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# *cis*-Pyridyl core-modified porphyrins for the synthesis of cationic water-soluble porphyrins and unsymmetrical non-covalent porphyrin arrays

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**Abstract**—Synthesis of a series of 21-thia and 21-oxoporphyrin building blocks containing two pyridyl functional groups at the *meso* positions in a *cis* fashion is reported. The building blocks were used to synthesize a series of cationic water-soluble 21-thia and 21-oxoporphyrins. An unsymmetrical non-covalent trimer containing two dissimilar porphyrin cores such as one $N_3S$ and two $N_4$ porphyrins cores was also constructed using the pyridyl porphyrin building blocks reported here. 

## 1. Introduction

Pyridyl porphyrins are versatile ligands toward a variety of metal ions and the well-known coordinating ability of pyridyl groups can be used to construct self-assembled systems.[1] Several polymeric or oligomeric structures based on a self assembly approach have been constructed using metalloporphyrin–pyridine interactions.[1] From the synthetic point of view, it is very important that the pyridine can be easily functionalized. Consequently, it can be readily built into the porphyrin *meso*-position(s). The use of mixed *meso*-substituted pyridyl/phenyl porphyrins as linkers for metal ion centres can provide the connection to as many as four metal centres by coordination of the *meso*-pyridyl groups. In addition, the pyridine ring offers three available carbon positions through which it can be attached to a porphyrin. This variability provides an additional route to control the spatial architecture of designed assemblies. There are several reports available of non-covalent porphyrin assemblies connected via pyridyl groups which are limited to normal porphyrin ($N_4$) systems.[2] Latos-Grazynski et al.[3] and Imamura et al.[4] separately reviewed all the work published on pyridine based non-covalent porphyrin arrays. Furthermore pyridyl porphyrins can be made water-soluble by methylating the pyridyl nitrogen. Water-soluble porphyrins have significant technological applications as sensitizers in photodynamic therapy of cancer,[5a] in opto-electronic devices[5b] and non-linear optics[5c] etc.

Recently, our group has been working on core-modified porphyrins[6] which can be generated by replacing one or more pyrrole rings by heterocyclic rings such as thiophene, furan, selenophene and tellurophene.[7] The core-modified porphyrins exhibit unique chemistry and different properties from $N_4$ porphyrin systems. One of the interesting features of core-modified porphyrins is their ability to stabilize metals in unusual oxidation states such as copper and nickel in +1 state.[8] In spite of their novel physico-chemical features, the reports of core-modified porphyrins are scarce and new systems are required to explore their potential. Interestingly, to the best of our knowledge, there is no report of core-modified porphyrins having pyridyl groups at the *meso* positions. As described above, pyridyl porphyrins are ideal building blocks to synthesize non-covalent multiporphyrin assemblies. Thus, in this paper, we report the synthesis and characterization of a series of 21-thia and 21-oxoporphyrin building blocks bearing two pyridyl functional groups at the *meso* positions in a *cis* fashion and their application towards the synthesis of cationic water-soluble porphyrins[6a] and non-covalent multiporphyrin arrays. The non-covalent porphyrin trimer reported in this paper is unsymmetrical, containing two dissimilar porphyrin cores; one $N_3S$ core and two $N_4$ porphyrin cores. There are several symmetrical porphyrin arrays that have been synthesized as model compounds for natural photosynthetic processes[9] to study photo-induced processes but very few reports are available on unsymmetrical porphyrin arrays containing two different porphyrin cores. The unsymmetrical porphyrin arrays reported to date are covalent systems having two different macrocycles such as porphyrin-corrole, porphyrin-chlorin and porphyrin-phthalocyanine.[10] We recently reported a covalent unsymmetrical porphyrin pentamer containing one $N_2S_2$ core and four $N_4$ porphyrin cores.[6c]

*Keywords*: water-soluble; porphyrins; 21-thiapyridyl porphyrins; 21-oxoporphyrin; unsymmetrical porphyrin arrays.

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The unsymmetrical porphyrin trimer containing one $N_3S$ and two $N_4$ porphyrin cores is the first example of a non-covalent multiporphyrin system having two different porphyrin cores.

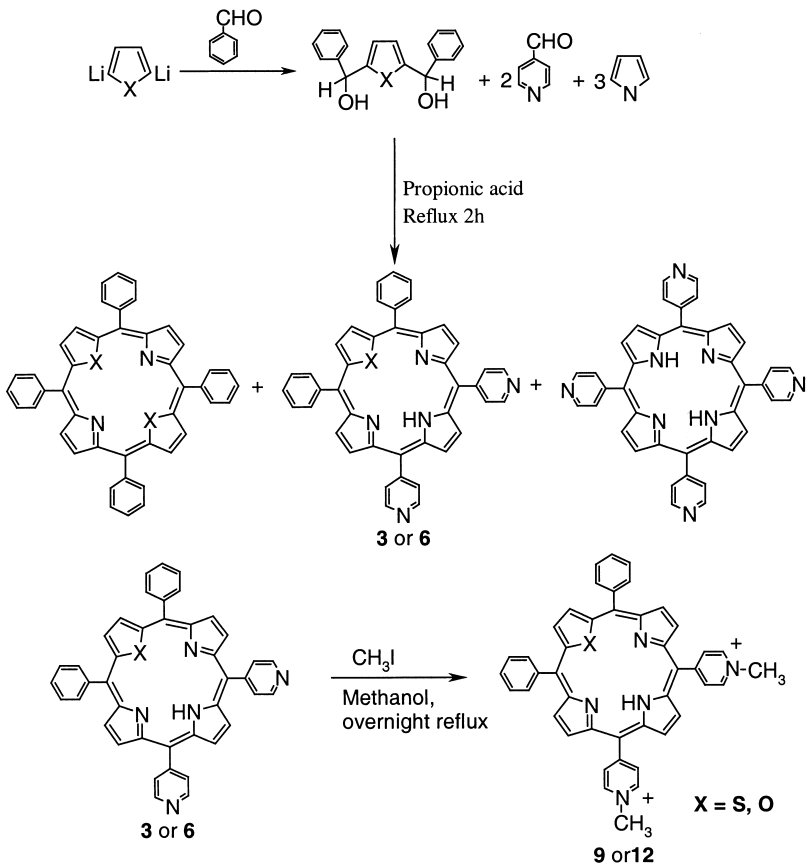
## 2. Results and discussion

### 2.1. *cis*-Pyridyl 21-thia and 21-oxaporphyrins (1–6)

The general synthetic scheme for the preparation of *cis*-pyridyl 21-thia and 21-oxaporphyrin building blocks is shown in Scheme 1. The required diols, 2,5-bis(phenyl hydroxymethyl) thiophene and 2,5-bis(phenylhydroxymethyl) furan were prepared by treating the dianion of thiophene with benzaldehyde as reported in the literature.[11] Initially the thiophene or furan diol was condensed with pyridine-2, 3 or 4-carboxaldehyde and pyrrole under Lindsey conditions[12a] which gave less than 1% of porphyrin. Hence the reaction was done under standard propionic acid conditions.[12b] The condensation of 1 equiv. of thiophene or furan diol with 2 equiv. of the appropriate pyridine carboxaldehyde and 3 equiv. of pyrrole in propionic acid at reflux for 2 h, followed by the removal of propionic acid under vacuum and thorough washing with warm water gave a crude mixture of three porphyrins as indicated by TLC analysis. As shown in Scheme 1, every condensation resulted in the formation of three porphyrins with different porphyrin cores: $N_4$, $N_3X$ and $N_2X_2$ (X=S, O). It is known that the absorption bands shift to the red as porphyrin core changes from $N_4$ to $N_3S$ to $N_2S_2$. Thus, it was very easy to identify the desired $N_3S$ or $N_3O$ pyridyl porphyrin building block using absorption spectroscopy. The mixture of three porphyrins was separated easily by silica gel column chromatography. The *cis*-pyridyl 21-thia or 21-oxoporphyrins, **1–6** always moved as the second band with $CH_2Cl_2$/3–5% $CH_3OH$ and afforded purple compounds in 10–15% yields (Table 1). Porphyrins **1–6** were characterized by NMR, mass spectrometry, elemental analysis, infra-red, absorption and emission spectroscopies. In $^1H$ NMR, for both 21-thia and 21-oxaporphyrin building blocks, the three pyrroles appeared as three separate signals and thiophene or furan appeared as one signal. Similar observations were made in the NMR of 5,10,15,20-tetraphenyl-21-thia or 21-oxaporphyrin.[7] This is due to the low symmetry of the porphyrins. The presence of a strong *m/z* peak at 634 for 21-thia and 617 for 21-oxaporphyrins confirmed the product. The absorption spectra of **1–6** showed four Q-bands and one Soret band (Table 2) and the bands were red shifted compared to 5,10,15,20-tetrapyridyl porphyrin (TPyP). The fluorescence spectra of **1–6** showed two bands which were more red shifted than TPyP and the quantum yields were much lower than TPyP (Table 2).

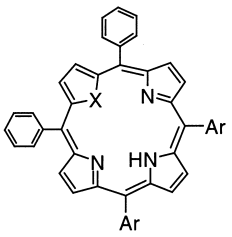
### 2.2. *cis*-Pyridyl cationic water-soluble 21-thia and 21-oxaporphyrins (7–12)

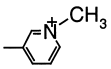
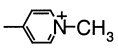
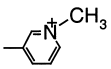
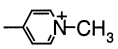
The *cis*-pyridyl 21-thia and 21-oxaporphyrins **1–6** were methylated to get water-soluble porphyrins **7–12**, respectively, by treating them with a 500-fold excess of $CH_3I$ in $CH_2Cl_2$ for overnight (Scheme 1). The water-soluble porphyrins **7–12** were precipitated out of the reaction




**Scheme 1.** General synthetic scheme of pyridyl porphyrin building blocks and their water-soluble porphyrins.

**Table 1**. 21-Thia and 21-oxoporphyrin building blocks and corresponding cationic water-soluble porphyrins




| Porphynin | X | Ar | Yield (%) |
|---|---|---|---|
| **1** | S |  | 10 |
| **2** | S |  | 13 |
| **3** | S |  | 12 |
| **4** | O |  | 11 |
| **5** | O |  | 15 |
| **6** | O |  | 13 |
| **7** | S |  | 42 |
| **8** | S |  | 49 |
| **9** | S |  | 52 |
| **10** | O |  | 40 |
| **11** | O |  | 57 |
| **12** | O |  | 51 |

mixture as the reaction progressed. The compounds were filtered and washed several times with $CH_2Cl_2$ and recrystallized two times from methanol/ether mixture to afford water-soluble porphyrins **7**–**12** in 40–57% yields (Table 1). Methylation was confirmed by NMR, FAB-MS and elemental analysis. It is known that water-soluble porphyrins aggregate in water but remain monomeric in dimethyl sulfoxide. $^1$H NMR spectra of **8** and **11** recorded in $(CD_3)_2SO$ are shown in Figures 1 and 2, respectively. The methylation of the pyridyl nitrogen resulted in a down-field shift of the inner NH, pyridyl, β-pyrrole and β-thiophene protons and maximum effects were observed for the pyridyl protons which were adjacent to the methylated nitrogen. For example in **9**, the 2,6 protons of *meso* pyridyl groups were shifted to down field by 0.39 ppm compared to **3** (Table 3). Furthermore, the methyl protons appeared as a singlet in **8** and **9** but in **7**, they appeared as two singlets. The methyl protons in **7** were down field shifted by 0.50 ppm compared to methyl protons of **8** and **9**. This suggests that in the case of **7**, due to the close proximity of pyridinium methyl group with the porphyrin ring resulted in a interaction which led to the formation of two atropisomers. This was further confirmed by $^{13}$C NMR which showed two equal intense signals for **7** at 48.5 and 52.8 ppm, whereas for **9**, only one signal at 47.9 ppm was observed. The methylation of the pyridyl nitrogen also resulted in a slight down field shift of β-pyrrole and β-thiophene protons and a slight upfield shift of inner NH. All these effects were attributed to the change in the porphyrin ring current on methylation. The compounds were further confirmed by FAB-MS which showed a molecular ion peak at 664 for **7**–**9** and 648 for **10**–**12**. The peaks corresponding to $M-CH_3$ and $M-2CH_3$ were also noted in the mass spectra. The absorption spectra of **7**–**12** (shown for **9** and **12** as an inset (b) in Figs. 1 and 2, respectively) exhibited four Q-bands and one Soret band and the bands were red shifted compared to tetrakis (*N*-methylpyridiniumyl) porphyrin, TMPyP (Table 2).[13] The porphyrins are highly soluble and showed aggregation behaviour above $10^{-4}$ M. The fluorescence bands of **7**–**12** were also red shifted compared to TMPyP (Table 2).[11]

### 2.3. Non-covalent unsymmetrical porphyrin arrays containing two dissimilar cores

The pyridyl 21-thia and 21-oxaporphyrin building blocks,

**Table 2**. Absorption and emission data of pyridyl porphyrins **1**–**6** and TPyP in toluene and water-soluble porphyrins **7**–**12** and TMPyP in water

| Porphyrin | Soret band λ (nm)×(ε×10$^{-4}$) | Absorption Q-bands, λ (nm)×(ε×10$^{-3}$) | | | | Fluorescence λ (nm) ($\lambda_{exc}$=510 nm) | | |
|---|---|---|---|---|---|---|---|---|
| | | IV | III | II | I | Q(0,0) (nm) | Q(0,1) (nm) | $\phi$ |
| **1** | 427(23.1) | 512(4.5) | 546(2.3) | 614(1.2) | 676(0.8) | 679 | 745 | 0.010 |
| **2** | 429(57.3) | 513(6.6) | 547(2.3) | 617(1.1) | 678(1.5) | 678 | 745 | 0.010 |
| **3** | 426(26.5) | 512(2.1) | 545(2.1) | 616(0.9) | 677(0.8) | 681 | 744 | 0.008 |
| **4** | 420(31.6) | 505(23.8) | 536(5.1) | 609(4.1) | 670(3.1) | 677 | 745 | 0.067 |
| **5** | 418(19.5) | 506(16.2) | 537(3.8) | 610(2.7) | 671(2.6) | 678 | 747 | 0.049 |
| **6** | 417(25.8) | 505(19.1) | 536(4.2) | 610(3.0) | 670(2.5) | 677 | 744 | 0.035 |
| **7** | 428(24.1) | 515(20.7) | 554(5.5) | 612(4.4) | 675(4.9) | 679 | 745 | 0.010 |
| **8** | 427(22.9) | 515(17.6) | 550(5.3) | 611(3.6) | 673(3.7) | 678 | 745 | 0.010 |
| **9** | 429(20.2) | 517(16.1) | 554(5.5) | 614(3.7) | 676(3.7) | 681 | 744 | 0.008 |
| **10** | 415(13.4) | 504(16.4) | 537(4.5) | 604(3.7) | 665(1.3) | 667 | 734 | 0.026 |
| **11** | 417(19.9) | 506(24.0) | 536(5.7) | 606(4.6) | 666(2.7) | 670 | 734 | 0.088 |
| **12** | 420(9.4) | 509(14.4) | 541(6.1) | 606(3.6) | 666(2.3) | 675 | 740 | 0.047 |
| **TPyP** | 416(15.6) | 513(1.0) | 545(0.2) | 588(0.3) | 643(0.1) | 649 | 713 | 0.072 |
| **TMPyP** | 421(15.6) | 518(10.0) | 554(3.7) | 583(4.1) | 638(0.9) | 675 | 705 | 0.047 |

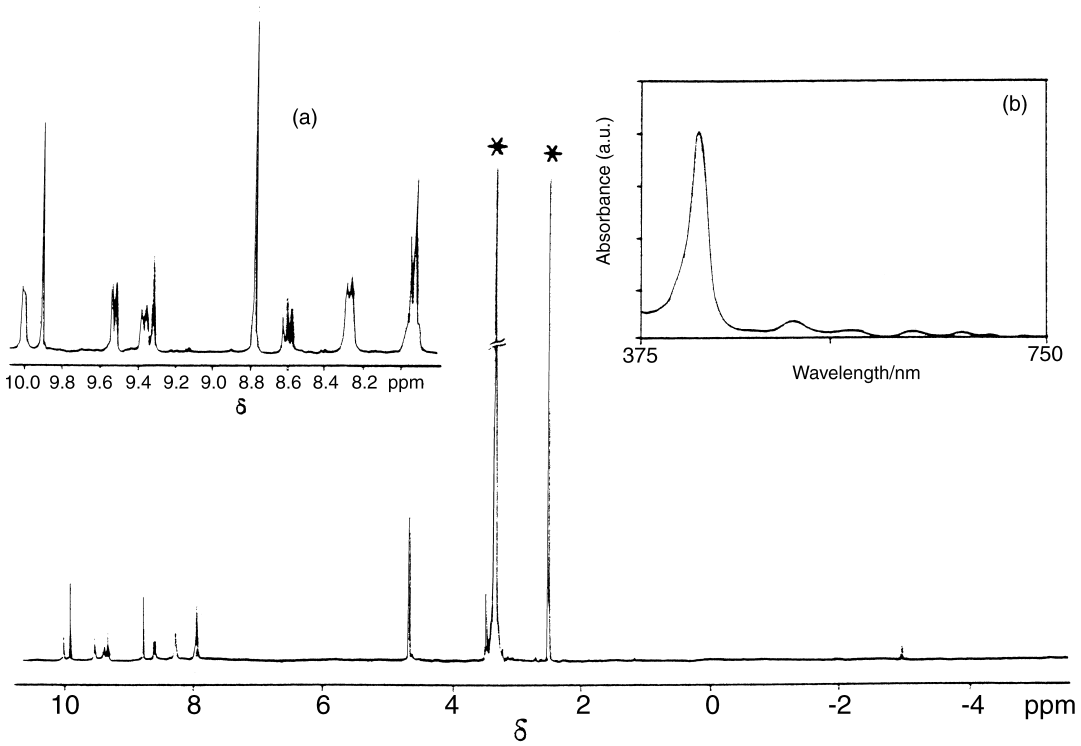



**Figure 1.** [1]H NMR spectrum of **8** recorded in $(CD_3)_2SO$. The expansion of the 7.8–10 ppm region is shown in inset (a). Solvent peaks marked with ∗. The absorption spectrum of **8** in water is shown in inset (b). The concentration used was $2\times10^{-5}$ M.

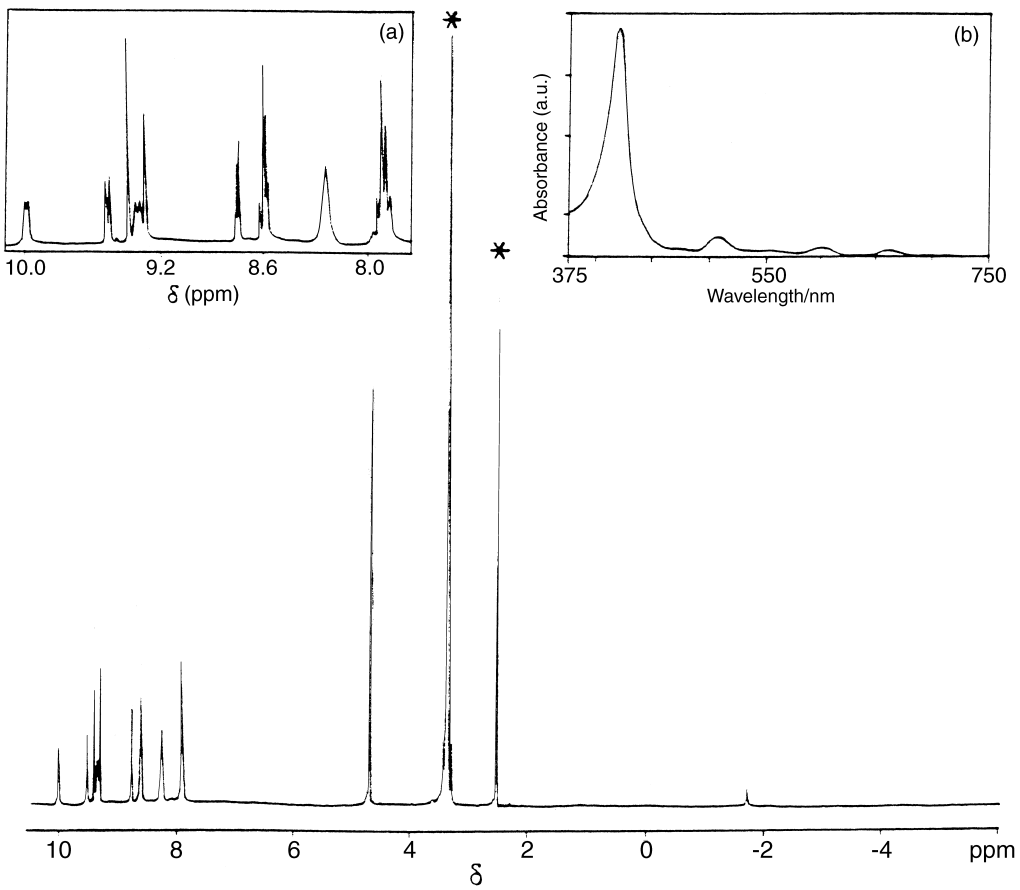


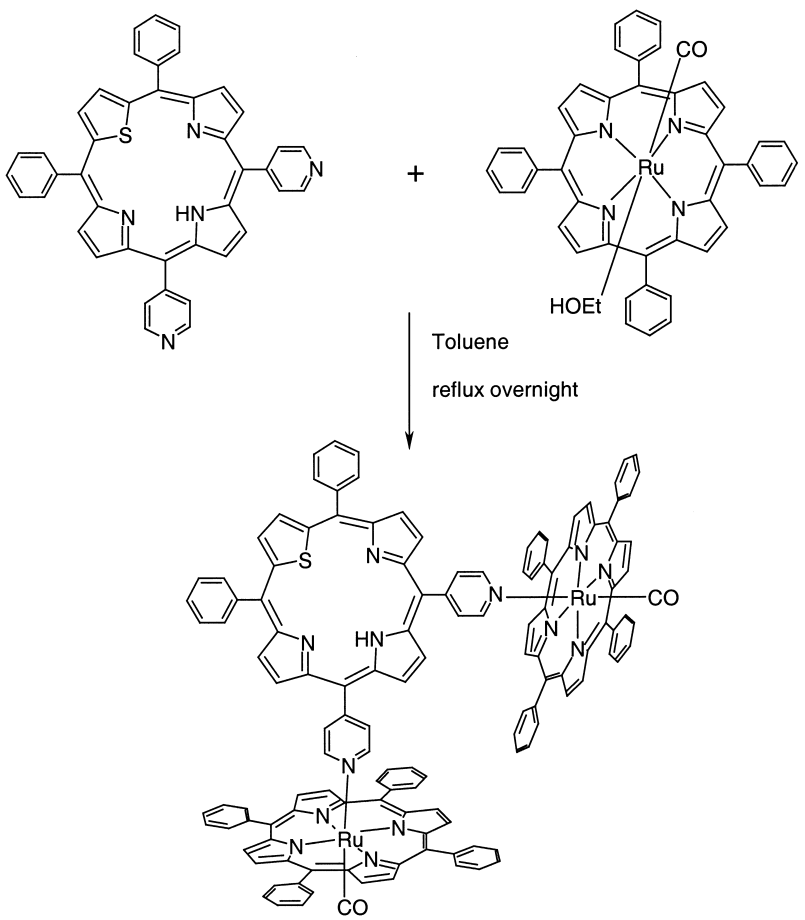

**Figure 2.** [1]H NMR spectrum of **11** recorded in $(CD_3)_2SO$. The expansion of the 7.8–10 ppm region is shown in inset (a). Solvent peaks marked with ∗. The absorption spectrum of **11** is shown in inset (b). The concentration used was $2\times10^{-5}$ M.

**Table 3**. $^1$H NMR chemical shift (ppm) values of selected protons of porphyrins **3**, **9** and **13**

| Porphyrin | 2,6-Pyridyl | 3,5-Pyridyl | Pyrrole | Thiophene | N–H |
|---|---|---|---|---|---|
| **3**[a] | 9.06(d) | 8.23(m) | 8.56(d), 8.74(d), 8.92(s) | 9.80(s) | −2.81(s) |
| **9**[b] | 9.45(d) | 8.70(d), 8.78(d) | 8.99(d), 9.25(m) | 9.89(s) | −2.99(s) |
| **13**[a] | 1.85(d) | 5.82(d) | 6.83(d), 7.01(d), 8.20(d) | 9.52(s) | −3.94(s) |

[a] In $CDCl_3$.
[b] In $(CD_3)_2$ SO.

**1**–**6** can be used to construct the non-covalent porphyrin arrays. The reports available in literature till now on non-covalent porphyrins arrays synthesized based on pyridyl porphyrins were restricted to $N_4$ porphyrins. The pyridyl $N_4$ porphyrins systems were only useful for synthesizing symmetrical non-covalent porphyrin arrays containing one kind of porphyrin core, i.e. a $N_4$ core. The advantage of $N_3S$ and $N_3O$ pyridyl porphyrins is that these building blocks are good synthons for synthesizing unsymmetrical non-covalent porphyrin arrays containing at least two different porphyrin cores such as $N_3S$ and $N_4$. To demonstrate the superiority of the pyridyl $N_3S$ and $N_3O$ porphyrins synthesized in this report, we used $N_3S$ porphyrin building block **3** to prepare an unsymmetrical non-covalent porphyrin trimer STPyP(RUTPP)$_2$ **13** containing one $N_3S$ porphyrin core and two $N_4$ porphyrin cores. To synthesize an unsymmetrical trimer **13**, we treated 1 equiv. of **3** with 2.2 equiv. of RuTPP(CO)(EtOH) in toluene at refluxing temperature overnight (Scheme 2). The progress of the reaction was followed by TLC. As the reaction progressed, the colour of the reaction mixture changed from bright red to brownish red. The reaction was stopped after complete consumption of **3** as judged by TLC. Compound **13** was purified by silica gel column chromatography using $CH_2Cl_2$/petroleum ether (1:1) followed by size exclusion chromatography using toluene. Trimer **13** was highly soluble in most solvents and characterized by NMR, LD-MS, elemental analysis, infrared and Uv–visible spectroscopy. The $^1$H NMR spectrum shown in Figure 3 confirms the coordination of the two *meso* pyridyl groups of **3** to the central ruthenium ion of the RuTPP(CO) core. The evidence of coordination mainly comes from the large upfield shifts of the 2,6- and 3,5-protons of the pyridyl groups, β-pyrrole and β-thiophene protons and inner NH protons of 21-thiaporphyrin part (i.e. $N_3S$ porphyrin building block **3**) in **13** (Table 3). The doublet signal observed for 2,6-pyridyl protons of **3** experienced a large upfield shift by 7.21 ppm in **13** compared to 2,6-pyridyl protons of free **3**. The 3,5- protons of the pyridyl group in **13** were also shifted upfield by 2.41 ppm compared to free **3**. Similar upfield shifts for




**Scheme 2.** Synthetic scheme for the preparation of **13**.

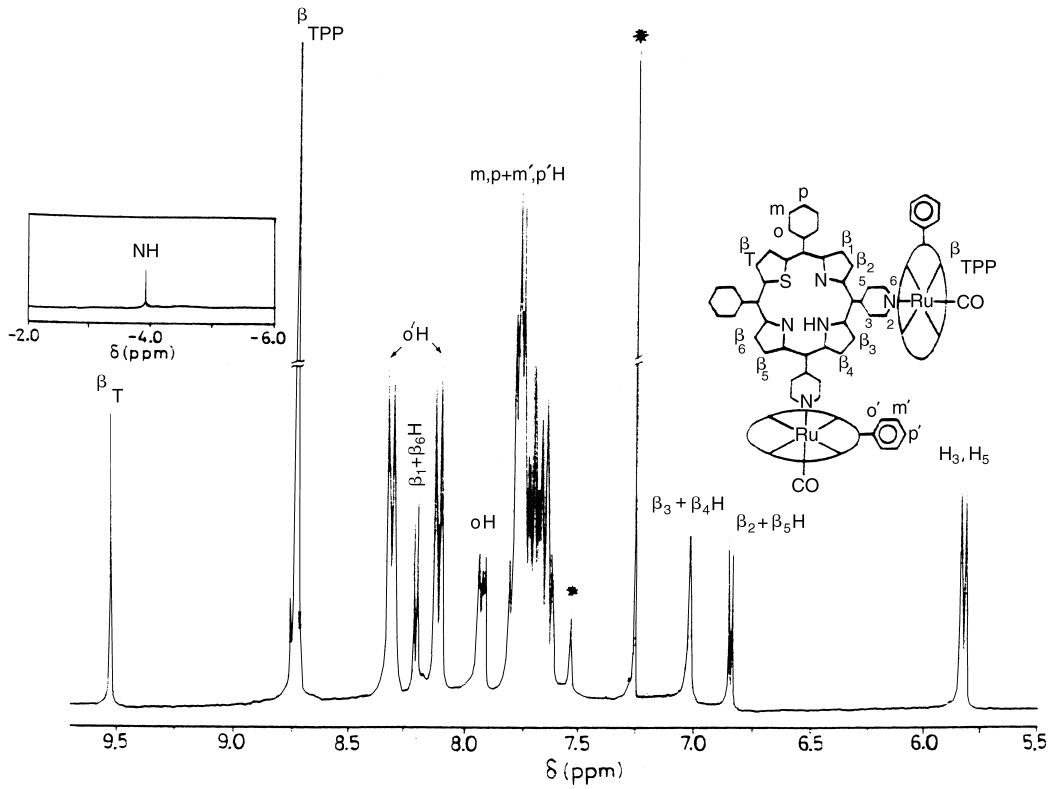



**Figure 3.** $^{1}$H NMR spectrum of **13** recorded in $CDCl_3$. Solvent and impurity peaks were marked with ∗. The NH signal is shown as an inset.

pyridyl protons were observed in non-covalent symmetrical porphyrin arrays reported in the literature.[3,4] The signals of β-pyrrole protons of part **3** in **13** also indicates the coordination of **3** to Ru(TPP)(CO). The three doublets observed for the three pyrroles of **3** (in **13**) were significantly upfield shifted compared to corresponding β-pyrrole protons in free **3** (Table 3). The NH proton of **3** (in **13**) was observed at −3.94 ppm compared to free **3** in which the NH was observed at −2.81 ppm. These results clearly indicate the coordination of **3** to the central ruthenium ion of the Ru(TPP)(CO) core through the pyridyl groups. The elemental analysis results and mass data were in agreement with the trimer formation. IR measurements showed the $\nu_{(CO)}$ stretch at 1953 $cm^{-1}$. The absorption spectra of trimer **13** along with a mixture of RuTPP(CO)(EtOH) and **3** in 2:1 ratio at the same concentration for both Q-bands and Soret band (inset) is shown in Figure 4. The trimer **13** showed the peaks corresponding to both monomers and it matched with the 2:1 mixture of Ru(TPP)(CO) and **3** indicating that there was no strong interaction between the porphyrin units. However, the intensity of peaks in **13** was much higher than the 2:1 mixture of porphyrins.

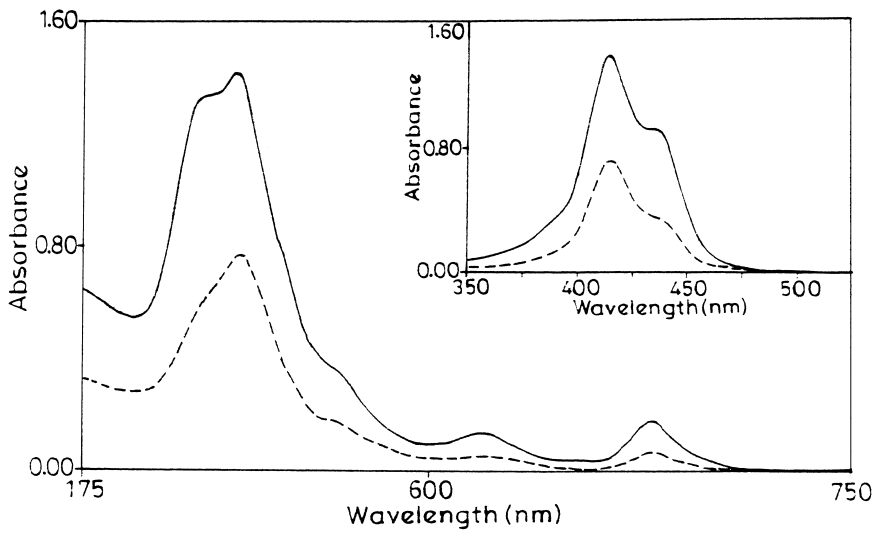



**Figure 4.** Q-bands and Soret band (inset) absorption spectra of **13** (solid line) and 2:1 mixture of RuTPP(CO)(EtOH) and **3** (dashed line) recorded in toluene. The concentrations used were: Soret band (inset), 5×10−$^{6}$ M; and Q-bands, 5×10−$^{5}$ M.

## 3. Conclusions

In summary, we synthesized a series 21-thia and 21-oxoporphyrin building blocks bearing two pyridyl functional groups at the *meso* positions in a *cis* fashion. The pyridyl porphyrin building blocks were methylated to prepare the cationic core-modified water-soluble porphyrins. The water soluble porphyrins could be tested as sensitizers for photodynamic therapy of cancer. The cationic water-souble porphyrins are also good synthons for generating unsymmetrical porphyrin aggregates by mixing the cationic porphyrins with anionic water-soluble N4 porphyrins. This kind of hetero aggregate has wide applications. We also showed that the pyridyl porphyrin building blocks can be used to construct non-covalent unsymmetrical porphyrin arrays containing two dissimilar porphyrin cores. We are presently exploring the synthesis of metal derivatives of water-soluble porphyrins to study their interaction with DNA and also use these building blocks to synthesize several non-covalent metal mediated multi-porphyrin arrays. Such studies are presently in progress in our laboratory.

## 4. Experimental

### 4.1. Data for compounds

**4.1.1. 5,20-Diphenyl-10,15-bis(2-pyridyl)-21-thiaporphyrin (1).** A solution of 2,5-bis(hydroxymethyl) thiophene (500 mg, 1.69 mmol), pyridine-2- carboxaldehyde (350 μl, 2.90 mmol) and pyrrole (335 μl, 5.16 mmol) were dissolved in 125 ml of propionic acid and refluxed for 3 h. The first band 5,10,15,20-tetraphenyl-21,23-dithiaporphyrin ($S_2$TPP) was removed by silica gel column chromatography with $CH_2Cl_2$ and the desired purple compound was obtained as the second band using $CH_2Cl_2$/3% $CH_3OH$ followed by recrystallization from $CH_2Cl_2$/petroleum ether (107 mg, 10%). Mp>300°C. $^1$H NMR ($CDCl_3$, $\delta$ in ppm) −2.81 (s, 1H, NH), 7.70–7.85 (m, 8H, *m*,*p*-phenyl and 5-pyridyl), 8.13 (t, 2H, pyridyl-4), 8.26 (m, 6H, *o*-phenyl, pyridyl-3), 8.57 (d, *J*=4.60 Hz, 2H, β-pyrrole), 8.73 (d, *J*=4.70 Hz, 2H, β-pyrrole), 8.93 (d, *J*=2 Hz, 2H, β-pyrrole), 9.17 (d, *J*=4.30 Hz, 2H, pyridyl-2), 9.78 (s, 2H, β-thiophene). FAB-MS $C_{42}H_{27}N_5S$ calcd av. mass 633.8, obsd *m*/*z* 634 ($M^+$, 52%). Anal. calcd: C, 79.59; H, 4.29; N, 11.10. Found: C, 79.29; H, 4.29; N, 11.30. IR (KBr, $\nu$ ($cm^{-1}$)) 3418, 967, 696.1.

**4.1.2. 5,20-Diphenyl-10,15-bis(3-pyridyl)-21-thiaporphyrin (2).** Samples of 2,5-bis(hydroxymethyl) thiophene (500 mg, 1.69 mmol), pyridine-3-carboxaldehyde (350 μl, 2.87 mmol) and pyrrole (335 μl, 5.16 mmol) were dissolved in 125 ml of propionic acid and refluxed for 3 h. Column chromatography with $CH_2Cl_2$/3% $CH_3OH$ gave the required purple compound. The compound was recrystallized from $CH_2Cl_2$/petroleum ether (139 mg, 13%). Mp>300°C. $^1$H NMR ($CDCl_3$, $\delta$ in ppm) −2.83 (s, 1H, NH), 7.82 (m, 8H, *m*,*p*-phenyl and 4-pyridyl), 8.24 (m, 4H, *o*-phenyl), 8.56 (m, 4H, 3-pyridyl and β-pyrrole), 8.74 (d, *J*=4.70 Hz, 2H, β-pyrrole), 8.92 (d, *J*=1.80 Hz, 2H, β-pyrrole), 9.05 (s, 2H, 2-pyridyl)), 9.45 (s, 2H, 6-pyridyl), 9.80 (s, 2H, β-thiophene). FAB-MS $C_{42}H_{27}N_5S$ calcd av. mass 633.8, obsd *m*/*z* 634 ($M^+$, 55%). Anal. calcd: C, 79.59; H, 4.29; N, 11.10. Found: C, 79.17; H, 4.32; N, 11.11. IR (KBr, $\nu$ ($cm^{-1}$)) 3429, 964, 697.

**4.1.3. 5,20-Diphenyl-10,15-bis(4-pyridyl)-21-thiaporphyrin (3).** Samples of 2,5-bis(hydroxymethyl) thiophene (1 g, 3.38 mmol), pyridine-4- carboxaldehyde (692 μl, 5.71 mmol) and pyrrole (335 μl, 5.16 mmol) were dissolved in 250 ml of propionic acid and refluxed for 3 h. Column chromatography with $CH_2Cl_2$/3% $CH_3OH$ and recrystallization from $CH_2Cl_2$/petroleum ether gave the desired porphyrin as purple solid (260 mg, 12%). Mp>300°C. $^1$H NMR ($CDCl_3$, $\delta$ in ppm) −2.81 (s, 1H, NH), 7.82 (m, 6H, *m*,*p*-phenyl), 8.17 (m, 4H, *o*-phenyl), 8.23 (m, 4H, 3,5-pyridyl), 8.56 (d, *J*=4.39 Hz, 2H, β-pyrrole), 8.74 (d, *J*=4.75 Hz, 2H, β-pyrrole), 8.92 (s, 2H, β-pyrrole), 9.06 (bs, 4H, 2,6-pyridyl), 9.80 (s, 2H, β-thiophene). $^{13}$C NMR (77.1 MHz, $CDCl_3$, $\delta$ in ppm) 29.8, 120.1, 127.8, 128.3, 129.3, 134.4, 135.2, 137.9, 140.7, 1438.0, 148.3, 150.7, 153.7, 157.8. FAB-MS $C_{42}H_{27}N_5S$ calcd av. mass 633.8, obsd *m*/*z* 634 ($M^+$, 100%). Anal. calcd: C, 79.59; H, 4.29; N, 11.10. Found: C, 79.82; H, 4.31; N, 11.14. IR (KBr, $\nu$ ($cm-^1$)) 3432, 963, 699.

**4.1.4. 5,20-Di(phenyl)-10,15-bis(2-pyridyl)-21-oxoporphyrin (4).** A solution of 2,5-bis(hydroxymethyl) furan (500 mg, 1.78 mmol) and pyridine-2-carboxaldehyde (340 μl, 2.82 mmol) and pyrrole (373 μl, 5.353 mmol) in 125 ml of propionic acid was refluxed for 3 h. Column chromatography on silica using $CH_2Cl_2$/5% $CH_3OH$ followed by recrystallization from $CH_2Cl_2$/petroleum ether gave the desired compound as purple solid (120 mg, 11%). Mp>250°C. $^1$H NMR ($CDCl_3$, $\delta$ in ppm) −2.94 (s, 1H, NH), 7.79 (m, 8H, *m*,*p*-phenyl+5-pyridyl), 8.06–8.21 (m, 8H, *o*-phenyl+3,4-pyridyl), 8.64 (m, 4H, β-pyrrole), 8.96 (s, 2H, β-pyrrole), 9.16 (d, *J*=4.0 Hz, 2H, 2-pyridyl), 9.24 (s, 2H, β-furan); FAB-MS $C_{42}H_{27}N_5O$ calcd av. mass 617, obsd 617 ($M^+$, 58%). Anal. calcd: C, 81.76; H, 4.40; N, 11.33. Found: C, 81.92; H, 4.42; N, 11.40. IR (KBr, $\nu$ ($cm^{-1}$)) 3425, 963, 706.

**4.1.5. 5,20-Diphenyl-10,15-bis(3-pyridyl)-21-oxoporphyrin (5).** Samples of 2,5-bis (hydroxymethyl) furan (500 mg, 1.784 mmol) and pyridine-3-carboxaldehyde (340 μl, 2.82 mmol) and pyrrole (373 μl, 5.353 mmol) in 125 ml propionic acid was refluxed for 3 h and purified by silica gel column chromatography with $CH_2Cl_2$/5% $CH_3OH$. The required compound was moved as a second band and the solvent was removed on rotary evaporator and the solid was recrystallized from $CH_2Cl_2$/petroleum ether to obtain **5** as a purple compound (165 mg, 15%). Mp>250°C. $^1$H NMR ($CDCl_3$, $\delta$ in ppm) −2.92 (s, 1H, NH), 7.78 (m, 6H, *m*,*p*-phenyl), 8.20 (m, 4H, *o*-phenyl), 8.51 (d, *J*=7.70 Hz, 2H, 2-pyridyl), 8.61 (m, 4H, 3,4-pyridyl), 8.86 (s, 2H, β-pyrrole), 9.03 (m, 4H, β-pyrrole), 9.26 (s, 2H, β-furan), 9.41 (s, 2H, 6-pyridyl); FAB-MS $C_{42}H_{27}N_5O$ calcd av. mass 617, obsd *m*/*z* 617 ($M^+$, 48%). Anal. calcd: C, 81.76; H, 4.40; N, 11.33. Found: C, 81.59; H, 4.39; N, 11.20. IR (KBr, $\nu$ ($cm^{-1}$)) 3414, 963, 706.

**4.1.6. 5,20-Diphenyl-10,15-bis(4-pyridyl)-21-oxoporphyrin (6).** Samples of 2,5-bis(hydroxymethyl) furan (500 mg, 1.784 mmol), pyridine-4-carboxaldehyde

(340 μl, 2.82 mmol) and pyrrole (373 μl, 5.353 mmol) were dissolved in propionic acid (125 ml) and refluxed for 3 h. The crude compound was purified by silica gel column chromatography using $CH_2Cl_2$/5% $CH_3OH$ and recrystallized from $CH_2Cl_2$/petroleum ether (150 mg, 13%). Mp>250°C. $^1$H NMR ($CDCl_3$, $\delta$ in ppm) −2.92 (s, 1H, NH), 7.78 (m, 6H, *m*,*p*-phenyl), 8.12 (m, 4H, *o*-phenyl), 8.17 (d, *J*=6.50 Hz, 4H, 3,5-pyridyl), 8.57 (d, *J*=4.90 Hz, 2H, β-pyrrole), 8.61 (d, *J*=4.35 Hz, 2H, β-pyrrole), 9.03 (d, *J*=6.62 Hz, 2H, 2,6-pyridyl), 9.24 (s, 2H, β-furan). $^{13}$C NMR (77.1 MHz, $CDCl_3$, $\delta$ in ppm) 29.8, 120.1, 127.2, 128.6, 129.5, 134.0, 134.4, 137.6, 141.5, 148.4, 149.7, 155.2, 158.6, 158.8. FAB-MS $C_{42}H_{27}N_5O$ calcd av. mass 617, obsd *m*/*z* 617 ($M^+$, 76%). Anal. calcd: C, 81.76; H, 4.40; N, 11.3. Found: C, 81. 57; H, 4.29; N, 11.31. IR (KBr, $\nu$ ($cm^{-1}$)) 3441, 982, 709.

**4.1.7. 5,20-Diphenyl-10,15-bis(2-*N*-methylpyridyl)-21-thiaporphyrin (7).** Compound **1** (100 mg, 0.158 mmol) and a 500-fold excess of $CH_3I$ (4.92 ml, 79 mmol) in $CH_2Cl_2$ was refluxed overnight. The compound was precipitated with $CH_3OH$ and recrystallized two times with methanol/diethyl ether to obtain a crystalline purple solid (44 mg, 42%). Mp>300°C. $^1$H NMR (($CD_3)_2SO$, $\delta$ in ppm)) −2.94 (s, 1H, NH), 4.10 (s, 3H, $NCH_3$), 4.14 (s, 3H, $NCH_3$), 7.92 (m, 6H, *m*,*p*-phenyl), 8.28 (m, 4H, *o*-phenyl), 8.68 (d, *J*=4.67 Hz, 2H, 5-pyridyl), 8.73 (m, 2H, β-pyrrole), 8.80 (d, *J*=4.65 Hz, 2H, β-pyrrole), 8.93 (m, 2H, 3-pyridyl), 9.03 (t, 2H, 4-pyridyl), 9.30 (m, 2H, β-pyrrole), 9.63 (d, *J*=6.38 Hz, 2H, 2-pyridyl), 9.92 (s, 2H, β-thiophene). $^{13}$C NMR (77.1 MHz, $CDCl_3$, $\delta$ in ppm) 48.5, 52.8, 128.1, 128.7, 128.8, 130.0, 133.7, 134.1, 134.6, 136.1, 136.9, 137.4, 139.1, 144.6, 148.2, 148.4, 153.1, 153.2, 157.1. FAB-MS $C_{44}H_{33}N_5S$ calcd av. mass 663.8, obsd *m*/*z* 664 ($M^+$, 95%), 648 ($M-CH_3$, 70%). Anal. calcd: C, 57.59; H, 3.62; N, 7.63. Found: C, 58.13; H, 3.59; N, 7.69. IR (KBr, $\nu$ ($cm^{-1}$)) 3433, 965, 709

**4.1.8. 5,20-Diphenyl-10,15-bis(3-*N*-methylpyridyl)-21-thiaporphyrin (8).** Compound **2** (100 mg, 0.158 mmol) was treated with a 500-fold excess of $CH_3I$ (4.92 ml, 79 mmol) in $CH_2Cl_2$ at reflux. Recrystallization with methanol/diethyl ether gave **8** as purple solid, (51 mg, 49%). Mp>300°C. $^1$H NMR (($CD_3)_2SO$, $\delta$ in ppm)) −2.99 (s, 1H, NH), 4.65 (s, 6H, $NCH_3$), 7.92 (m, 6H, *m*,*p*-phenyl), 8.26 (m, 4H, *o*-phenyl), 8.59 (m, 2H, 3-pyridyl), 8.77 (s, 4H, β-pyrrole), 9.32 (m, 2H, β-pyrrole), 9.37 (d, *J*=7.60 Hz, 2H, 4-pyridyl), 9.52 (d, *J*=6.04 Hz, 2H, 2-pyridyl), 9.91 (s, 2H, β-thiophene), 10.65 (bs, 2H, 6-pyridyl). FAB-MS $C_{44}H_{33}N_5S$ calcd av. mass 663.8, obsd *m*/*z* 664 ($M^+$, 53%), 648 ($M-CH_3$, 50%). Anal. calcd: C, 57.59; H, 3.62; N, 7.63. Found: C, 57.90; H, 3.61; N, 7.68. IR (KBr, $\nu$ ($cm^{-1}$)) 3430, 965, 706

**4.1.9. 5,20-Diphenyl-10,15-bis(4-*N*-methylpyridyl)-21-thiaporphyrin (9).** A solution of **3** (150 mg, 0.234 mmol) in 40 ml of $CH_2Cl_2$ was refluxed with a 500-fold excess of $CH_3I$ (7.3 ml, 117 mmol). The compound was purified by recrystallization from methanol/ether (85 mg, 54%). Mp>300°C. $^1$H NMR (($CD_3)_2SO$, $\delta$ in ppm)) −2.99 (s, 1H, NH), 4.70 (s, 6H, $NCH_3$), 7.93 (m, 6H, *m*,*p*-phenyl), 8.27 (m, 4H, *o*-phenyl), 8.70 (d, *J*=6.59 Hz, 2H, 3,5-pyridyl), 8.78 (d, *J*=6.51 Hz, 2H, 3,5-pyridyl), 8.99 (d, *J*=4.61 Hz, 4H, β-pyrrole), 9.25 (m, 2H, β-pyrrole), 9.45 (d, *J*=6.31 Hz, 4H, 2,6-pyridyl), 9.89 (s, 2H, β-thiophene). $^{13}$C NMR (77.1 MHz, $CDCl_3$, $\delta$ in ppm) 47.9, 117.1, 128.0, 128.6, 129.7, 131.9, 133.2, 134.0, 134.7, 135.3, 136.1, 136.7,139.4, 144.1, 147.5, 152.5, 157.0, FAB-MS $C_{44}H_{33}N_5S$ calcd av. mass 663.8, obsd *m*/*z* 664 ($M^+$, 88%), 648 ($M-CH_3$, 51%). Anal. calcd: C, 57.59; H, 3.62; N, 7.63. Found: C, 57.92; H, 3.58; N, 7.61. IR (KBr, $\nu$ ($cm^{-1}$)) 3429, 963, 706.

**4.1.10. 5,20-Diphenyl-10,15-bis(2-*N*-methylpyridyl)-21-oxoporphyrin (10).** Compound **4** (50 mg, 0.0809 mmol) was dissolved in 20 ml of $CH_2Cl_2$ and a 500-fold excess of $CH_3I$ (2.52 ml, 40 mmol) was added. The reaction mixture was refluxed overnight. Recrystallization from methanol/diethyl ether gave **10** as purple solid (21 mg, 40%). Mp>300°C. $^1$H NMR (($CD_3)_2SO$, $\delta$ in ppm) −1.75 (bs, 1H, NH), 4.05 (s, 3H, $CH_3$), 4.10 (s, 3H, $CH_3$), 7.92 (m, 6H, *m*,*p*-phenyl), 8.26 (m, 4H, *o*-phenyl), 8.71 (m, 6H, β-pyrrole+4,5-pyridyl), 8.91 (t, 2H, 3-pyridyl), 9.03 (m, 4H, β-pyrrole), 9.24 (s, 2H, β-furan), 9.62 (bs, 2H, 2-pyridyl); FAB-MS $C_{44}H_{33}N_5O$ calcd av. mass 648, obsd *m*/*z* 648 ($M^+$, 90%), 633 ($M-CH_3$, 100%), 618 ($M-2CH_3$, 60%). Anal. calcd: C, 58.60; H, 3.68; N, 7.76. Found: C, 58.70; H, 3.69; N, 7.78. IR (KBr, $\nu$ ($cm^{-1}$)) 3415, 2849, 1245, 709.

**4.1.11. 5,20-Diphenyl-10,15-bis(3-*N*-methylpyridyl)-21-oxoporphyrin (11).** Samples of compound **5** (50 mg, 0.0809 mmol) and $CH_3I$ (2.52 ml, 40 mmol) in 20 ml $CH_2Cl_2$ was refluxed for 12 h. The product was obtained as purple solid after recrystallization from methanol/diethyl ether (29 mg, 57%). Mp>300°C. $^1$H NMR (($CD_3)_2SO$, $\delta$ in ppm) −1.73 (s, 1H, NH), 4.67 (s, 6H, $CH_3$), 7.90 (m, 6H, *m*,*p*-phenyl), 8.23 (m, 4H, *o*-phenyl), 8.58 (m, 4H, 3,4-pyridyl), 8.74 (d, *J*=4.90 Hz, 2H, β-pyrrole), 9.28 (s, 2H, β-pyrrole), 9.33 (d, *J*=4.80 Hz, 2H, β-pyrrole), 9.38 (s, 2H, β-furan), 9.51 (d, *J*=6.54 Hz, 2H, 2-pyridyl), 9.99 (bs, 2H, 6-pyridyl); FAB-MS $C_{44}H_{33}N_5O$ calcd av. mass 648, obsd *m*/*z* 648 ($M^+$, 92%), 633 ($M-CH_3$, 98%), 618 ($M-2CH_3$, 60%); Anal. calcd: C, 58.60; H, 3.66; N, 7.73. Found: C, 58.65; H, 3.66; N, 7.73. IR (KBr, $\nu$ ($cm^{-1}$)) 3418, 2850, 1244, 1223, 709.

**4.1.12. 5,20-Diphenyl-10,15-bis(4-*N*-methylpyridyl)-21-oxoporphyrin (12).** A solution of compound **6** (50 mg, 0.0809 mmol) and $CH_3I$ (2.52 ml, 40 mmol) in 20 ml $CH_2Cl_2$ was refluxed overnight. Recrystallization from methanol/diethyl ether gave a purple solid (26 mg, 51%). Mp>300°C. $^1$H NMR (($CD_3)_2SO$, $\delta$ in ppm) −1.73 (bs, 1H, NH), 4.72 (s, 6H, $CH_3$), 7.89 (m, 6H, *m*,*p*-phenyl), 8.23 (m, 4H, *o*-phenyl), 8.64 ($AA'BB'$, 4H, 3,5-pyridyl), 8.98 (m, 4H, β-pyrrole), 9.21 (s, 2H, β-pyrrole), 9.43 (s, 2H, β-furan), 9.48 (m, 4H, 2,6-pyridyl); FAB-MS $C_{44}H_{33}N_5O$ calcd av. mass 648, obsd 648 ($M^+$, 90%), 633 ($M-CH_3$, 65%), 618 ($M-2CH_3$, 30%); Anal. calcd: C, 58.60; H, 3.68; N, 7.76. Found: C, 58.94; H, 3.63; N, 7.71. IR (KBr, $\nu$ ($cm^{-1}$)) 3428, 1241, 1223.

**4.1.13. STPyP(RUTPP)$_2$ (13).** The thiaporphyrin building block, **3** (20 mg, 0.0316 mmol) was dissolved in 40 ml of toluene in two necked 100 ml round bottomed flask and argon was purged for 10 min. RuTPP(CO)(EtOH) (55 mg,

0.070) was then added and the solution was refluxed under stirring overnight. The colour of the reaction changed from bright red to dark brownish red as the reaction progressed. The reaction was monitored with TLC. The TLC analysis after 12 h showed complete consumption of **3**. Heating was stopped and the solvent was removed on a rotary evaporator under reduced pressure. The crude compound was dissolved in a minimum amount of $CH_2Cl_2$ and a dry slurry powder was prepared by adding a small amount of silica gel followed by the removal of the traces of solvent under reduced pressure. The slurry was loaded on a silica gel column and eluted with petroleum ether. An excess of unreacted RuTPP(CO)(EtOH) eluted as the first band and collected with petroleum ether/$CH_2Cl_2$ (3:2). The desired trimer, **13** was eluted as second band and collected with petroleum ether/$CH_3OH$ (1:1). The trimer **13** was then subjected to a second silica gel column under same solvent conditions and the compound was obtained as a purple solid (45% yield). Mp>250°C. $^1$H NMR ($CDCl_3$, $\delta$ in ppm) −3.94 (s, 1H, NH), 1.85 (d, $J$=1.37 Hz, 4H, 2,6-pyridyl), 5.82 (d, $J$=1.37 Hz, 4H, 3,5-pyridyl), 6.83 (d, $J$=4.50 Hz, 2H, β-pyrrole of **3**), 7.01 (d, $J$=1.78 Hz, 2H, β-pyrrole of **3**), 7.60–7.78 (m, 30H, *m*,*p*-phenyl of **3**+*m*′,*p*′-phenyl of TPP), 7.90 (m, 4H, *o*-phenyl of **3**), 8.11 (d, $J$=7.55 Hz, 8H, o′-H of TPP), 8.20 (d, $J$=4.50 Hz, 2H, β-pyrrole of **3**), 8.33 (d, $J$=7.00 Hz, 8H, o′-H of TPP), 8.72 (s, 16H, β-pyrrole of TPP), 9.52 (s, 2H, β-thiophene). $^{13}$C NMR (77.1 MHz, $CDCl_3$, $\delta$ in ppm) 29.9, 117.5, 121.9, 126.5, 126.7, 126.8, 127.1, 127.5, 127.6, 128.3, 132.1, 132.5, 133.5, 134.1, 134.5, 135.1, 135.9, 140.1, 142.5, 142.8, 143.9, 147.7, 148.5, 157.2. LD-MS $Ru_2C_{132}H_{83}N_{13}O_2S$ calcd av. mass 2117.4, obsd *m*/*z* 2118.2. Anal. calcd: C, 74.87; H, 3.95; N, 8.59. Found: C, 74.95; H, 3.91; N, 8.62. IR (KBr): $\nu$ (CO) 1953 cm$^{-1}$. UV–vis. ($\lambda_{max}$, in nm and $\varepsilon\times10^3$) 429 (191.4), 411 (391.2), 516 (24.1), 530 (26.2), 565 (6.38), 618 (2.56), 679 (3.22).

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