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Synthesis of 21-thia and 21-oxaporphyrin building blocks and boron–dipyrrin appended systems

D. Kumaresan, Neeraj Agarwal, Iti Gupta and M. Ravikanth*

Department of Chemistry, Indian Institute of Technology, Powai, Mumbai 400076, India

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Abstract—A series of 21-thia and 21-oxaporphyrin building blocks bearing iodo-, ethynyl-and aldehyde functional groups were synthesized and characterized. These porphyrins are ideal building blocks for the construction of unsymmetrical porphyrin arrays containing two dissimilar porphyrin cores. The building blocks were used to construct boron–dipyrrin appended core-modified porphyrin systems under mild palladium coupling conditions. A preliminary steady state fluorescence measurements suggested that boron–dipyrrin unit transfers the energy to both 21-oxaporphyrin and 21-thiaporphyrin and the efficiency depends on the orientation of the boron–dipyrrin units and the core structure of the porphyrin. © 2002 Elsevier Science Ltd. All rights reserved.

1. Introduction

Core-modified porphyrins resulting from the replacement of pyrrole with heterocycles such as thiophene, furan, selenophene and tellurophene have received less attention inspite of their novel properties such as stabilization of metals in unusual oxidation states.[1] Most of the studies on core modified chemistry has been directed towards the synthesis and stabilization of metals such as copper, nickel and rhodium in unusual oxidation states.[2] For example, it has been shown that 5,10,15,20-tetraphenyl-21-thiaporphyrin (N_3S core) can stabilize copper in +1 oxidation state which is not possible with a normal 5,10,15,20-tetraphenyl porphyrin (N_4 core). Though in recent times, few papers have appeared on new 21-thiaporphyrin systems, the reports on 21-oxaporphyrin (N_3O) core are also still rare.[3] We have been interested in synthesis and chemistry of new core modified porphyrins to use them for biorganic and materials chemistry applications and in this direction, we have recently reported the synthesis of an unsymmetrical porphyrin pentamer containing one central dithiaporphyrin (N_2S_2 core) which was connected covalently by diaryl ethyne bridges to peripheral normal porphyrin systems.[4] We demonstrated an efficient energy transfer from peripheral N_4 systems to the central N_2S_2 system. We have also reported the synthesis of β-substituted 21-thiaporphyrins[5a] and water-soluble 21-oxaporphyrins.[5b] In continuation of our study on core modified porphyrin chemistry, in this paper, we report the synthesis and characterization of a series of 21-thia and 21-oxaporphyrin building blocks[6] bearing iodo-, ethyne- and aldehyde functional groups and their application towards the construction of energy donor appended 21-thia and 21-oxaporphyrin systems. A boron–dipyrrin (BDPY) unit was used as energy donor. A preliminary steady state fluorescence study indicates that there is an energy transfer from boron–dipyrrin units to 21-oxaporphyrin and 21-thiaporphyrin and the efficiency of energy transfer depends on the orientation and distance of boron–dipyrrin and porphyrin units as well as the structure of the porphyrin core.

2. Results and discussion

2.1. 21-Thiaporphyrin building blocks

The required thiophene diol, 2,5-bis(phenyl hydroxymethyl)thiophene was prepared in 65% yield by the double alkylation of the dianion of thiophene with benzaldehyde.[7] The other precursors such as 3- or 4-[2-(trimethylsilyl)-ethynyl]benzaldehyde,[8a] 3- or 4-iodobenzaldehyde[8b] and 2-(5,5-dimethyl-1,3-dioxacyclohex-2-yl) benzaldehyde[8c] were prepared by following literature procedures. The condensation of 1 equiv. of 2,5-bis(phenyl hydroxymethyl) thiophene with 2 equiv. of appropriate aldehyde and 3 equiv. of pyrrole gave a crude porphyrin mixture. The tlc analysis clearly showed the formation of three porphyrins. It is interesting to note that the above condensation resulted in the formation of three porphyrins with three different porphyrins cores: N_2S_2, N_3S and N_4. For example, as shown in the Scheme 1, the condensation of 2,5-bis(phenyl hydroxymethyl)thiophene, 4-iodobenzaldehyde and pyrrole gave three porphyrins: 5,10,15,20-tetraphenyl-21,23-dithiaporphyrin (N_2S_2, 2%), a desired 5,10-diphenyl-15,20-bis(4-iodophenyl)21-thiaporphyrin, **5** (N_3S, 17%) and 5,10,15,20-tetra(4-iodophenyl)porphyrin (N_4, 3%).

Keywords: porphyrin building blocks; core modified porphyrins; boron–dipyrrin; energy transfer.

* Corresponding author. Fax: +91-22-576-7152; e-mail: ravikanth@chem.iitb.ernet.in

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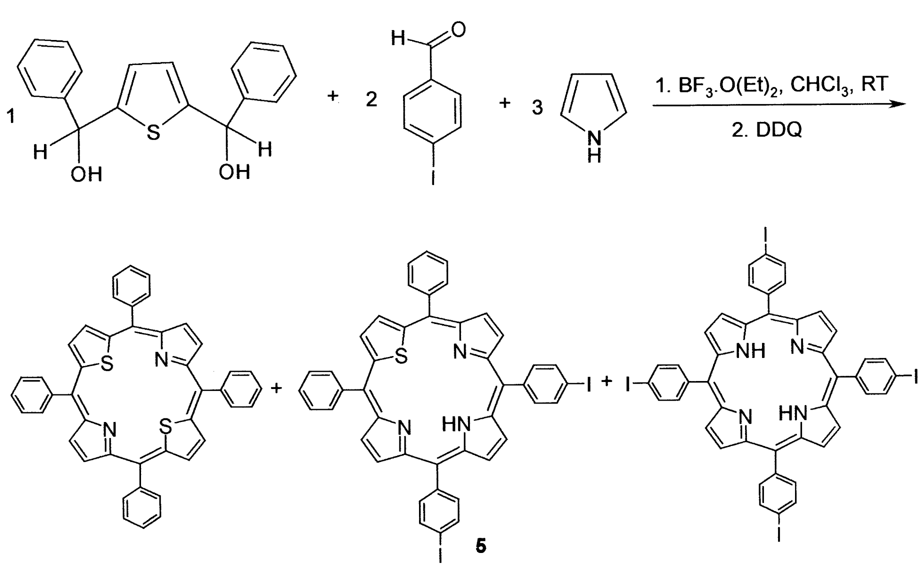
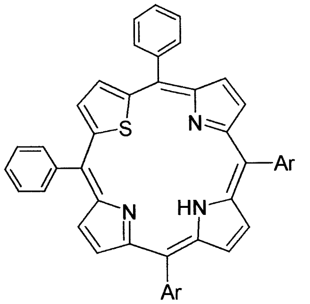
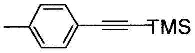
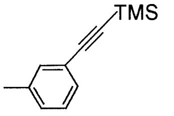
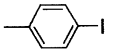
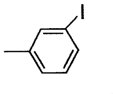
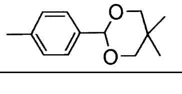


Scheme 1. Synthetic scheme of 21-thiaporphyrin building block, **5**.

Absorption spectroscopy is a very good tool for identifying the three porphyrins since the absorption bands (both soret and Q-bands) of all three porphyrins are very different from each other. The bands are red shifted as core changes from N_4 to N_3S to N_2S_2. Thus absorption spectroscopy is a fast and easy way to identify the required 21-thiaporphyrin building blocks. The mixture of three porphyrins was separated by silica gel column chromatography. Generally, the dithiaporphyrin moves as the first band followed by the desired 21-thiaporphyrin building block as the second band. The building blocks with iodo- and CCTMS-functional groups were obtained in 10–17% yields (Table 1). The deprotection of the trimethyl silyl group of **1** and **3** was carried out by treating with K_2CO_3 in THF–methanol (3:1) giving **2** and **4**, respectively, in 80% yield.[8a] The building block with formyl functional group **8** was prepared by deprotecting **7** with trifluoroacetic acid in the presence of dilute H_2SO_4. **7** was prepared in 3% yield by condensing 2,5-bis(phenyl hydroxymethyl) thiophene with 2-(5,5-dimethyl-1,3-dioxacyclohex-2-yl) benzaldehyde and pyrrole in $CHCl_3$ using TFA as catalyst. Use of $BF_3{\cdot}O(Et)_2$ as catalyst in this reaction gave very small amounts of porphyrin.

Table 1. 21-Thiaporphyrin building blocks



Porphyrin	Ar	Yield (%)
1		15
3		14
5		17
6		11
7		3

All 21-thiaporphyrin building blocks with iodo-, ethynyl- and aldehyde groups were characterized by ^1H NMR, mass spectroscopy, C, H, N analysis, absorption and fluorescence spectroscopy. The ^1H NMR spectrum of **8** is shown in Fig. 1(a). In all 21-thiaporphyrin building blocks, the thiophene protons appeared as singlet and three pyrroles appeared as three separate signals. This indicates the low symmetric nature of the porphyrin building blocks. The FAB-MS spectra showed a molecular ion peak confirming the product. Absorption spectra exhibited one Soret and four Q-bands and the peak positions were in close match with 5,10,15,20-tetraphenyl-21-thiaporphyrin. C, H, N analyses was also in agreement with the expected porphyrin building blocks.

2.2. 21-Oxaporphyrin building blocks

2,5-Bis(phenyl hydroxymethyl)furan was synthesized similarly to the synthesis of 2,5-bis(phenyl hydroxymethyl)thiophene by the double alkylation of the dianion of furan with benzaldehyde.[1b] The condensation of 2,5-bis(phenyl hydroxymethyl)furan with corresponding aldehyde and pyrrole gave a mixture of three porphyrins: 5,10,15,20-tetraphenyl-21,23-dioxoporphyrin (N_2O_2), the required 21-oxaporphyrin with –I, or –CCTMS groups (N_3S) and tetraphenyl porphyrin with –I or –CCTMS groups (N_4). The 21-oxaporphyrin building blocks were obtained in 10–15%

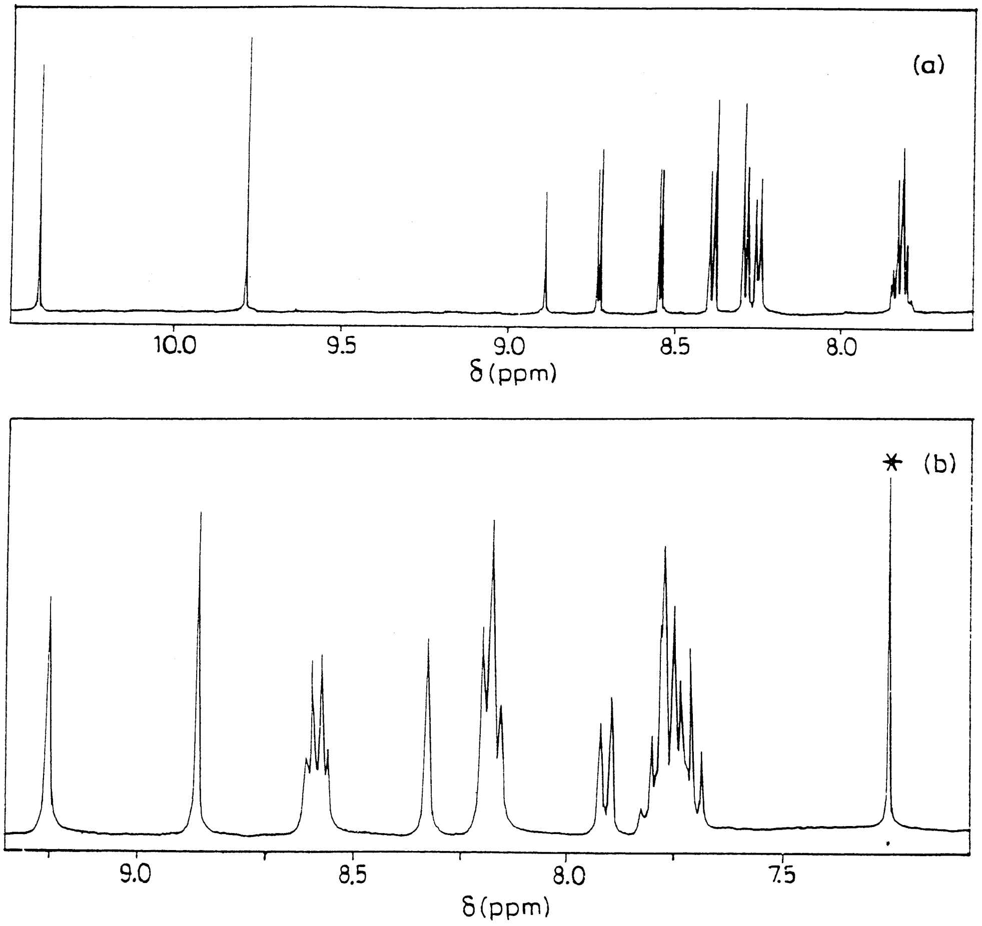
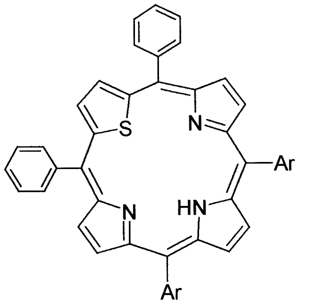
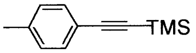
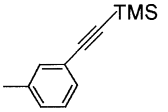
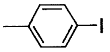
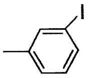
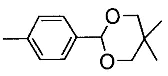


Figure 1. ^{1}H NMR spectra of: (a) **8** and (b) **12** recorded in $CDCl_3$.

Table 2. 21-Oxaporphyrin building blocks

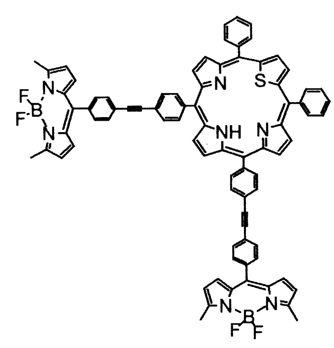


Porphyrin	Ar	Yield (%)
9		15
11		10
13		14
14		11
15		5

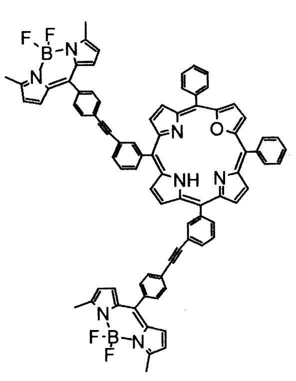
yields (Table 2). The deprotection of the trimethyl silyl group in **9** and **11** was carried out in THF–methanol in the presence of K_2CO_3 gave **10** and **12**, respectively,[8a] Porphyrin building block **15** was prepared in relatively low yield using TFA as catalyst. The deprotection of **15** with trifluoroacetic acid in the presence of dilute H_2SO_4 gave **16** in 55% yield. All building blocks were characterized using spectroscopic techniques. The ^{1}H NMR spectra (Fig. 1(b)) show a singlet for furan and the three pyrroles appear as two or three signals indicating the low symmetry nature of porphyrins. FAB-MS and C, H, N analyses further confirmed the products. Absorption spectra of the other two side products (N_2O_2 and N_4 porphyrins) were very different from the required porphyrin and hence useful in identifying the right compound.

2.3. Boron–dipyrrin appended 21-thia and 21-oxaporphyrins

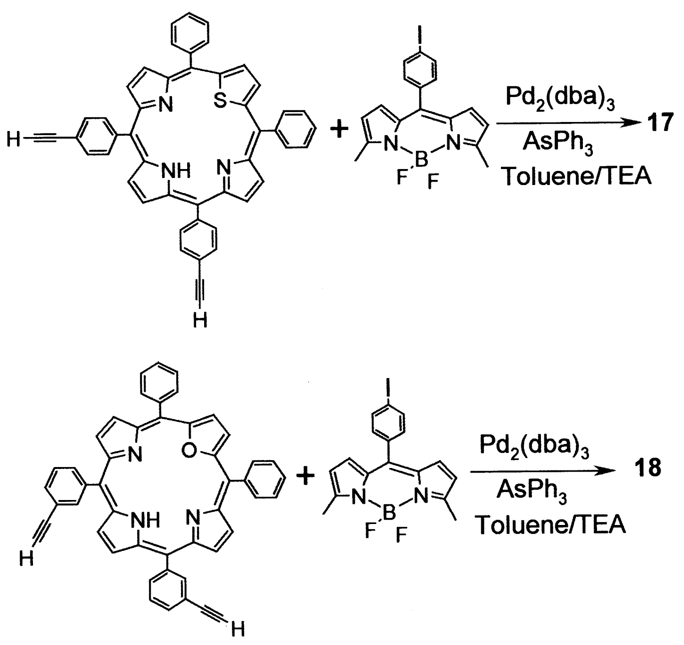
The porphyrin building blocks with –I, –CCH and –CHO functional groups are very useful for preparing series of unsymmetrical porphyrin arrays and donor appended porphyrin systems.[6] Thus we used the core modified porphyrin building blocks to synthesize boron–dipyrrin appended porphyrin systems **17** and **18** as outlined in Scheme 2. Coupling of **2** with *N*,*N*-difluoroboryl-1,9-dimethyl-5-(4-iodophenyl)-dipyrrin (BDPY-I) in toluene/triethylamine at 35°C in the presence of $Pd_2(dba)_3$ and



17



18



Scheme 2. Synthetic scheme for **17** and **18**.

$AsPh_3$ gave **17** in 28% yield and coupling of **12** with BDPY-I under same conditions gave **18** in 17% yield.[9] Both **17** and **18** were characterized using ^1H NMR, FAB-MS, absorption and emission spectroscopies. ^1H NMR spectra of **17** and **18** are shown in Fig. 2. In both cases, the pyrroles of the porphyrin ring appear as three separate signals. The pyrrole protons of BDPY unit appear upfield as two doublets in **17** and as two multiplets in **18**. The β-thiophene in **17** and β-furan in **18** appear as singlets. The FAB-MS showed a molecular ion peak confirming that the porphyrin systems are appended with two BDPY units. The absorption spectra (Fig. 3) show four bands; one Soret and three Q-bands. The peak at 515 nm which is mainly due to BDPY units[10] is much larger in intensity than the other two Q-bands which are mainly due to the porphyrin ring. The emission spectra recorded at 485 nm for both **17** and **18** are shown in Fig. 4. As evident from Fig. 4, both **17** and **18** excited at 485 nm where BDPY absorbs predominantly resulted in emission from both BDPY and porphyrin units. Though in the case of **18**, the strong emission was from 21-oxoporphyrin unit with a comparatively weak emission from BDPY unit indicating a clear transfer of energy from BDPY unit to 21-oxoporphyrin unit, the quantum yield data suggest that the energy transfer from boron–dipyrrin to porphyrin unit was also evident in **17**. The quantum yield of BDPY unit in both **17** ($\phi=0.0306$) and **18** ($\phi=0.0198$) was decreased from the free BDPY ($\phi=0.18$) supporting the above observation.[10] The efficiency of energy transfer appears to be greater in **18** than **17**. However, it is difficult to compare these two systems since the distance and the orientation of BDPY units with the porphyrin unit are different in **17** and **18**. In case of **17**, the distance between the boron–dipyrrin and porphyrin is longer than **18** and the orientation of BDPY units w.r.t porphyrin is also different. A detailed study of the photodynamics of these systems taking the distance and orientation of donor and acceptor into consideration would help to understand the difference of energy transfer in **17** and **18**.

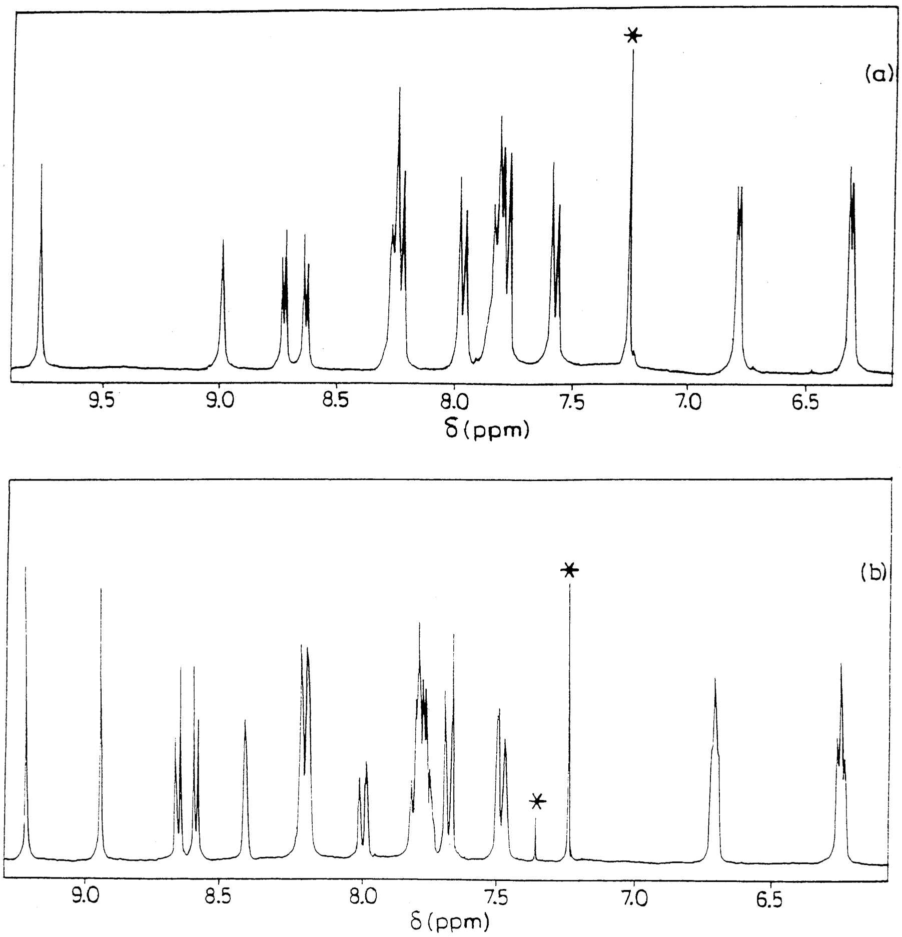


Figure 2. ^{1}H NMR spectra of: (a) **17** and (b) **18** recorded in $CDCl_3$. (*) indicates solvent and its impurity.

3. Conclusions

In conclusion, we have prepared a series of 21-thia and 21-oxaporphyrin building blocks bearing iodo-, ethyne- and aldehyde functional groups. The *cis*-porphyrin building blocks reported here are very difficult to make with N_4 porphyrin systems. However, the core modified porphyrin building blocks with functional groups in *cis* fashion were very easy to synthesize. Spectroscopic techniques like absorption and fluorescence spectroscopy were sufficient to identify and isolate the core modified building blocks in reasonable yields. We have also shown the use of these core modified building blocks to synthesize energy donor appended systems under mild palladium coupling conditions. Much more extensive studies would be required to understand the energy transfer dynamics in these systems.

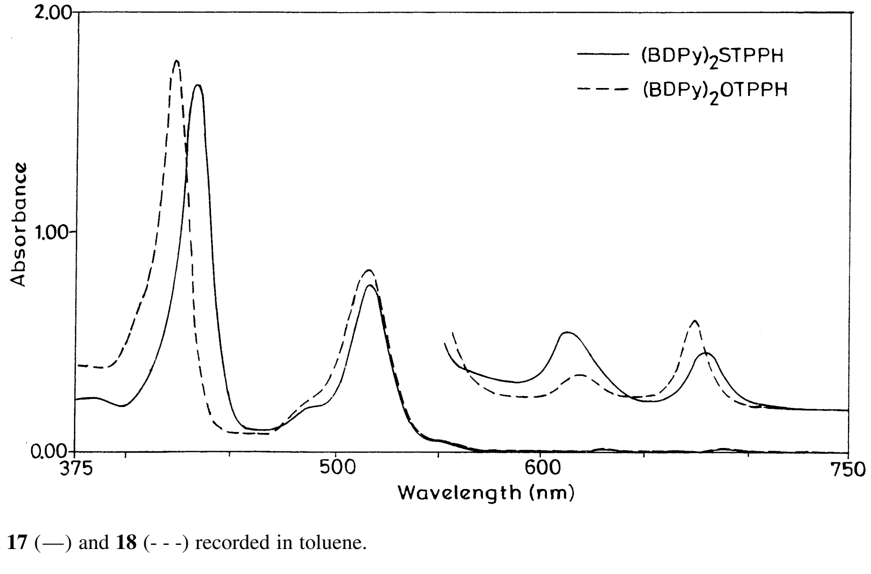


Figure 3. UV–Vis spectra **17** (—) and **18** (- - -) recorded in toluene.

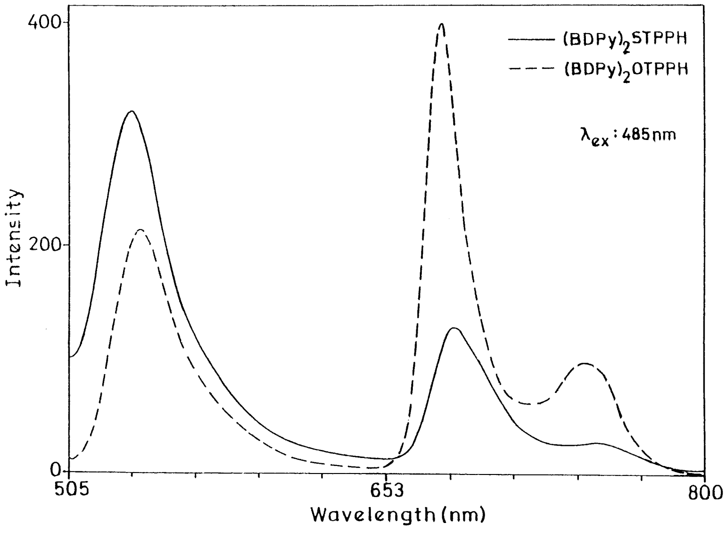


Figure 4. Fluorescence spectra of **17** (—) and **18** (- - -) recorded in toluene at λ_{ex}=515 nm.

The building blocks can also be used to synthesize unsymmetrical porphyrin arrays containing core modified porphyrin and normal porphyrin which are ideal systems to understand the electron and energy transfer reactions of photosynthesis. The synthesis and study of such unsymmetrical porphyrin arrays are presently under investigation in our laboratory.

4. Experimental

4.1. General

^{1}H NMR spectra were recorded on a varian 300 MHz using tetramethylsilane as internal standard. Absorption and fluorescence spectra were obtained with Shimadzu-160 and Spex Fluoromax respectively. The FAB mass spectra were recorded on a JEOL SX 102/DA-6000 mass spectrometer using Argon/Xenon as the FAB gas. Toluene, THF and triethylamine were obtained from S.D Fine chemicals, India, and dried by standard procedures before use. All general chemicals were obtained from Qualigens, India. Benzaldehyde and pyrrole were obtained from Lancaster. Column chromatography was performed using 60–120 mesh silica obtained from Sisco Research Laboratories, India. Size exclusion chromatography was performed using Bio-Beads SX-1 in toluene obtained from Biorad, USA.

4.2. General method for the synthesis and purification of porphyrin building blocks (1, 3, 5, 6, 9, 11, 13 and 14)

Samples of 1 equiv. of 2,5-bis(phenyl hydroxymethyl)thiophene or -furan and 2 equiv. of appropriate aldehyde (3- or 4-substituted benzaldehyde with –I, –CCTMS groups) were dissolved in $CHCl_3$ under argon in a one neck round bottom flask. After 10 min purging with argon, 3 equiv. of pyrrole were added and $BF_3{\cdot}O(Et)_2$ (3.3 mM) was added to initiate the condensation. The reaction mixture was stirred for 1 h under an argon atmosphere. Then DDQ was added and stirring was continued for an additional 1 h. The formation of porphyrin(s) was verified by absorption spectroscopy. The tlc analysis of crude reaction mixture indicated the formation of three expected pophyrins. The solvent was removed under reduced pressure and crude solid was dissolved in $CHCl_3$. A dark powdered slurry was then prepared by adding silica gel and dried. The powder was loaded on a silica column and slow gravity elution with pet ether/CH_2Cl_2 or CH_2Cl_2/CH_3OH was started. The desired porphyrin was the second band in all porphyrin building block reactions. Absorption and fluorescence spectroscopy were used to identify the required compound. The desired porphyrin was rechromatographed in an identical manner for final purification.

4.2.1. 5,10-Diphenyl-15,20-bis {4-[2-(trimethylsilyl)-ethynyl]phenyl}-21-thiaporphyrin (1). A solution of 2,5-bis(hydroxymethyl)thiophene (500 mg, 1.69 mmol), 4-[2-(trimethylsilyl)ethynyl] benzaldehyde (683 mg, 0.675 mmol) and pyrrole (352 μl, 5.083 mmol) in 250 ml $CHCl_3$ were condensed in the presence of $BF_3{\cdot}O(Et)_2$ (330 μl of 2.5 M stock solution, 3.3 mM). After 1 h, DDQ (573 mg, 0.748 mmol) was added and stirred for 1 h. Chromatography with pet ether/CH_2Cl_2 (1:1) gave the required purple compound (218 mg, 15%). ^{1}H NMR ($CDCl_3$, δ in ppm) -2.76 (s, 1H, NH), 0.39 (s, 18H, CH_3), 7.83 (m, 10H, Ar), 8.15 (m, 4H, Ar), 8.26 (m, 4H, Ar), 8.57 (d, 2H, J=4 Hz, β-pyrrole), 8.70 (d, 2H, J=4 Hz, β-pyrrole), 8.90 (d, 2H, J=4 Hz, β-pyrrole), 9.76 (s, 2H, β-thiophene). FAB-MS $C_{54}H_{45}N_3SSi_2$ calcd mass, 823.2. obsd. m/z 823. Anal. calcd: C, 78.8; H, 5.50; N, 5.09. Found: C, 79.2; H, 5.42; N, 4.89. IR (KBr, ν (cm^{-1})) 3323, 3030, 2943, 2154, 705. UV–Vis (λ_{max} (nm), ε (dm^3 mol^{-1} cm^{-1})) 431 (272,000), 514 (18760), 549 (5900), 619 (2360), 679 (3840).

4.2.2. 5,10-Diphenyl-15,20-bis(4-ethynylphenyl)-21-thiaporphyrin (2). Compound **1** (66 mg, 0.0802 mmol) was dissolved in 30 ml of THF and K_2CO_3 in CH_3OH (200 mg in 10 ml of CH_3OH) was added to it. The reaction mixture was heated to reflux for 6 h. The deprotection of trimethyl silyl group was followed by tlc. The solvent was removed and the compound was purified by silica gel column chromatography using CH_2Cl_2 gave **2** as a purple solid (53 mg, 80%). ^{1}H NMR ($CDCl_3$, δ in ppm) -2.75 (s, 1H, NH), 3.25 (s, 2H, CCH), 7.81 (m, 10H, Ar), 8.15 (m, 4H, Ar), 8.25 (m, 4H, Ar), 8.55 (d, 2H, J=4 Hz, β-pyrrole), 8.69 (d, 2H,

J=4 Hz, β-pyrrole), 8.91 (d, 2H, J=4 Hz, β-pyrrole), 9.78 (s, 2H, β-thiophene). FAB-MS $C_{48}H_{29}N_3S$ calcd mass 679.2, obsd. *m/z* 679. Anal. calcd: C, 84.9; H, 4.30; N, 6.18. Found: C, 84.2; H, 4.14; N, 6.08. IR (KBr, ν (cm^{-1})) 3335, 3295, 2927, 2854, 2111, 702. UV–Vis (λ_{max} (nm), ε (dm^{3}mol^{-1} cm^{-1})) 431 (321,800), 514 (26,920), 548 (7740), 619 (3400), 679 (5260).

4.2.3. 5,10-Diphenyl-15,20-bis {3-[2-(trimethylsilyl)-ethynyl]phenyl}-21-thiaporphyrin (3). Samples of 2,5-bis(phenyl hydroxymethyl)thiophene (200 mg, 0.676 mmol), 3-[2-(trimethylsilyl)ethynyl] benzaldehyde (273 mg, 1.35 mmol) and pyrrole (140 μl, 2.027 mmol) in 100 ml $CHCl_3$ were treated with $BF_3{\cdot}O(Et)_2$ (132 ml of 2.5 M stock solution, 3.3 mM) under argon for 1 h. DDQ (229 mg, 1.013 mmol) was added and stirring was continued for extra 1 h. Chromatography with pet ether/CH_2Cl_2 (3:1) afforded a purple solid (79 mg, 14%). ^{1}H NMR ($CDCl_3$, δ in ppm) −2.76 (s, 1H, NH), 0.26 (s, 18H, CH_3), 7.68 (t, 2H, J=6.5 Hz, Ar), 7.79 (m, 6H, Ar), 7.89 (m, 2H, Ar), 8.13 (m, 2H, Ar), 8.22–8.28 (m, 4H, Ar), 8.33 (s, 2H, Ar), 8.58 (d, 2H, J=4.5 Hz, β-pyrrole), 8.69 (d, 2H, J=4.5 Hz, β-pyrrole), 8.92 (s, 2H, β-pyrrole), 9.76 (s, 2H, β-thiophene). FAB-MS $C_{54}H_{45}N_3SSi_2$ calcd mass 823.2, obsd. *m/z* 824. Anal. calcd: C, 78.8; H, 5.50; N, 5.09. Found: C, 78.1; H, 5.43; N, 4.91. UV–Vis (λ_{max} (nm), ε (dm^3 mol^{-1} cm^{-1})) 430 (370,610), 514 (33,052), 548 (7636), 618 (4165), 678 (5688).

4.2.4. 5,10-Diphenyl-15,20-bis(3-ethynylphenyl)-21-thiaporphyrin (4). Compound **3** (50 mg, 0.0607 mmol) in 10 ml dry THF was treated with K_2CO_3 (84 mg, 0.607 mmol) in 3 ml of CH_3OH at reflux temperature for 6 h. Chromatography on silica with CH_2Cl_2 gave **4** as a purple solid (34 mg, 82%). ^{1}H NMR ($CDCl_3$, δ in ppm) −2.75 (s, 1H, NH), 3.16 (s, 2H, CCH), 7.71 (t, 2H, J=6.5 Hz, Ar), 7.81 (m, 6H, Ar), 7.92 (m, 2H, Ar), 8.22–8.28 (m, 4H, Ar), 8.35 (s, 2H, Ar), 8.58 (d, 2H, J=4.5 Hz, β-pyrrole), 8.71 (d, 2H, J=4.5 Hz, β-pyrrole), 8.92 (d, 2H, J=4.5 Hz, β-pyrrole), 9.77 (s, 2H, β-thiophene). FAB-MS $C_{48}H_{29}N_3S$ calcd mass 679.2, obsd. *m/z* 680. Anal. calcd: C, 84.9; H, 4.30; N, 6.18. Found: C, 84.3; H, 4.21; N, 6.05. UV–Vis (λ_{max} (nm), ε (dm^3 mol^{-1} cm^{-1})) 430 (345,280), 514 (31,872), 547 (7380), 617 (4070), 677 (5457).

4.2.5. 5,10-Diphenyl-15,20-bis(4-iodophenyl)-21-thiaporphyrin (5). A solution of 2,5-bis(phenyl hydroxymethyl)thiophene (100 mg, 0.337 mmol), 4-iodobenzaldehyde (156 mg, 0.675 mmol) and pyrrole (70 μl, 1.013 mmol) in 25 ml of $CHCl_3$ was treated with $BF_3{\cdot}O(Et)_2$ (66 μl of 2.5 M stock solution, 3.3 mM). After 1 h, DDQ (150 mg, 0.663) was added and stirring was continued for additional 1 h. Chromatography with pet ether/CH_2Cl_2 (1:1) gave purple compound, **5** (53 mg, 17%). ^{1}H NMR ($CDCl_3$, δ in ppm) −2.75 (s, 1H, NH), 7.82 (m, 6H, Ar), 7.91 (m, 4H, Ar), 8.13 (m, 4H, Ar), 8.25 (m, 4H, Ar), 8.58 (d, 2H, J=4.5 Hz, β-pyrrole), 8.70 (d, 2H, J=4.5 Hz, β-pyrrole), 8.93 (d, 2H, J=4.5 Hz, β-pyrrole), 9.77 (s, 2H, β-thiophene). FAB-MS $C_{44}H_{27}N_3SI_2$ calcd mass 883.0, obsd. *m/z* 884. Anal. calcd: C, 59.8; H, 3.07; N, 4.77. Found: C, 60.5; H, 3.01; N, 4.63. UV–Vis (λ_{max} (nm), ε (dm^3 mol^{-1} cm^{-1})) 430 (424,000), 513 (26,420), 548 (7340), 618 (3300), 679 (4920).

4.2.6. 5,10-Diphenyl-15,20-bis(3-iodophenyl)-21-thiaporphyrin (6). A solution of 2,5-bis(phenyl hydroxymethyl)thiophene (100 mg, 0.337 mmol), 3-iodobenzaldehyde (156 mg, 0.675 mmol) and pyrrole (70 μl, 1.013 mmol) in 50 ml of CH_2Cl_2 was treated with $BF_3{\cdot}O(Et)_2$ (66 μl of 2.5 M stock solution, 3.3 mM). After 1 h, DDQ (170 mg, 0.5066 mmol) was added and left the reaction for stirring for 1 h in air. Chromatography with pet ether/CH_2Cl_2 (1:1) gave **6** as a purple solid (31 mg, 11%). ^{1}H NMR ($CDCl_3$, δ in ppm) −2.76 (s, 1H, NH), 7.48 (t, 4H, J=6.5 Hz, Ar), 7.82 (m, 6H, Ar), 8.13–8.33 (m, 6H, Ar), 8.61 (m, 4H+2H, Ar+β-py), 8.72 (d, 2H, J=4.5 Hz, β-pyrrole), 8.96 (bs, 2H, β-pyrrole), 9.78 (s, 2H, β-thiophene). FAB-MS $C_{44}H_{27}N_3SI_2$ calcd mass 883.0, obsd. *m/z* 884. Anal. calcd: C, 59.8; H, 3.07; N, 4.77. Found: C, 60.4; H, 3.01; N, 4.48. IR (KBr, ν (cm^{-1})) 3328, 3052, 2927, 2848, 709. UV–Vis (λ_{max} (nm), ε (dm^3 mol^{-1} cm^{-1})) 430 (420,000), 513 (28,500), 547 (6840), 618 (3420), 678 (4720).

4.2.7. 5,10-Diphenyl-15,20-bis[4-(5,5-dimethyl-1,3-dioxacyclohex-2-yl)phenyl]-21-thiaporphyrin (7). Samples of 2,5-bis (phenyl hydroxymethyl)thiophene (100 mg, 0.337 mmol), 4-(5,5-dimethyl-1,3-dioxacyclohex-2-yl)-benzladehyde (165 mg, 0.749 mmol) and pyrrole (100 μl, 1.441 mmol) were dissolved in 25 ml of $CHCl_3$ and stirred at room temperature under argon for 10 min. Trifluoroacetic acid (100 μl, 0.0013 mmol) was added to initiate the condensation and the reaction mixture was stirred for 1 h under argon atmosphere. DDQ (100 mg, 0.441 mmol) was then added and the reaction mixture was stirred for additional 1 h in air. The solvent was removed in vacuo and the crude compound was loaded on silica and eluted with CH_2Cl_2. The desire compound was the second band with CH_2Cl_2/diethyl ether (85:15). The solvent was removed on a rotary evaporator to afford **7** as dark purple solid in 3% (8.7 mg) yield. ^{1}H NMR ($CDCl_3$, δ in ppm) −2.75 (s, 1H, NH), 1.54 (s, 12H, CH_3), 3.86 (d, 4H, J=6.6 Hz, CH_2), 3.97 (d, 4H, J=6.6 Hz, CH_2), 5.76 (s, 2H, CH), 7.79 (m, 6H, Ar), 7.90 (m, 4H, Ar), 8.21 (m, 8H, Ar), 8.59 (d, 2H, J=2.4 Hz, β-py), 8.66 (d, 2H, J=2.4 Hz, β-pyrrole), 8.91 (m, 2H, β-pyrrole), 9.74 (s, 2H, β-thiophene). FAB-MS $C_{56}H_{49}N_3O_4S$ calcd mass 860.1, obsd. *m/z* 861. Anal. calcd: C, 78.2; H, 5.74; N, 4.88. Found: C, 77.6; H, 5.85; N, 4.79. IR (KBr, ν (cm^{-1})) 3336, 2953, 2861, 1110, 715. UV–Vis (λ_{max} (nm), ε (dm^3 mol^{-1} cm^{-1}) 429 (83,470), 513 (7638), 547 (225), 616 (1037), 678 (1441).

4.2.8. 5,10-Diphenyl-15,20-bis(4-formylphenyl)-21-thiaporphyrin (8). The acetal group in **7** was hydrolyzed to give the formyl substituted porphyrin **8**. The acetal porphyrin **7** (50 mg, 0.0581), trifluoroacetic acid (7 ml), 10% aqueous sulfuric acid (2 ml) in 20 ml CH_2Cl_2 was refluxed for 7 h. The deprotection was monitored by tlc. The reaction mixture was cooled to room temperature and poured into water. The organic layer was washed successively with water, aqueous sodium bicarbonate and brine and dried over anhydrous sodium sulfate. The solvent was removed and the residue was dissolved in CH_2Cl_2. Column chromatography on silica with CH_2Cl_2 gave **8** as a dark purple solid in 65% yield (25 mg). ^{1}H NMR ($CDCl_3$, δ in ppm) −2.73 (s, 1H, NH), 7.81 (m, 6H, Ar), 8.23 (m, 4H, Ar), 8.27 (AA′BB′, 4H, Ar), 8.38 (AA′BB′, 4H, Ar), 8.54 (d, 2H, J=2.4 Hz, β-py), 8.72 (d, 2H, J=2.4 Hz, β-pyrrole), 8.89 (m, 2H, β-pyrrole), 9.79 (s, 2H, β-thiophene). FAB-MS $C_{46}H_{29}N_3O_2S$ calcd mass 687.2, obsd. m/z 688. Anal. calcd: C, 83.7; H, 4.43; N, 6.36. Found: C, 82.8; H, 4.37; N, 6.19. IR (KBr, ν (cm^{-1})) 3325, 2934, 2852, 1704, 720. UV–Vis (λ_{max} (nm), ε (dm^3 mol^{-1} cm^{-1})) 431 (43,924), 514 (4233), 549 (1388), 618 (614), 678 (853).

4.2.9. 5,10-Diphenyl-15,20-bis {4-[2-(trimethylsilyl)-ethynyl]phenyl}-21-oxaporphyrin (9). A solution of 2,5-bis(phenyl hydroxymethyl)furan (600 mg, 2.126 mmol), 4-[2-(trimethylsilyl)ethynyl]benzaldehyde (860 mg, 4.253 mmol) and pyrrole (442 μl, 6.364 mmol) in 300 ml $CHCl_3$ was treated with $BF_3{\cdot}O(Et)_2$ (396 μl of 2.5 M stock solution, 3.3 mM). After 1 h, DDQ (721 mg, 3.189 mmol) was added. Chromatography on silica with CH_2Cl_2/CH_3OH (97:3) gave a purple solid (270 mg, 15%). ^{1}H NMR ($CDCl_3$, δ in ppm) 0.38 (s, 18H, CH_3), 7.78 (m, 6H, Ar), 7.88 (m, 4H, Ar), 8.12 (d, 4H, J=6.5 Hz, Ar), 8.20 (d, 4H, J=6.5 Hz, Ar), 8.65 (bs, 4H, β-pyrrole), 8.86 (s, 2H, β-pyrrole), 9.25 (s, 2H, β-furan). FAB-MS $C_{54}H_{45}N_3OSi_2$ calcd mass 807.3, obsd. m/z 808. Anal. calcd: C, 80.1; H, 5.61; N, 5.19. Found: C, 79.6; H, 5.39; N, 5.09. IR (KBr, ν (cm^{-1})) 3052, 2940, 2154, 705. UV–Vis (λ_{max} (nm), ε (dm^3 mol^{-1} cm^{-1})) 423 (140,565), 508 (19,964), 540 (6752), 614 (3828), 675 (4253).

4.2.10. 5,10-Diphenyl-15,20-bis(4-ethynylphenyl)-21-oxaporphyrin (10). Compound **9** (100 mg, 0.124 mmol) was dissolved in 20 ml THF and K_2CO_3 (171 mg, 1.237 mmol) in CH_3OH (6 ml) was added to it. The reaction mixture was refluxed for 8 h. Chromatography on silica with CH_2Cl_2/CH_3OH (97:3) gave purple solid, **10** (70 mg, 85%). ^{1}H NMR ($CDCl_3$, δ in ppm) 3.31 (s, 2H, CCH), 7.79 (m, 6H, Ar), 7.89 (m, 4H, Ar), 8.17 (m, 8H, Ar), 8.55 (d, 2H, J=4.5 Hz, β-pyrrole), 8.59 (d, 2H, J=4.5 Hz, β-py), 8.85 (s, 2H, β-pyrrole), 9.20 (s, 2H, β-furan). FAB-MS $C_{48}H_{29}N_3O$ calcd mass 663.2, obsd. m/z 664. Anal. calcd: C, 86.8; H, 4.40; N, 6.35. Found: C, 86.3; H, 4.32; N, 6.09. IR (KBr, ν (cm^{-1})) 3242, 2115, 702. UV–Vis (λ_{max} (nm), ε (dm^3 mol^{-1} cm^{-1})) 422 (330,119), 508 (33,805), 540 (7664), 614 (4539), 675 (5931).

4.2.11. 5,10-Diphenyl-15,20-bis {3-[2-(trimethylsilyl)-ethynyl]phenyl}-21-oxaporphy-rin (11). Samples of 2,5-bis(phenyl hydroxymethyl)furan (100 mg, 0.357 mmol), 3-[2-(trimethylsilyl)ethynyl]benzaldehyde (144 mg, 0.714 mmol) and pyrrole (74 μl, 1.071 mmol) in 50 ml $CHCl_3$ were condensed in the presence of $BF_3{\cdot}O(Et)_2$ (66 μl of 2.5 M stock solution, 3.3 mM). After 1 h, DDQ (121 mg, 0.535 mmol) was added and stirred for an additional 1 h. Chromatography on silica using CH_2Cl_2/CH_3OH (97:3) gave purple solid, **11** (29 mg, 10%). ^{1}H NMR ($CDCl_3$, δ in ppm) 0.39 (s, 18H, CH_3), 7.68 (t, 2H, J=6 Hz, Ar), 7.79 (m, 6H, Ar), 7.89 (d, 2H, J=4 Hz, Ar), 8.10 (d, 2H, J=4 Hz, Ar), 8.19 (d, 4H, J=4 Hz, Ar), 8.31 (s, 2H, Ar), 8.57 (m, 4H, β-pyrrole), 8.85 (s, 2H, β-pyrrole), 9.20 (s, 2H, β-furan). FAB-MS $C_{54}H_{45}N_3Si_2O$ calcd mass, 807.3, obsd. m/z 808. Anal. calcd: C, 80.1; H, 5.61; N, 5.19. Found: C, 79.3; H, 5.90; N, 5.42. UV–Vis (λ_{max} (nm), ε (dm^3 mol^{-1} cm^{-1})) 423 (128,567), 444 (46,728), 507 (18,110), 538 (3687), 612 (2601), 673 (2753).

4.2.12. 5,10-Diphenyl-15,20-bis(3-ethynylphenyl)-21-oxaporphyrin (12). Compound **11** (46 mg, 0.0694 mmol) was dissolved in 12 ml of THF. K_2CO_3 (50 mg, 0.361 mmol) in 3 ml of CH_3OH was added and refluxed for 6 h. Chromatography on silica using CH_2Cl_2/CH_3OH (97:3) afforded **12** as a purple solid (38 mg, 82%). ^{1}H NMR ($CDCl_3$, δ in ppm) 3.20 (s, 2H, CCH), 7.75 (m, 8H, Ar), 7.91 (m, 2H, Ar), 8.18 (m, 6H, Ar), 8.32 (s, 2H, Ar), 8.57 (m, 4H, β-pyrrole), 8.86 (m, 2H, β-pyrrole), 9.20 (s, 2H, β-furan). FAB-MS $C_{48}H_{29}N_3O$ calcd mass, 663.2, obsd. m/z 664. Anal. calcd: C, 86.8; H, 4.40; N, 6.35. Found: C, 85.9; H, 4.39; N, 6.18. UV–Vis (λ_{max} (nm), ε (dm^3 mol^{-1} cm^{-1})) 421 (171,856), 443 (33,833), 507 (16,747), 538 (4930), 612 (2716), 674 (2456).

4.2.13. 5,10-Diphenyl-15,20-bis(4-iodophenyl)-21-oxaporphyrin (13). Samples of 2,5-bis(phenyl hydroxymethyl)furan (100 mg, 0.357 mmol), 3-iodobenzaldehyde (165 mg, 0.714 mmol) and pyrrole (74 μl, 1.071 mmol) in $CHCl_3$ (50 ml) was treated with $BF_3{\cdot}O(Et)_2$ (66 μl of 2.5 M stock solution, 3.3 mM). After 1 h, DDQ (121 mg, 0.535 mmol) was added. Chromatography on silica with CH_2Cl_2/CH_3OH (94:6) gave purple solid, **13** (43 mg, 14%). ^{1}H NMR ($CDCl_3$, δ in ppm) 7.79 (m, 6H, Ar), 7.93 (m, 4H, Ar), 8.12 (AA′BB′, 4H, Ar), 8.22 (AA′BB′, 4H, Ar), 8.72 (bs, 4H, β-pyrrole), 8.87 (m, 2H, β-pyrrole), 9.33 (s, 2H, β-furan). FAB-MS $C_{44}H_{27}N_3OI_2$ calcd mass, 867.0, obsd. m/z 868. Anal. calcd: C, 60.9; H, 3.13; N, 4.84. Found: C, 61.5; H, 3.34; N, 4.67. IR (KBr, ν (cm^{-1})) 3052, 2940, 715. UV–Vis (λ_{max} (nm), ε (dm^3 mol^{-1} cm^{-1})) 423 (205,404), 443 (53,560), 507 (25,896), 539 (5195), 614 (3347), 674 (4338).

4.2.14. 5,10-Diphenyl-15,20-bis(3-iodophenyl)-21-oxaporphyrin (14). A solution of 2,5-bis(phenyl hydroxymethyl) furan (100 mg, 0.357 mmol), meta-iodobenzaldehyde (165 mg, 0.714 mmol) and pyrrole (74 μl, 1.071 mmol) in $CHCl_3$ (50 ml) was treated with $BF_3{\cdot}O(Et)_2$ (66 μl of 2.5 M stock solution, 3.3 mM). After 1 h, DDQ (121 mg, 0.535 mmol) was added. Chromatography on silica with CH_2Cl_2/CH_3OH (94:6) gave purple solid, **14** (34 mg, 11%). ^{1}H NMR ($CDCl_3$, δ in ppm) 7.58 (t, 2H, J=3.6 Hz Ar), 7.89 (m, 6H, Ar), 8.20–8.39 (m, 8H, Ar), 8.65 (s, 2H, Ar), 8.85 (s, 2H, β-pyrrole), 9.07 (m, 4H, β-pyrrole), 9.64 (s, 2H, β-furan). FAB-MS $C_{44}H_{27}N_3OI_2$ calcd mass 867.0, obsd. m/z 868. Anal. calcd: C, 60.9; H, 3.13; N, 4.84. Found: C, 61.1; H, 3.42; N, 4.58. IR (KBr, ν (cm^{-1})) 2924, 2853, 705. UV–Vis (λ_{max} (nm), ε (dm^3 mol^{-1} cm^{-1})) 421 (119,667), 507 (14,750), 538 (3434), 613 (2205), 674 (2241).

4.2.15. 5,10-Diphenyl-15,20-bis[4-(5,5-dimethyl-1,3-dioxacyclohex-2-yl)phenyl]-21-oxaporphyrin (15). A solution of 2,5-bis(phenyl hydroxymethyl)furan (500 mg, 1.784 mmol), 2-(5,5-dimethyl-1,3-dioxacyclohex-2-yl)benzladehyde (825 mg, 3.74 mmol) and pyrrole (373 μl, 5.353 mmol) were dissolved in 25 ml of $CHCl_3$ and stirred at room temperature under argon for 10 min. Trifluoroacetic acid (1 ml, 0.0130 mmol) was added to initiate the condensation and the reaction mixture was stirred for 1 h under argon atmosphere. DDQ (635 mg, 2.797 mmol) was then added and the reaction mixture was stirred for an additional 1 h in air. The solvent was removed in vacuo and the crude compound was loaded on silica and eluted with CH_2Cl_2. The desired compound moved as a second band with CH_2Cl_2/5% CH_3OH to afford purple solid, **15** in 5% yield. (75 mg). ^{1}H NMR ($CDCl_3$, δ in ppm) 1.46 (s, 12H, CH_3), 3.85 (d, 4H, J=6.6 Hz, CH_2), 3.96 (d, 4H, J=6.6 Hz, CH_2), 5.75 (s, 2H, CH), 7.77 (m, 6H, Ar), 7.90 (m, 4H, Ar), 8.19 (m, 8H, Ar), 8.56 (d, 2H, J=4.5 Hz, β-pyrrole), 8.65 (d, 2H, J=4.5 Hz, β-pyrrole), 8.85 (m, 2H, β-pyrrole), 9.20 (s, 2H, β-furan). FAB-MS $C_{56}H_{49}N_3O_5$ calcd mass 843.3, obsd. *m/z* 844. Anal. calcd: C, 79.7; H, 5.85; N, 4.98. Found: C, 79.1; H, 5.94; N, 4.89. IR (KBr, ν (cm^{-1})) 2924, 2850, 1103, 711. UV–Vis (λ_{max} (nm), ε (dm^3 mol^{-1} cm^{-1})) 421 (112,761), 507 (16,380), 539 (5776), 612 (3982), 673 (3349).

4.2.16. 5,10-Diphenyl-15,20-bis(4-formylphenyl)-21-oxaporphyrin (16). The acetal porphyrin **15** (50 mg, 0.05924), trifluoroacetic acid (7 ml), 10% aqueous sulfuric acid (2 ml) in 20 ml CH_2Cl_2 was refluxed for 7 h. The deprotection was monitored with tlc. The reaction mixture was cooled to room temperature and poured into water. The organic layer was washed successively with water, aqueous sodium bicarbonate and brine and dried over anhydrous sodium sulfate. The solvent was removed and the residue was dissolved in CH_2Cl_2. Column chromatography on silica with CH_2Cl_2 gave purple solid, **16** in 55% yield (22 mg). ^{1}H NMR ($CDCl_3$, δ in ppm) 7.81 (m, 6H, Ar), 8.23 (m, 4H, Ar), 8.29 (m, 4H, Ar), 8.39 (m, 4H, Ar), 8.61 (d, 4H, J=4.5 Hz, β-pyrrole), 8.81 (m, 2H, β-pyrrole), 9.26 (s, 2H, β-furan), 10.38 (s, 2H, CHO). FAB-MS $C_{46}H_{29}N_3O_3$ calcd mass 671.2, obsd. *m/z* 672. Anal. calcd: C, 82.2; H, 4.35; N, 6.25. Found: C, 82.8; H, 4.25; N, 6.18. IR (KBr, ν (cm^{-1})) 2927, 2841, 1703, 702. UV–Vis (λ_{max} (nm), ε (dm^3 mol^{-1} cm^{-1})) 420 (109,761), 509 (14,581), 539 (5423), 611 (3889), 672 (3257).

4.2.17. $(BDPY)_2$STPPH (17). Samples of **2** (28 mg, 0.0412 mmol) and BDPY-I (76 mg, 0.1935 mmol) were dissolved in 36 ml of toluene/triethylamine (5:1). $AsPh_3$ (28 mg, 0.0918 mmol) was then added and the solution was deaerated with argon for 15 min. A catalytic amount of $Pd_2(dba)_3$ (12 mg, 0.0132 mmol) was added to initiate the coupling reaction. The reaction mixture was stirred at 35°C under argon for 3 h. The reaction was monitored with tlc at regular intervals and the reaction was stopped after the consumption of **2**. The solvent was removed on rotary evaporator under reduced pressure and the crude material was dissolved in CH_2Cl_2 and passed through short silica column using CH_2Cl_2 as solvent to remove the palladium species, triphenylarsine, excess BDPY-I and other side products. The compound was then passed through size exclusion chromatography with toluene to remove any undesired high molecular weight materials. The compound with very small amounts of impurities was passed through silica column using pet ether/CH_2Cl_2 (1:1) to afford the reddish product in 28% yield (15 mg). ^{1}H NMR ($CDCl_3$, δ in ppm) −2.69 (s, 1H, NH), 1.25 (s, 12H, CH_3), 6.32 (d, 4H, J=4.5 Hz, BDPY pyrrole), 6.78 (d, 4H, J=4.5 Hz, BDPY pyrrole), 7.57 (d, 4H, J=4 Hz, Ar), 7.79 (m, 10H, Ar), 7.96 (d, 4H, J=4 Hz, Ar), 8.25 (m, 8H, Ar), 8.68 (d, 2H, J=4.5 Hz, β-pyrrole), 8.72 (d, 2H, J=4.5 Hz, β-pyrrole), 8.98 (s, 2H, β-pyrrole), 9.77 (s, 2H, β-thiophene). FAB-MS $C_{82}H_{55}N_7SB_2F_4$ calcd mass 1267.4, obsd. *m/z* 1268. Anal. calcd: C, 77.7; H, 4.37; N, 7.73. Found: C, 78.1; H, 4.65; N, 7.79. IR (KBr, ν (cm^{-1})) 2925, 2855, 1555, 711. UV–vis (λ_{max} (nm), ε (10^3 dm^3 mol^{-1} cm^{-1})) 432 (233.4), 515 (110.9), 619 (2.58), 679 (4.45).

4.2.18. $(BDPY)_2$OTPPH (18). Samples of **12** (10 mg, 0.0151 mmol), BDPY-I (20.7 mg, 0.0527 mmol) and $AsPh_3$ (11 mg, 0.0361 mmol) were dissolved in 12 ml of toluene/triethylamine (5:1) and purged argon for 15 min. $Pd_2(dba)_3$ (4.1 mg, 0.00452 mmol) was added and reaction mixture was stirred at 35°C under argon for 3 h. The solvent was removed in vacuo and the crude compound was loaded on silica column and eluted with dichloromethane. The excess BDPY-I, $AsPh_3$ and other side products were removed and the desired compound was then eluted with CH_2Cl_2/ethyl acetate (85:15). The compound was then passed through a size exclusion chromatography with toluene and recrystallized with CH_2Cl_2/CH_3OH to afford **18** as a reddish compound in 17% yield (3.2 mg). ^{1}H NMR ($CDCl_3$, δ in ppm) 1.25 (s, 12H, CH_3), 6.35 (m, 4H, BDPY pyrrole), 6.70 (m, 4H, BDPY pyrrole), 7.48 (m, 4H, Ar), 7.67 (m, 4H, Ar), 7.78 (m, 8H, Ar), 7.99 (m, 2H, Ar), 8.21 (m, 6H, Ar), 8.42 (s, 2H, Ar) 8.65 (d, 2H, J=4.5 Hz, β-pyrrole), 8.93 (s, 2H, β-pyrrole), 9.22 (s, 2H, β-furan). FAB-MS $C_{82}H_{55}N_7OB_2F_4$ calcd mass 1251.4, obsd. *m/z* 1251. Anal. calcd: C, 78.6; H, 4.42; N, 7.86. Found: C, 77.8; H, 4.35; N, 7.78. IR (KBr, ν (cm^{-1})) 2922, 2848, 1556, 705. UV–vis (λ_{max} (nm), ε (10^3 dm^3 mol^{-1} cm^{-1})) 443 (34.2), 425 (180.5), 515 (150.2), 611 (3.89), 673 (3.89).

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