9.58(d), 9.71(s), 9.73(d)	9.06(bs), 9.50(bs)	7.80(m), 8.55(d)
8	6.84(d), 8.16(d), 8.64(d)	8.30(d), 9.38(d), 9.58(d), 9.62(d)	1.90(d), 2.22(s)	6.98(t), 7.38(d)
3	8.60(d), 8.69(s), 8.73(d)	9.57(d), 9.73(m)	9.07(bs)	8.19(m)
9	7.08(d), 7.92(d), 8.50(d), 8.58 (d)	8.06(d), 9.21(d), 9.47(d), 9.50(d)	1.92(d)	6.00(d)

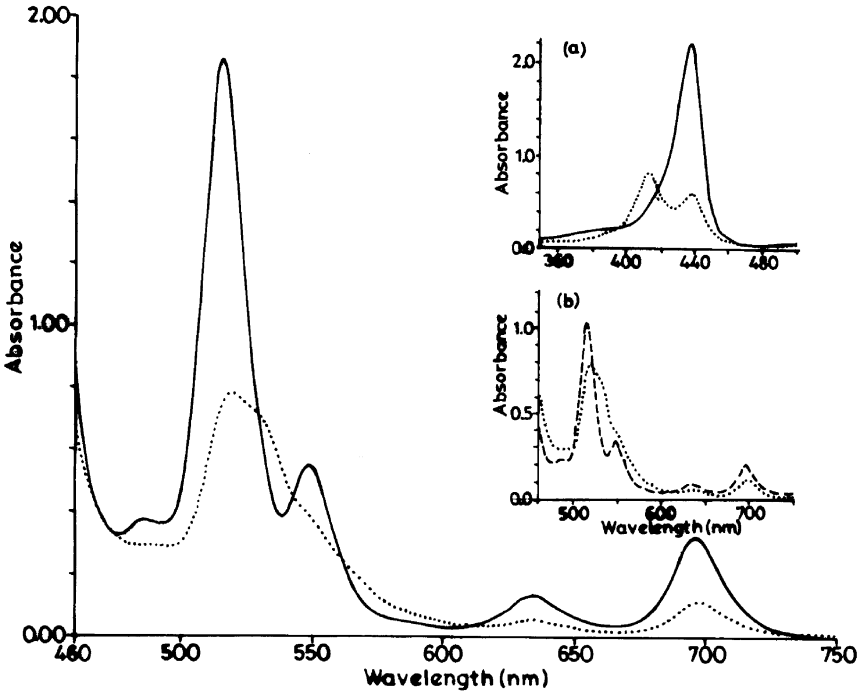
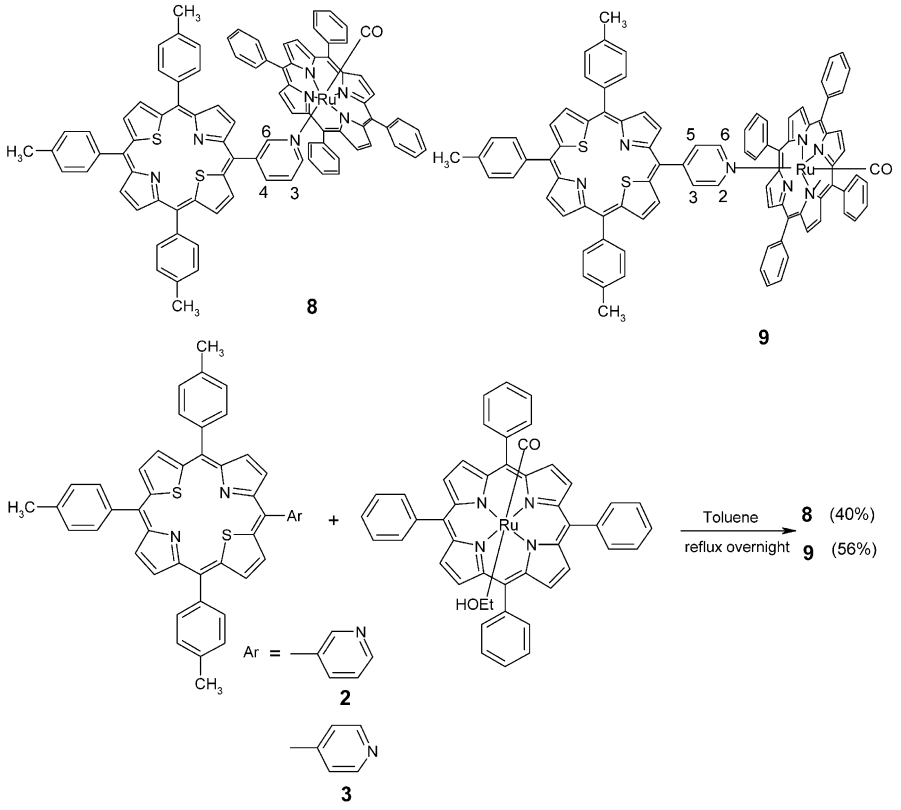


Figure 2. Q-bands and Soret band (inset a) absorption spectra of **3** (solid line) and **9** (dotted line). The inset b shows the absorption spectra of dimer **9** (dotted line) and 1:1 mixture of **3** and RuTPP(CO)(EtOH) (dashed line). All were recorded in toluene and the concentrations used were: Soret band, 5×10^{-6} M; and Q-bands, 5×10^{-5} M.

1 equiv. of RuTPP(CO)(EtOH) in toluene at refluxing temperature for 12 h (Scheme 3). As the reaction progressed, the colour of the reaction mixture changed from bright red to brownish red. The reaction progress was monitored with TLC and the reaction was stopped after complete disappearance of **2** as judged by TLC. The solvent was removed under vacuum and the crude compound was subjected to silica gel column chromatography using petroleum ether/dichloromethane (80:20). The fast moving unreacted RuTPP(CO)(EtOH) was removed and the desired dimer **8** was then collected with petroleum ether/dichloromethane (60:40) as a purple solid in 40% yield. Similarly, treating the porphyrin **3** with RuTPP(CO)(EtOH) under same conditions gave the dimer **9** in 56% yield (Scheme 3). Interestingly, porphyrin **1** did not form any dimer which may be due to steric hindrance. Furthermore, porphyrins **1**–**3** when treated with ZnTPP under different reaction conditions also did not form a dimer. The dimers **8** and **9** were highly soluble in most organic solvents and characterized by NMR spectroscopy, mass spectrometry, elemental analysis, infrared and Uv–visible spectroscopy. The ^{1}H NMR spectrum of dimer **9** comparing with monomer **3** shown in Figure 1 clearly demonstrated the formation of dimer. The signals of dimers **8** and **9** were composed of the parts of RuTPP and N_2S_2 porphyrin **2** and **3** respectively. The pyrrole and phenyl protons of the RuTPP part of dimers **8** or **9** appeared at almost the same chemical shifts of starting monomer RuTPP(CO)(EtOH). It is well-known that the porphyrin ring current changes the chemical shifts of the protons located near the porphyrin plane. The protons of mono pyridyl N_2S_2 porphyrin were shifted upfield from its parent porphyrin because of the RuTPP ring current. The pyrrole and thiophene protons of N_2S_2 porphyrin unit of dimers **8** and **9** were shifted upfield compared to their corresponding monomers **2** and **3**, respectively (Fig. 1 and Table 1). However, the maximum upfield shifts were observed for the 2,6- and 3,4-/3,5-pyridyl protons of the N_2S_2 porphyrin unit implying the coordination of pyridyl

Table 2. Absorption data of mono *meso*-pyridyl 21,123-dithiaporphyrins recorded in toluene

Porphyrin	Soret band λ (nm) ($\varepsilon\times10^{-4}$)	Absorption Q-bands λ (nm) ($\varepsilon\times10^{-3}$)			
		IV	III	II	I
1	437 (28.5)	515 (28.4)	549 (8.2)	634 (2.2)	697 (4.8)
2	437 (13.1)	515 (13.4)	549 (5.0)	634 (1.4)	697 (2.5)
3	437 (37.5)	515 (32.2)	549 (9.6)	634 (2.4)	697 (5.6)
8	438 (136.5)	520 (19.3)	552 (9.9)	635 (1.7)	698 (3.1)
	412 (204.3)	531 (sh)	567 (sh)		
1:1 Mixture of **2** and RuTPP(CO)(EtOH)	437 (128.6)	516 (15.5)	548 (7.7)	633 (2.4)	697 (3.3)
	413 (67.1)				
9	437 (204.2)	519 (28.1)	550 (sh)	634 (2.1)	697 (4.1)
	412 (292.9)	531 (sh)	567 (sh)		
1:1 Mixture of **3** and RuTPP(CO)(EtOH)	437 (217.1)	515 (26.8)	548 (8.8)	633 (2.5)	697 (5.1)
	411 (66.3)				



Scheme 3. Synthetic scheme for the preparation of non-covalent unsymmetrical dimer **8** and **9**.

group with central ruthenium ions. The large upfield shifts of 2,6-pyridyl protons compared with 3,4-/3,5-pyridyl protons indicate that these protons experienced large ring current effect of RuTPP because of their proximity to the RuTPP core. The elemental analysis and mass data were in agreement with dimer formation. IR measurements showed the $\nu_{(CO)}$ stretch at 1943 cm^{-1}. The absorption spectra of dimers **8** and **9** were compared with 1:1 mixture of RuTPP(CO)(EtOH) and **2** and **3**, respectively. The absorption spectra indicated that the dimers exhibited bands corresponding to both the units whereas, 1:1 mixture showed bands corresponds mainly to the mono-pyridyl N_2S_2 porphyrin unit. Furthermore, in the dimer **8** or **9**, the extinction coefficient of the Soret band of RuTPP unit was three times to that of the RuTPP unit of a 1:1 mixture, supporting the co-ordination of the pyridyl group of N_2S_2 porphyrin to the central ruthenium ion of the Ru(TPP)(CO) (Table 2).

3. Conclusions

In summary, we synthesized mono *meso*-pyridyl 21,23-dithiaporphyrins using readily available precursors. The porphyrins were obtained as single products in good yields by following any one of the two methods mentioned in this paper. The mono-*meso*-pyridyl porphyris were used to construct the non-covalent unsymmetrical porphyrin dimers containing N_4 and N_2S_2 porphyrin units. We are presently exploring the synthesis of other mono-functionalized 21,23-dithiaporphyrin building blocks for the synthesis of unsymmetrical covalent dimers using the methodology reported in this paper.

4. Experimental

4.1. General

^1H and ^{13}C NMR spectra were recorded using a Varian 400 MHz instrument using tetramethylsilane as an internal standard. Absorption and fluorescence spectra were obtained with Perkin–Elmer Lambda-35 and Lambda-55 instruments, respectively. The IR spectra were recorded with a Nicolet Impact-400 FT-IR spectrometer and the ES MS mass spectra were recorded with a Q-Tof micro (YA-105) mass spectrometer. Toluene, THF and diethylether were obtained from S.D. Fine chemicals, India, and were dried by standard procedures before use. All general chemicals were obtained from Qualigens, India. *p*-Tolualdehyde, thiophene, pyrrole, pyridine carboxaldehydes were obtained from Lancaster. Column chromatography was performed using 60–120 mesh silica obtained from Sisco Research Laboratories, India.

4.1.1. 2-(2-Pyridylhydroxymethyl)-5-(*p*-tolylhydroxymethyl) thiophene (4). A distilled diethylether (30 mL) was taken in a dry 250 mL three necked round-bottomed flask equipped with a rubber septum, gas inlet and gas outlet tube and a positive pressure of N_2 was maintained. A monool (2-(*p*-tolylyhydroxymethyl) thiophene) (1 g, 4.90 mmol) followed by *n*-BuLi (6.1 mL of ca. 15% solution in hexane) were added to it at 0 °C and stirring was continued for 1 h.

Then the ice-cold solution of 2-pyridine carboxaldehyde (0.93 mL, 9.79 mmol) in dry THF (20 mL) was added to the stirred solution. The reaction mixture was stirred at 0 °C for 15 min and then brought to room temperature. The reaction was quenched by adding an ice-cold NH_4Cl solution (50 mL, ca. 1 M). The organic layer was washed with water and brine solution and dried 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 2-pyridine carboxaldehyde, unreacted mono-ol and the desired diol **4**. In addition to the major spot of diol, we have also noted one minor spot just above the major diol spot, which was not characterized. The aldehyde, the mono-ol and the minor unidentified fractions were removed by silica gel column chromatography (1–3% CH_3OH/CH_2Cl_2) and the major diol fraction **4** was collected (609 mg, 40%) with 4% CH_3OH/CH_2Cl_2 as a white solid, mp 121–122 °C; [Found: C, 69.19; H, 5.20; N, 4.32; S, 10.11. $C_{18}H_{17}NO_2S$ requires C, 69.43; H, 5.50; N, 4.50; S, 10.30%]; R_f (4% CH_3OH/CH_2Cl_2) 0.51; ν_{max} (KBr) 3457, 3357, 3059, 2871, 1488, 1437, 1054, 806, 760, 692 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 8.52–8.55 (1H, bs, pyridyl), 7.66 (1H, t, $J=7.5$ Hz, pyridyl), 7.28 (2H, d, $J=8.1$ Hz, *o*-tolyl), 7.20–7.22 (2H, m, pyridyl), 7.13 (2H, d, $J=8.1$ Hz, *m*-tolyl), 6.83 (1H, d, $J=4.4$ Hz, thiophene), 6.70 (1H, d, $J=4.4$ Hz, thiophene), 5.91 (2H, s, C*H*OH), 2.32 (3H, s, *Me*); δ_C (400 MHz, $CDCl_3$) 148.2, 147.6, 140.2, 137.8, 137.6, 129.3, 126.4, 126.3, 125.0, 124.5, 123.1, 121.6, 72.5, 70.9, 21.3; ES MS 312 (8 MH^+), 295 (12), 294 (100), 175 (10), 119 (18%).

4.1.2. 2-(3-Pyridylhydroxymethyl)-5-(*p*-tolylhydroxymethyl) thiophene (5). To a three-necked 250 mL round-bottomed flask containing mono-ol (1 g, 4.90 mmol) in ether (30 mL), was added *n*-BuLi (6.1 mL of a 15% solution in hexane) under the same experimental conditions as mentioned above. 3-Pyridine carboxaldehyde (0.93 mL, 9.67 mmol) in dry THF (20 mL) was added slowly to the reaction mixture followed by workup and chromatography to afford the desired diol **5** (624 mg, 41%) as a white solid, mp 120–122 °C; [Found: C, 69.12; H, 5.25; N, 4.37; S, 10.20. $C_{18}H_{17}NO_2S$ requires C, 69.43; H, 5.50; N, 4.50; S, 10.30%]; R_f (4% CH_3OH/CH_2Cl_2) 0.48; ν_{max} (KBr) 3440, 3352, 3050, 3020, 2868, 1600, 1481, 1432, 809, 761, 692 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 8.23 (1H, bs, pyridyl), 8.16–8.18 (1H, m, pyridyl), 7.58–7.60 (1H, m, pyridyl), 7.21 (2H, d, $J=8.2$ Hz, *o*-tolyl), 7.04–7.06 (1H, m, pyridyl), 7.01 (2H, d, $J=8.2$ Hz, *m*-tolyl), 6.52 (1H, d, $J=4.4$ Hz, thiophene), 6.49 (1H, d, $J=4.4$ Hz, thiophene), 5.76 (2H, s, C*H*OH), 2.24 (3H, s, *Me*); δ_C (400 MHz, $CDCl_3$) 149.6, 147.9, 147.2, 144.7, 137.5, 134.9, 129.1, 128.3, 124.7, 124.3, 123.7, 123.5, 71.9, 69.7, 21.3; *m*/*z* (ES MS) 312 (8 MH^+), 294 (100), 219 (12), 174 (15), 119 (10), 102 (17%).

4.1.3. 2-(4-Pyridylhydroxymethyl)-5-(*p*-tolylhydroxymethyl) thiophene (6). The diol **6** was prepared following the same method given for diols **4** and **5** by adding *n*-BuLi (6.1 mL of a 15% solution in hexane) to mono-ol (1 g, 4.90 mmol) in diethylether (30 mL) followed by ice cold solution of 4-pyridine carboxaldehyde (0.93 mL, 9.79 mmol) in dry THF (20 mL). Purification of the crude product by silica gel column chromatography (4% CH_3OH/CH_2Cl_2) gave the desired diol **6** (685 mg, 45%) as an off-white semi-solid, mp 125–126 °C; [Found: C, 69.28; H, 5.41; N, 4.30; S, 10.18. $C_{18}H_{17}NO_2S$ requires C, 69.43; H, 5.50; N, 4.50; S, 10.30%]; R_f (4% CH_3OH/CH_2Cl_2) 0.47; ν_{max} (KBr) 3457, 3350, 3050, 3022, 2872, 1484, 1438, 1050, 806, 760, 692 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 8.18 (2H, d, $J=8.8$ Hz, pyridyl), 7.21–7.25 (4H, m, tolyl), 7.06 (2H, d, $J=8.8$ Hz, pyridyl), 6.62 (1H, d, $J=5.2$ Hz, thiophene), 6.59 (1H, d, $J=5.2$ Hz, thiophene), 5.82 (2H, s, C*H*OH), 2.27 (3H, s, *Me*); δ_C (400 MHz, $CDCl_3$) 148.6, 146.4, 146.2, 140.7, 137.4, 129.4, 126.3, 124.7, 124.3, 123.1, 121.4, 71.9, 70.4, 21.1; *m*/*z* (ES MS) 312 (5 MH^+), 294 (100), 194 (32%).

4.1.4. 5-(4-Pyridyl)-10-(*p*-tolyl)15,17-dihydro-16-thiatripyrrin (7). A mixture of **6** (500 mg, 1.61 mmol) and pyrrole (4.5 mL, 64.3 mmol) were degassed by bubbling with N_2 for 10 min. $BF_3 \cdot OEt_2$ (202 μL, 1.61 mmol) was added and the reaction mixture was stirred for 30 min at room temperature. The solution was diluted with CH_2Cl_2 (100 mL), then washed with 0.1 M NaOH, followed by water. 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. TLC analysis of the crude mixture showed no other product formation except small amounts of polymeric material at the origin. The resulting dark yellow viscous liquid was purified by column chromatography (silica gel 60–120 mesh, ethyl acetate/petroleum ether (50:50) to afford tripyrrin **7** (263 mg, 40%) as an orange oily liquid; [Found: C, 76.44; H, 5.46; N, 10.10; S, 7.70. $C_{26}H_{23}N_3S$ requires C, 76.24; H, 5.66; N, 10.26; S, 7.83%]; R_f (50% ethyl acetate/petroleum ether) 0.49; ν_{max} (KBr) 3403, 3290, 3091, 2968, 2864, 1615, 1602, 1462, 1072, 861, 762, 741 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 8.40 (2H, d, $J=8.0$ Hz, pyridyl), 8.30 (2H, bs, N*H*), 7.60 (2H, d, $J=8.0$ Hz, pyridyl) 7.09–7.11 (4H, m, tolyl), 6.71–6.73 (4H, m, pyrrole), 6.54–6.56 (2H, m, pyrrole), 6.05 (1H, s, thiophene), 5.84 (1H, s, thiophene), 5.81 (1H, s, C*H*), 5.46 (1H, s, C*H*), 2.27 (3H, s, *Me*); δ_C (400 MHz, $CDCl_3$) 150.2, 147.7, 145.9, 137.3, 136.7, 133.3, 128.3, 128.2, 125.3, 122.9, 122.4, 121.3, 117.2, 108.2, 107.3, 45.7, 36.9, 21.1; *m*/*z* (ESMS) 409 (100 $M-H^+$), 394 (40), 252 (8), 237 (15), 239 (10), 169 (12%).

4.1.5. 5-(2-Pyridyl)-10,15,20-tris(*p*-tolyl)-21,23-dithiaporphyrin (1). A solution of **4** (367 mg, 1.18 mmol) and symmetrical 16-thiatripyrrin (5,10-ditolyl-16-thia-15,17-dihydrotripyrrin) (500 mg, 1.18 mmol) in 125 mL of propionic acid was refluxed for 3 h. The progress of the reaction was checked by absorption spectroscopy, which showed bands characteristic of the desired porphyrin. The excess propionic acid was removed under vacuum and the resultant black solid was washed several times with warm water and dried in an oven at 100 °C. The crude product was then purified by silica gel column chromatography using CH_3OH/CH_2Cl_2 (2:98) as eluent, to afford the desired porphyrin **1** (67 mg, 8.2%) as a purple solid, mp > 300 °C; [Found: C, 80.03; H, 4.95; N, 6.24; S, 9.44. $C_{46}H_{33}N_3S_2$ requires C, 79.82; H, 4.92; N, 6.07; S, 9.25%]; R_f (2% CH_3OH/CH_2Cl_2) 0.44; ν_{max} (KBr) 2929, 2864, 1456, 976, 794; δ_H (400 MHz, $CDCl_3$) 9.70–9.73 (4H, m, β-thiophene), 9.20–9.22 (1H, bs, pyridyl), 8.69–8.71 (4H, m, β-pyrrole), 8.27–8.29 (2H, m, pyridyl), 8.12–8.14 (6H, m, *o*-tolyl), 7.71–7.73 (1H, m, pyridyl), 7.60–7.62 (6H, m, *m*-tolyl),

2.70 (9H, s, *Me*); δ_C (400 MHz, $CDCl_3$) 156.8, 149.5, 148.4, 147.9, 147.6, 138.4, 137.9, 136.2, 135.7, 135.0, 134.8, 134.5, 131.2, 130.3, 129.5, 128.3, 128.0, 122.6, 21.6; *m/z* (ES MS) 692 (100% M^+).

4.1.6. 5-(3-Pyridyl)-10,15,20-tris(*p*-tolyl)-21,23-dithiaporphyrin (2). Condensation of **5** (367 mg, 1.18 mmol) with symmetrical 16-thiatripyrrin (500 mg, 1.18 mmol) in propionic acid (125 mL) using similar reaction and purification methods as mentioned for **1**, gave the desired porphyrin **2** (86 mg, 10.5%) as a purple solid, mp > 300 °C; [Found: C, 79.64; H, 4.77; N, 6.20; S, 9.11. $C_{46}H_{33}N_3S_2$ requires C, 79.82; H, 4.92; N, 6.07; S, 9.25%]; R_f (2% CH_3OH/CH_2Cl_2) 0.46; ν_{max} (KBr) 2926, 2860, 1450, 982, 794; δ_H (400 MHz, $CDCl_3$) 9.73 (1H, d, $J=5.1$ Hz, β-thiophene), 9.71 (2H, s, β-thiophene), 9.58 (1H, d, $J=5.1$ Hz, β-thiophene), 9.50 (1H, bs, pyridyl), 9.06 (1H, bs, pyridyl), 8.74–8.76 (1H, d, $J=4.5$ Hz, β-pyrrole), 8.69 (2H, s, β-pyrrole), 8.61 (1H, d, $J=4.5$ Hz, β-pyrrole), 8.55 (1H, d, $J=7.5$ Hz, pyridyl), 8.13–8.15 (6H, m, *o*-tolyl), 7.79–7.81 (1H, m, pyridyl), 7.60–7.62 (6H, m, *m*-tolyl), 2.70 (9H, s, *Me*); δ_C (400 MHz, $CDCl_3$) 156.7, 153.3, 149.1, 148.4, 148.1, 147.9, 147.7, 141.2, 140.1, 136.1, 135.9, 135.3, 134.8, 134.3, 133.7, 128.9, 128.3, 128.0, 122.8, 21.6; *m/z* (ES MS) 692 (100% M^+).

4.1.7. 5-(4-Pyridyl)-10,15,20-tris(*p*-tolyl)-21,23-dithiaporphyrin (3). Condensation of **6** (367 mg, 1.18 mmol) with symmetrical 16-thiatripyrrin (500 mg, 1.18 mmol) in propionic acid (125 mL) using similar reaction and purification methods as mentioned for **1**, gave the desired porphyrin **3** (90 mg, 11%) as a purple solid. The compound **3** was also prepared by following method B. Condensation of 2,5-bis (*p*-tolylhydroxymethyl) thiophene (200 mg, 0.617 mmol) with 5-(4-pyridyl)-10-(*p*-tolyl)-15,17-dihydro-16-thiatripyrrin **7** (253 mg, 0.617 mmol) in propionic acid followed by chromatography gave **3** (26 mg, 6.1%) as a purple solid, mp > 300 °C; [Found: C, 79.71; H, 4.77; N, 6.28; S, 9.10. $C_{46}H_{33}N_3S_2$ requires C, 79.82; H, 4.92; N, 6.07; S, 9.25%]; R_f (2% CH_3OH/CH_2Cl_2) 0.50; ν_{max} (KBr) 2930, 2860, 1455, 982, 798; δ_H (400 MHz, $CDCl_3$) 9.72–9.74 (3H, m, β-thiophene), 9.57 (1H, d, $J=5.2$ Hz, β-thiophene), 9.07 (2H, bs, pyridyl), 8.73 (1H, d, $J=4.8$ Hz, β-pyrrole), 8.69 (2H, s, β-pyrrole), 8.60 (1H, d, $J=4.8$ Hz, β-pyrrole), 8.18–8.19 (2H, m, pyridyl), 8.12–8.14 (6H, m, *o*-tolyl), 7.61–7.63 (6H, m, *m*-tolyl), 2.69 (9H, s, *Me*); δ_C (400 MHz, $CDCl_3$) 157.0, 156.6, 155.1, 150.9, 149.8, 148.7, 148.5, 147.6, 146.9, 138.0, 136.1, 135.7, 135.1, 134.9, 134.7, 133.6, 129.5, 128.3, 21.6; *m/z* (ES MS) 692 (100% M^+).

4.1.8. Unsymmetrical non-covalent dimer (8). The dithiaporphyrin building block, **2** (20 mg, 0.0289 mmol) was dissolved in 30 mL of toluene in a two necked 100 mL round-bottomed flask and was purged with N_2 for 10 min. RuTPP(CO)(EtOH) (23 mg, 0.0289 mmol) was then added and the solution was refluxed with stirring overnight. The reaction was monitored with TLC and absorption spectroscopy. The TLC analysis after 12 h showed complete consumption of **2**, and absorption spectroscopy showed characteristic splittings and shifts in soret and in Q-bands. The heating was stopped and the solvent was removed under reduced pressure. The crude compound was purified by silica gel column chromatography using petroleum ether/dichloromethane (60:40) as solvent and afforded dimer **8** (17 mg, 40%) as a purple solid, mp > 300 °C; [Found: C, 76.30; H, 4.50; N, 6.70; S, 4.50. $C_{46}H_{33}N_3S_2$ requires C, 76.36; H, 4.29; N, 6.84; S, 4.47%]; R_f (60% pet ether/dichloromethane) 0.48; ν_{max} (KBr) 2930, 2858, 1943, 1443, 1358, 1267, 1177, 1021, 800, 755; δ_H (400 MHz, $CDCl_3$) 9.62 (1H, d, $J=4.8$ Hz, β-thiophene), 9.58 (1H, d, $J=4.8$ Hz, β-thiophene), 9.38 (1H, d, $J=4.8$ Hz, β-thiophene), 8.77 (8H, s, β-pyrrole of TPP), 8.64 (1H, d, $J=5.0$ Hz, β-pyrrole of **2**), 8.54 (4H, d, $J=8$ Hz, o'-Ph of TPP), 8.50 (4H, d, $J=8$ Hz, o'-Ph of TPP), 8.30 (1H, d, $J=4.8$ Hz, β-thiophene), 8.14 (2H, d, $J=5.2$ Hz, β-pyrrole of **2**), 7.58–7.64 (14H, m, *o*-tolyl of **2** + *m*-Ph of TPP), 7.42–7.50 (10H, m, *m*-tolyl of **2** + p'-Ph of TPP), 7.38 (1H, d, $J=4.4$ Hz, 4-pyridyl), 6.98 (1H, t, $J=2.0$, 4.4 Hz, 3-pyridyl), 6.84 (1H, d, $J=5.0$ Hz, β-pyrrole of **2**), 2.65 (9H, s, *Me*), 2.22 (1H, s, 6-pyridyl), 1.90 (1H, d, $J=2.0$ Hz, 2-pyridyl); δ_C (400 MHz, $CDCl_3$) 157.2, 156.0, 153.4, 152.0, 150.9, 148.5, 147.9, 147.6, 146.3, 146.1, 145.8, 144.5, 143.9, 142.7, 141.5, 139.2, 138.0, 136.7, 135.7, 134.6, 134.1, 132.5, 131.6, 128.9, 128.4, 125.3, 123.6, 120.3, 22.8, 21.6; *m/z* (ES MS) 1435 (15 M^+), 741 (40), 713 (10), 692 (100%).

4.1.9. Unsymmetrical non-covalent dimer (9). Compound **3** (20 mg, 0.0289 mmol) was treated with RuTPP(CO)(EtOH) (23 mg, 0.0289 mmol) in toluene under the same reaction condition as for **8** to yield the dimer **9** (23 mg, 56%) as a purple solid, mp > 300 °C; ν_{max} (KBr) 1943 (CO); δ_H (400 MHz, $CDCl_3$) 9.50 (1H, d, $J=4.8$ Hz, β-thiophene), 9.47 (1H, d, $J=4.8$ Hz, β-thiophene), 9.21 (1H, d, $J=4.8$ Hz, β-thiophene), 8.66 (8H, s, β-pyrrole of TPP), 8.58 (1H, d, $J=5.2$ Hz, β-pyrrole of **3**), 8.50 (1H, d, $J=5.2$ Hz, β-pyrrole of **3**), 8.20–8.30 (4H, m, o'-ph of TPP), 8.10–8.18 (4H, m, o'-phl of TPP), 8.06 (1H, d, $J=4.8$ Hz, β-thiophene), 7.92 (1H, d, $J=5.2$ Hz, β-pyrrole of **3**), 7.84 (4H, t, $J=7.6$ Hz, *p*-ph of TPP), 7.58–7.70 (m, m'-ph of TPP + *o*-tolyl of **3**), 7.43–7.47 (6H, m, *m*-tolyl of **3**), 7.08 (1H, d, $J=5.2$ Hz, β-pyrrole of **3**), 6.00 (2H, d, $J=2.4$ Hz, 3,5-pyridyl), 2.61 (6H, s, *Me*), 2.26 (3H, s, *Me*), 1.92 (2H, d, $J=2.4$ Hz, 2,6-pyridyl); δ_C (400 MHz, $CDCl_3$) 157.0, 156.6, 153.4, 152.2, 150.9, 149.8, 148.5, 147.6, 156.9, 146.3, 145.8, 143.9, 142.7, 141.5, 139.7, 139.2, 138.0, 136.1, 135.8, 134.1, 132.6, 132.1, 131.1, 129.0, 128.4, 126.3, 123.0, 119.3, 22.8, 21.6; *m/z* (ES MS) 1435 (17 M^+), 713 (10), 692 (100%).

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