Synthesis of N_3S, N_3O, N_2S_2, N_2O_2, N_2SO and N_2OS Porphyrins with One *meso*-Unsubstituted Carbon

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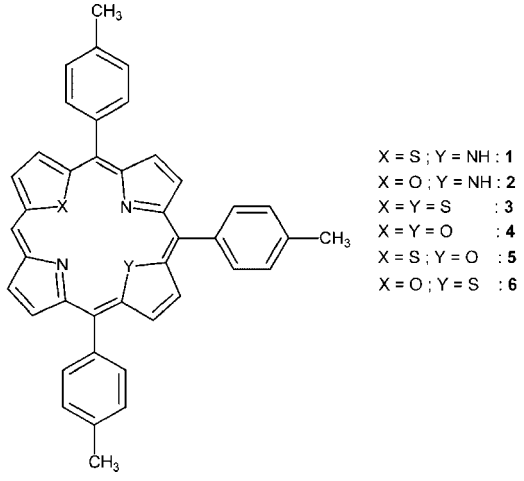
A simple straightforward synthesis of N_3S, N_2S_2, N_2O_2, N_2SO and N_2OS porphyrins and an improved method for the synthesis of an N_3O porphyrin with one *meso*-unsubstituted carbon atom are reported from readily available precursors. The reactivity of the *meso*-unsubstituted carbon atom was demonstrated by carrying out bromination followed by Heck coupling reactions.

Introduction

Porphyrins with *meso*-unsubstituted carbon(s) play a vital role in synthetic porphyrin chemistry since they are ideal precursors for the synthesis of more complex systems with special physical and chemical properties due to the high reactivity of the *meso* carbon bridge.[1] *meso*-Unsubstituted porphyrins with substituents at the β-pyrrole carbons, such as octaethylporphyrin (OEP), are in general very stable to handle for further chemistry. However, β-unsubstituted *meso*-unsubstituted porphyrins are difficult to synthesize, hence reports on β-unsubstituted *meso*-unsubstituted porphyrins are scarce.[2] Recently Neya et al.[2c] reported a very simple high-yielding method to synthesize porphine (N_4 core) with four *meso*-unsubstituted carbons by cleaving the bulkier *tert*-butyl groups of 5,10,15,20-tetra(*tert*-butyl)porphyrin with H_2SO_4/1-butanol at 90 °C for 15 min. However, reports on porphyrins with a single *meso*-unsubstituted carbon are very scarce, and the available synthetic routes are long and tedious.[3] Recently we reported the synthesis of β-substituted 21,23-dithiaporphyrins (N_2S_2) and 21-monothiaporphyrins (N_3S) with two and four *meso*-unsubstituted carbons and demonstrated the reactivity of these *meso*-unsubstituted porphyrins by carrying out a series of reported reactions.[4] In the same paper, we also reported the synthesis of a β-unsubstituted N_3S porphyrin with one *meso*-unsubstituted carbon from an unsymmetrical thiophene diol. This is a more useful porphyrin precursor than porphyrins having two or more *meso*-unsubstituted carbon atoms for performing selective chemistry. Chemieleski et al.[5] have reported the synthesis of an N_3O porphyrin with one *meso*-unsubstituted carbon. However, this method involves more steps and slightly complicated purification procedures. To the best our knowledge, there are no other reports of core-modified porphyrins with one *meso*-unsubstituted carbon. It would be highly useful to have access to a mono *meso*-unsubstituted porphyrin with a range of porphyrin cores. In this paper, we wish to report the synthesis of six mono *meso*-unsubstituted porphyrins with different porphyrin cores such as N_3S (**1**), N_3O (**2**), N_2S_2 (**3**), N_2O_2 (**4**) and N_2SO (**5**) and N_2OS (**6**) (Scheme 1).



Scheme 1. Mono *meso*-unsubstituted core-modified porphyrins **1**–**6**

Porphyrins with a single *meso*-unsubstituted carbon can be used as precursors to prepare a series of compounds, including the Ag^I-catalysed synthesis of *meso*-*meso* coupled dimers.[3] The *meso*-unsubstituted carbon is also highly reactive towards electrophilic- and nucleophilic-substitution reactions.[6] The reactivity of porphyrins **1**–**6** was tested by

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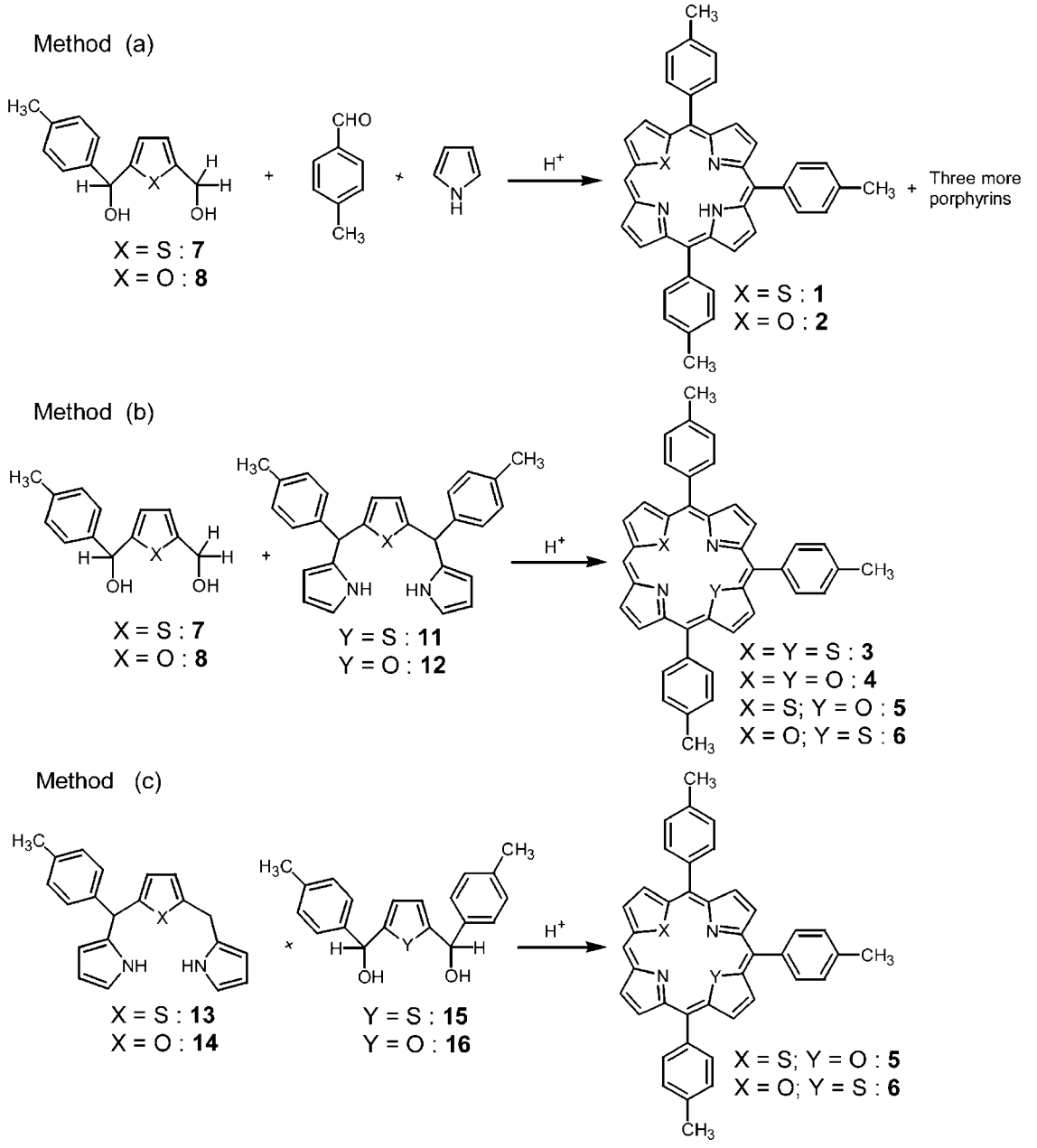
treating the porphyrins with *N*-bromosuccinimide and the resulting bromoporphyrins were subjected to Heck coupling to synthesize porphyrins with one ethynyl functional group. Both the bromo and ethynyl functional groups are highly desirable for the synthesis of a series of unsymmetrical porphyrin dimers containing two different porphyrin cores as well as to synthesize donor-appended porphyrin systems.

Table 1. Method of preparation and yields of mono *meso*-unsubstituted porphyrins **1**−**6**

Porphyrin	Method of preparation	Yield (%)
1	Scheme 2 (a)	6
2	Scheme 2 (a)	7
3	Scheme 2 (b)	14
4	Scheme 2 (b)	2
5	Scheme 2 (b), 2 (c)	5, 2.7
6	Scheme 2 (b), 2 (c)	7, 3

Results and Discussion

Porphyrins **1**−**6** were synthesized by following three different routes, as shown in Scheme 2 (see also Table 1). Porphyrins **1** and **2** were prepared from the unsymmetrical thiophenediol **7** and furandiol **8**, respectively (Scheme 2, a). The unknown unsymmetrical diols **7** and **8** were synthesized[4,5] in two steps starting from 2-thiophenecarboxaldehyde and 2-furancarboxaldehyde, respectively. The 2-thiophene- and 2-furancarboxaldehydes were first treated



Scheme 2. Synthetic scheme showing three different methods of preparation of mono *meso*-unsubstituted porphyrins **1**−**6**

Table 2. Absorption and emission data for porphyrins **1**−**6** recorded in toluene

Porphyrin	Soret band λ (nm) (ε × 10^{-4})	Absorption Q-bands λ (nm) (ε × 10^{-3})				Fluorescence λ (nm) (λ_{exc} = 430 nm)		
		IV	III	II	I	Q(0.0)	Q(0.1)	φ
1	424 (5.31)	508 (4.26)	542 (3.62)	609 (3.41)	669 (3.37)	675	742	0.0099
2	415 (5.31)	503 (4.25)	561 (3.33)	606 (3.51)	664 (3.47)	668	732	0.0319
3	431 (5.37)	509 (4.36)	541 (3.74)	628 (3.28)	691 (3.52)	697	770	0.0079
4	414 (4.86)	518 (4.18)	553 (3.31)	660 (3.21)	701 (3.40)	652	716	0.0436
5	424 (5.18)	507 (4.28)	537 (3.55)	637 (3.17)	702 (3.62)	706	780	0.0046
6	423 (5.12)	505 (4.34)	537 (3.72)	636 (3.12)	701 (3.63)	705	778	0.0048

with $NaBH_4$ in dry methanol followed by work up with CH_2Cl_2 to give light yellow liquids of 2-(α-hydroxymethyl)thiophene (**9**) and 2-[α-hydroxymethyl)furan (**10**), respectively (mono-ols). The mono-ols **9** and **10** were then treated with two equivalents of *n*BuLi followed by addition of 1.2 equivalents of *p*-tolualdehyde in THF at 0 °C. TLC analysis of the crude reaction mixture indicated the formation of the diols **7** and **8**, respectively, along with small amounts of the mono-ol and unchanged aldehyde. The crude reaction mixture was purified by silica gel column chromatography and afforded pure unsymmetrical diols **7** and **8** as light yellow solids in about 41% yields. We varied the number of equivalents of *n*BuLi and the best yields were observed when we used two equivalents of *n*BuLi. Both diols **7** and **8** were characterized by NMR and IR spectroscopy, mass spectrometry and elemental analysis.

To synthesize porphyrin **1**, one equivalent of diol **7** was condensed with two equivalents of *p*-tolualdehyde and three equivalents of pyrrole in CH_2Cl_2 in the presence ofa catalytic amount of $BF_3{\cdot}OEt_2$, followed by oxidation with DDQ. The solvent was removed under vacuum and the crude compound was passed through a short silica-gel column using CH_2Cl_2 as eluent to remove the non-porphyrinic materials. TLC analysis showed the formation of a mixture of four porphyrins: the desired N_3S porphyrin **1**, a mixture of two isomers (*cis* and *trans*) of N_2S_2 porphyrins and one N_4 porphyrin (H_2TPP). The porphyrin mixture was subjected to silica gel column chromatography to afford the N_3S porphyrin **1** in 6% yield. Porphyrin **1** was characterized by NMR, absorption and fluorescence spectroscopy, mass spectrometry and elemental analysis. In the ^1H NMR spectrum, the *meso*-H appears at δ = 10.68 ppm. The thiophene protons appear as two separate signals that are shifted slightly with respect to the signals of *meso*-5,10,15,20-tetraphenyl-21-thiaporphyrin (STPPH),[7] in which they appear as a singlet, indicating the unsymmetrical substitution of porphyrin **1** at the *meso* carbons. The absorption spectrum of **1** shows four defined Q-bands and one Soret band and is blue-shifted with respect to STTPH,[7] supporting the absence of the aryl group at the *meso* carbon. The fluorescence bands of **1** also show blue shifts and a reduction in quantum yields relative to STPPH (Table 2).

The N_3O porphyrin **2** was also prepared under similar conditions from the furan diol **8**. TLC analysis of the crude reaction mixture showed the formation of only two compounds: the desired N_3O porphyrin **2** and N_4 porphyrin (H_2TTP). We did not observe the formation of the N_2O_2 porphyrin in this reaction. The mixture was separated by silica gel column chromatography and the expected N_3O porphyrin **2** was isolated in 7% yield. The porphyrin **2** has also been synthesized previously by Chmielewski et al.[5] from the same unsymmetrical furan diol **8**. However, the diol **8** was prepared from 2,5-bis(hydroxymethyl)furan, which was first oxidized and then reacted with a Grignard reagent. In this method, the diol **8** was formed along with large amounts of the symmetric diol, 2,5-bis(phenylhydroxymethyl)furan. The mixture of diols was used without separation for the porphyrin condensation reaction. Thus, the diol **8** was not isolated in pure form. However, with our method the diol **8** can be prepared in pure form in decent yields and the N_3O porphyrin **2** can be obtained easily by simple condensation followed by purification. The appearance of more signals for the furan and pyrrole protons than in *meso*-5,10,15,20-tetraphenyl-21-oxaporphyrin (OTPPH)[7] confirms the unsymmetrical substitution of the porphyrin **2** at the *meso* positions. The signal at δ = 10.14 ppm in the ^1H NMR spectrum and the molecular-ion peak in the mass spectrum also confirm the structure of the product. The absorption and fluorescence bands experience blue shifts, with slight changes in ε values and fluorescence yields, compared to OTPPH (Table 2).

The N_2S_2 porphyrin **3** with one *meso*-unsubstituted carbon was synthesized from the unsymmetrical diol **7** (Scheme 2, b). To the best of our knowledge, there is no report of an N_2S_2 porphyrin with one free *meso* carbon, which is useful for constructing complex N_2S_2 porphyrin systems. Diol **7** was condensed with known[8] 5,10-ditolyl-15,17-dihydro-16-thiatripyrrin (16-thiatripyrrin) **11** in propionic acid at reflux temperature for 1 h. The propionic acid was then removed under vacuum and the residue washed thoroughly with water, and dried. The crude black compound was passed through a silica gel column with petroleum ether/dichloromethane (6:4) as eluent. TLC analysis showed a single yellow spot corresponding to the N_2S_2 porphyrin **3**. We did not observe any scrambling product in this reaction. The crude compound was chromatographed again and pure **3** was obtained as a purple solid in 14% yield. This reaction also works with BF_3. OEt_2 but with slightly lower yields. The structure of the porphyrin **3** was confirmed by NMR spectroscopy, mass spectrometry and other

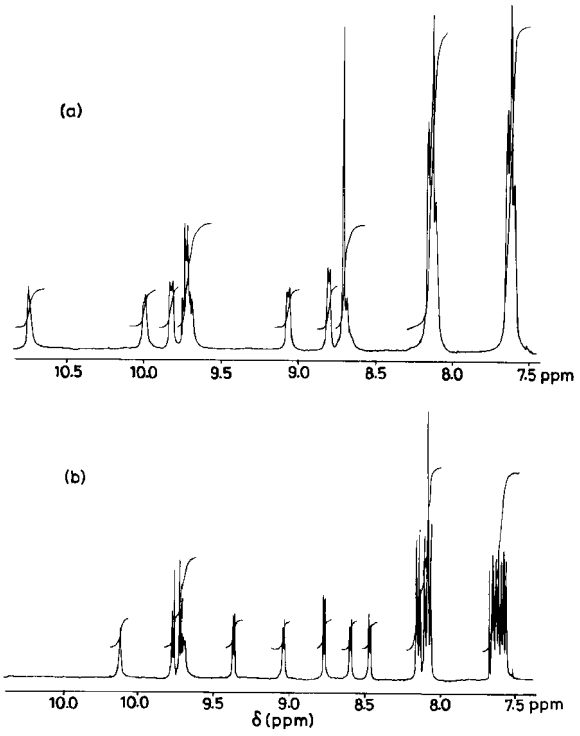


Figure 1. ^{1}H NMR spectra of **3** (a) and **6** (b) recorded in $CDCl_3$

spectral analysis. The ^{1}H NMR spectrum of **3**, presented in Figure 1, shows two signals for the thiophene moiety and four signals for the pyrrole, whereas the pyrrole and thiophene protons in *meso*-5,10,15,20-tetraphenyl-21,23-dithiaporphyrin (S_2TPP)[7] appear as two singlets. The *meso*-H in **3** appears as a singlet at $\delta = 10.74$ ppm. The pyrrole and thiophene protons of **3** show slight downfield shifts compared to S_2TPP.[7] The absorption and emission bands also show a blue shift compared to S_2TPP, indicating the absence of an aryl group at the *meso* carbon (Table 2).

The N_2O_2 porphyrin **4** was obtained by condensing one equivalent of diol **8** with symmetric 5,10-ditolyl-15,17-dihydro-16-oxatripyrrin (16-oxatripyrrin)[8] **12** in propionic acid. The absorption spectrum of the crude reaction mixture indicated the formation of **4** only in trace amounts and the purification of **4**, unlike that of **3**, was found to be very tedious. Pure **4** was obtained in only 2% yield after repeated column chromatography using silica gel as well as basic alumina. The presence of a strong *m*/*z* peak at 582.7 in the ES-MS, a clean ^{1}H NMR spectrum and a good C, H, N analysis confirmed its structure. The unsymmetrical substitution at the *meso* carbon is evident from the appearance of *meso*-H at $\delta = 10.16$ ppm and the larger number of signals for furan and pyrrole protons compared to *meso*-5,10,15,20-tetraphenyl-21,23-dioxaporphyrin (O_2TPP)[7] in the ^{1}H NMR spectrum. The absence of one aryl group is also evident from shifts in the absorption and emission bands (Table 2).

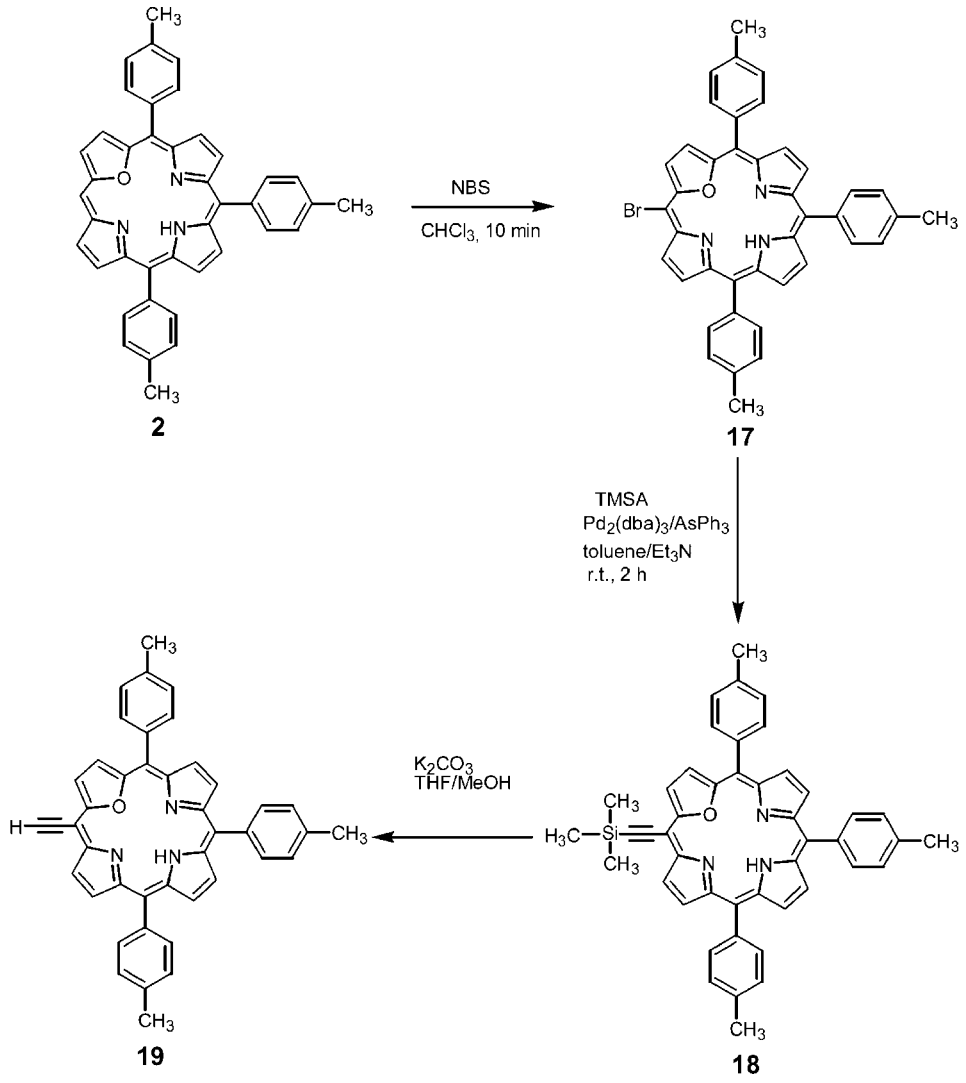
There are two possible N_2SO porphyrins with one *meso*-unsubstituted carbon: the N_2SO porphyrin with the free *meso* carbon adjacent to the thiophene ring (**5**) and the N_2SO porphyrin with the free *meso* carbon adjacent to the furan ring (**6**). Both **5** and **6** were prepared by following methods (b) and (c) as shown in Scheme 2.

The condensation of unsymmetrical diols **7** and **8** with 16-thiatripyrrin[8] **11** and 16-oxatripyrrin[8] **12**, respectively, under Adler's or Lindsey's porphyrin-forming conditions gave the desired products **5** and **6** in 5−7% yields as a single product. Alternatively, porphyrins **5** and **6** were also prepared from the unknown unsymmetrical thia- **13** and oxatripyrrin **14**, respectively. The tripyrrins **13** and **14** were synthesized by treating one equivalent of the diol **7** and **8**, respectively, with 40 equivalents of pyrrole in CH_2Cl_2 in the presence of a catalytic amount of $BF_3{\cdot}OEt_2$.[8] The tripyrrins were purified by flash silica gel column chromatography and isolated as orange solids in 30% yield.

The condensation of **13** and **14** with symmetric diols[9] **15** and **16**, respectively, under porphyrin-forming conditions, followed by usual workup and silica gel column chromatography purification, gave the porphyrins **5** and **6** in about 3% yield. Both **5** and **6** were characterized by the usual spectroscopic and mass spectrometric methods. For both **5** and **6**, the larger number of signals for the pyrrole, thiophene and furan protons in the ^{1}H NMR spectrum and the blue shifts of the absorption and emission bands relative to the symmetrically substituted *meso*-5,10,15,20-tetraphenyl-23-oxa-21-thiaporphyrin (N_2SO)[7] indicate the absence of an aryl group at the *meso* carbon (Table 2).

Although the yields of **1**−**6** are not very high, these porphyrins were previously inaccessible and, using the methods reported in this paper, all porphyrins can be prepared in sufficient amounts from easily available precursors.

The mono *meso*-unsubstituted porphyrins **1**−**6** are suitable precursors to construct novel core-modified porphyrin systems. The free *meso* carbon is highly reactive and, in principle, one can introduce any desirable functional group depending on the required application. To test this reactivity, we carried out bromination and Heck coupling reactions as shown in Scheme 3 for N_3O porphyrin **2**. Porphyrin **2** was treated with 1.2 equivalents of *N*-bromosuccinimide[10] at room temperature for 10 min. The progress of the reaction was monitored by TLC and absorption spectroscopy. After complete consumption of **2** (as confirmed by TLC) the reaction was stopped and the solvent was removed under vacuum. The crude compound was subjected to silica gel column chromatography with CH_2Cl_2 as eluent and the pure bromo compound **17** was isolated in 71% yield. The disappearance of the *meso*-H signal in the ^{1}H NMR spectrum and the *m*/*z* peak in the mass spectrum confirmed the nature of the product. The ethynyl derivative **19** was prepared[11] in 30% yield by treating **17** with trimethylsilylacetylene in the presence of a catalytic amount of $Pd_2(dba)_3$ in THF/triethylamine to afford **18** after deprotection with K_2CO_3 in THF/CH_3OH. The introduction of the bromo and ethynyl groups at the *meso* carbons resulted in large red-shifts of the absorption bands (Figure 2). These bromo and ethynyl derivatives are very useful to synthesize unsymmetrical porphyrin dimers[12] containing two different porphyrin cores, such as N_3O-N_3S, $N_2S_2-N_3O$, $N_2S_2-N_2SO$, $N_3O-N_2S_2$ etc.



Scheme 3. Synthetic scheme for the preparation of porphyrin **17**, **18** and **19**

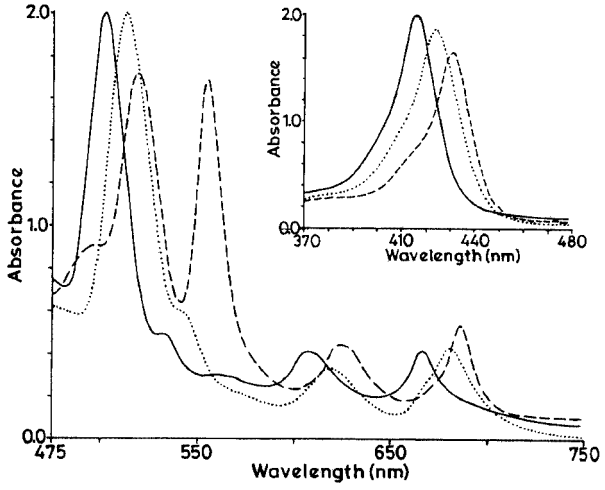


Figure 2. Q-bands and Soret band (inset) absorption spectra of **2** (−), **17** (···) and **18** (------) recorded in toluene

In conclusion, we have synthesized six porphyrins, with one free *meso* carbon having five different N_3S, N_3O, N_2S_2, N_2O_2 and N_2SO cores, from easily available precursors. Except for one report on N_3O and one report by us on N_3S, there are no reports available on any other porphyrin cores having one free *meso* carbon. This method gives the first synthetic access to N_2S_2, N_2O_2 and N_2SO porphyrins with one reactive free *meso* carbon. We have also shown the use of the free *meso* porphyrins by introducing functional groups such as bromo and ethyne groups, which have wide applications. The porphyrins reported in this paper could help in constructing some novel core-modified porphyrin-based systems.

Experimental Section

General: ^1H and ^{13}C NMR spectra were recorded with 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 mass spectra were recorded with a Q-Tof micro (YA-105) mass spectrometer. Toluene, THF and diethyl ether 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, furan, pyrrole, 2-thiophenecarboxaldehyde and 2-furancarboxaldehyde were obtained from Lancaster. Column chromatography was performed using 60−120 mesh silica and basic alumina, obtained from Sisco Research Laboratories, India.

2-(α-Hydroxymethyl)thiophene (9): Distilled 2-thiophenecarboxaldehyde (5 mL, 53.50 mmol) was mixed with 40 mL of distilled methanol in a 250 mL round-bottomed flask. After stirring at −10 °C for 10 min, $NaBH_4$ (2.84 g, 74.90 mmol) was added very slowly and the stirring was continued for another 15 min. Product formation was checked by TLC. Regular workup was done with CH_2Cl_2. The solvent was then removed on a rotary evaporator. The crude product was purified by silica gel column chromatography using petroleum ether/ethyl acetate (95:5) as eluent. The mono-ol **9** was collected as a yellow oily compound (4.15 g, 68%). B.p. 207 °C. IR (neat, cm^{-1}): $\tilde{\nu}$ = 3355 (OH). ^1H NMR ($CDCl_3$): δ = 4.50 (s, 2 H, CH_2), 5.98 (d-d, *J* = 5.2 Hz, 3.6 Hz, 1 H, thiophene) 6.22 (d, *J* = 3.6 Hz, 1 H, thiophene), 6.43 (d, *J* = 5.2 Hz, 1 H, thiophene) ppm. ESMS: C_5H_6OS calcd. av. mass 114.2, obsd. 97.2 [M − 17] (100%). C_5H_6OS (114.2): calcd. C 52.59, H 5.30, S 28.08; found C 52.63, H 5.35, S 28.18.

2-(α-Hydroxymethyl)furan (10): The reduction of 2-furancarboxaldehyde (5.1 mL, 59.84 mmol) with $NaBH_4$ (3.18 g, 83.77 mmol) under the same experimental conditions as for **9** gave the furan mono-ol **10** as a yellow oily compound (4.11 g, 70%). B.p.170 °C. IR (neat, cm^{-1}): $\tilde{\nu}$ = 3360 (OH). ^1H NMR ($CDCl_3$): δ = 4.43 (s, 2 H, CH_2), 5.90 (d-d, *J* = 1.8 Hz, 3.2 Hz, 1 H, furan) 6.10 (d, *J* = 3.2 Hz, 1 H, furan), 6.38 (d, *J* = 1.8 Hz, 1 H, furan) ppm. ESMS: $C_5H_6O_2$ calcd. av. mass 98.1, obsd. 81.1 [M − 17] (100%). $C_5H_6O_2$ (98.1): calcd. C 61.22, H 6.16; found C 61.30, H 6.25.

2-(Hydroxymethyl)-5-[hydroxy(*p*-tolyl)methyl]thiophene (7): Dry, distilled diethyl ether (30 mL) was added to a 250 mL three-necked round-bottomed flask equipped with rubber septum, gas inlet and gas outlet tube. A positive pressure of N_2 was maintained and after purging N_2 gas for 5 min, TMEDA (5.9 mL, 39.42 mmol) and *n*BuLi (24.6 mL of ca. 15% solution in hexane) were added to the stirred solution. The mono-ol **9** (2 mL, 15.77 mmol) was then added and the solution was stirred at 0 °C for 1 h. An ice-cold solution of *p*-tolualdehyde (4.6 mL, 39.42 mmol) in dry THF (20 mL) was then 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 with anhydrous Na_2SO_4. The solvent was removed on a rotary evaporator under reduced pressure to afford the crude compound. TLC analysis showed three spots corresponding to the unchanged *p*-tolualdehyde, unchanged mono-ol **9** and the desired diol **7**. The aldehyde and the mono-ol were removed by silica gel column chromatography with 5−15% ethyl acetate/petroleum ether as eluent and the diol **7** was collected with 25% ethyl acetate/petroleum ether as a white solid (1.5 g, 41%). M.p. 92−95 °C. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3466 cm^{-1} (OH). ^1H NMR ($CDCl_3$): δ = 2.31 (s, 3 H, CH_3), 4.72 (s, 2 H, CH_2), 5.91 (s, 1 H, *meso*), 6.72 (d, *J* = 3.6 Hz, 1 H, thiophene), 6.81 (d, *J* = 3.6 Hz, 1 H, thiophene), 7.24 (d, *J* = 8 Hz, 2 H, *m*-tolyl), 7.31 (d, *J* = 8 Hz, 2 H, *o*-tolyl) ppm. ^{13}C NMR ($CDCl_3$): δ = 21.3, 60.2, 72.5, 112.3, 113.5, 125.4, 126.3, 137.8, 140.1, 144.3, 146.6, 149.1 ppm. ESMS: $C_{13}H_{14}O_2S$ calcd. av. mass 234.3, obsd. 217.1 [M − 17] (100%). $C_{13}H_{14}O_2S$ (234.3): calcd. C 66.64, H 6.02, S 13.69; found C 66.701, H 5.92, S 13.61.

2-(Hydroxymethyl)-5-[hydroxy(*p*-tolyl)methyl]furan (8): In a three-necked 250 mL round-bottomed flask, the furan mono-ol **10** (2 mL, 23.14 mmol) in diethyl ether (30 mL) was treated with *n*BuLi (36 mL of a 15% solution in hexane) in the presence of TMEDA (8.7 mL, 57.85 mmol) under the same experimental conditions as for **7**. *p*-Tolualdehyde (6.8 mL, 57.85 mmol) was added slowly to the reaction mixture followed by workup and chromatography to afford the furan-diol **8** as a yellow solid (2.1 g, 42%). M.p. 98−100 °C. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3440 cm^{-1} (OH). ^1H NMR ($CDCl_3$): δ = 2.32 (s, 3 H, CH_3), 4.43 (s, 2 H, CH_2), 5.66 (s, 1 H, *meso*), 5.96 (d, *J* = 3.2 Hz, 1 H, furan), 6.11 (d, *J* = 3.2 Hz, 1 H, furan), 7.20 (d, *J* = 8.4 Hz, 2 H, *m*-tolyl), 7.32 (d, *J* = 8.4 Hz, 2 H, *o*-tolyl) ppm. ^{13}C NMR ($CDCl_3$): δ = 21.3, 57.2, 69.8, 108.3, 108.5, 126.7, 129.2, 137.8, 140.7, 149.0, 154.1, 156.3 ppm. ESMS: $C_{13}H_{14}O_3$ calcd. av. mass 218.3, obsd. 201.1 [M − 17])100%). $C_{13}H_{14}O_3$ (218.3): calcd. C 71.53, H 6.46; found C 71.48, H 6.48.

5,10-Di(*p*-tolyl)-15,17-dihydro-16-thiatripyrrin (11): This compound was synthesized according to the literature method.[8]

5,10-Di(*p*-tolyl)-15,17-dihydro-16-oxatripyrrin (12): Compound **12** was synthesized by the literature method.[8]

5-(*p*-Tolyl)-10,15,17-trihydro-16-thiatripyrrin (13): A mixture of **7** (500 mg, 2.13 mmol) and pyrrole (5.7 mL, 85.6 mmol) was degassed by bubbling with N_2 for 10 min. $BF_3{\cdot}OEt_2$ (268 μL, 2.136 mmol) was added and the reaction mixture was stirredat room temperature for 30 min. It was then diluted with CH_2Cl_2 (100 mL) and washed with 0.1 M NaOH (50 mL) and water (50 mL). The organic layer was dried with anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the unchanged pyrrole was removed by vacuum distillation at room temperature. The resulting viscous dark yellow liquid was purified by column chromatography (silica gel 60−120 mesh, ethyl acetate/petroleum ether (10:90). After the initial tailing material a pale orange band eluted which gave an orange solid, identified as **13**, in 30% yield (212 mg). M.p. 80−82 °C. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3402 cm^{-1} (NH). ^1H NMR ($CDCl_3$): δ = 2.32 (s, 3 H, CH_3), 4.03 (s, 2 H, CH_2), 5.52 (s, 1 H, *meso*), 5.89 (s, 1 H, thiophene), 5.99 (s, 1 H, thiophene), 6.08−6.11 (m, 2 H, pyrrole), 6.57−6.60 (m, 4 H, pyrrole), 7.09 (m, 4 H, tolyl), 7.81 (br. s, 2 H, NH) ppm. ESMS: $C_{21}H_{20}N_2S$ calcd. av. mass 332.5, obsd. 331.6 $[M]^+$ (100%). $C_{21}H_{20}N_2S$: calcd. C 75.86, H 6.06, N 8.43, S 9.64; found C 75.80, H 6.06, N 8.48, S 9.70.

2,5-[Hydroxy(*p*-tolyl)methyl]thiophene (15): Compound **15** was synthesized by the reported method.[9a]

2,5-[Hydroxy(*p*-tolyl)methyl]furan (16): Compound **16** was prepared by the literature method.[9b]

10,15,20-Tris(*p*-tolyl)-21-thiaporphyrin (1): A solution of the diol **7** (335 mg, 1.43 mmol), pyrrole (320 μL, 4.70 mmol) and *p*-tolualdehyde (350 μL, 2.91 mmol) in CH_2Cl_2 (150 mL) was added to a 250 mL one-necked round-bottomed flask fitted with a N_2 gas bubbler. After purging with N_2 for 15 min, condensation of the diol, aldehyde and pyrrole was initiated at room temperature by addition of a catalytic amount of $BF_3{\cdot}OEt_2$ (100 μL of 2.5 M stock solution). The progress of the reaction was checked at regular intervals by oxidizing a small amount of the reaction mixture with DDQ in toluene and recording the absorption spectrum. After stirring

for 1 h, DDQ (240 mg, 1.07 mmol) was added and the reaction mixture was stirred at room temperature in air for an additional hour. The solvent was removed on a rotary evaporator under low pressure and analysis of the crude compound showed the formation of four porphyrins. This mixture was separated by silica gel column chromatography using CH_2Cl_2 as eluent to afford **1** as a purple solid (48 mg, 6%). M.p. > 300 °C. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3410, 2928, 2860, 1472, 967, 820. ^1H NMR ($CDCl_3$): δ = −2.91 (s, 1 H, NH) 2.71 (s, 9 H, CH_3), 7.55−7.65 (m, 6 H, *m*-tolyl), 8.17−8.25 (m, 6 H, *o*-tolyl), 8.65 (m, 4 H, β-pyrrole), 9.04 (m, 2 H, β-pyrrole), 9.95 (s, 1 H, β-thiophene), 10.00 (s, 1 H, β-thiophene), 10.68 (s, 1 H, *meso*) ppm. ^{13}C NMR ($CDCl_3$): δ = 21.6, 116.1, 123.6, 124.6, 127.3, 128.5, 129.3, 131.4, 132.9, 133.4, 134.1, 135.6, 137.6, 138.1, 138.8, 139.5, 146.6, 148.4, 154.1, 154.9, 156.9, 157.6 ppm. ESMS: $C_{41}H_{31}N_3S$ calcd. av. mass 597.8, obsd. *m*/*z* = 598.2 $[M]^+$ (100%). $C_{41}H_{31}N_3S$: calcd. C 82.38, H 5.23, N 7.03, S 5.36; found C 82.63, H 5.35, N 6.88, S 5.57.

10,15,20-Tris(*p*-tolyl)-21-oxaporphyrin (2): Diol **8** (500 mg, 2.29 mmol), pyrrole (500 μL, 7.31 mmol) and *p*-tolualdehyde (590 μL, 5.06 mmol) were dissolved in 200 mL of CH_2Cl_2 in a 250 mL round-bottomed flask under N_2. After stirring for 15 min, $BF_3{\cdot}OEt_2$ (100 μL of 2.5 M stock solution) was added as an acid catalyst to initiate the reaction. The reaction mixture was stirred for 1 h under a N_2 atmosphere. DDQ (520 mg, 2.32 mmol) was then added and the reaction mixture was stirred for another 1 h in air. The absorption spectrum and TLC analysis of the crude mixture showed the formation of N_4 porphyrin (H_2TTP) along with the desired N_3O porphyrin **2**. The solvent was removed and the crude compound was purified by basic alumina column chromatography with CH_2Cl_2 as eluent. The desired porphyrin **2** was isolated as a fluorescent green solid (93 mg, 7%). M.p > 250 °C. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3422, 2929, 2851, 1469, 956, 813. ^1H NMR ($CDCl_3$): δ = −2.82 (s, 1 H, NH), 2.70 (s, 9 H, CH_3), 7.52−7.58 (m, 6 H, *m*-tolyl), 8.03−8.09 (m, 6 H, *o*-tolyl), 8.61 (d, *J* = 3.2 Hz, 1 H, β-pyrrole), 8.65 (d, *J* = 4.8 Hz, 1 H, β-pyrrole), 8.85 (d, *J* = 3.2 Hz, 1 H, β-pyrrole), 8.92 (d-d, *J* = 4.8 Hz, 4.6 Hz, 2 H, β-pyrrole), 9.12 (d, *J* = 4.6 Hz, 1 H, β-pyrrole), 9.37 (d, *J* = 4.8 Hz, 1 H, β-furan), 9.70 (d, *J* = 4.8 Hz, 1 H, β-furan), 10.14 (s, 1 H, *meso*) ppm. ^{13}C NMR ($CDCl_3$): δ = 21.1, 117.5, 117.9, 123.0, 124.3, 125.8, 127.3, 127.7, 128.7, 129.1, 134.3, 134.5, 134.6, 135.0, 137.4, 137.5, 137.8, 138.4, 138.7, 139.1, 141.9, 153.8, 154.2 ppm. ESMS: $C_{41}H_{31}N_3O$ calcd. av. mass 581.7, obsd. *m*/*z* = 582.2 $[M]^+$ (100%). $C_{41}H_{31}N_3O$: calcd. C 84.66, H 5.37, N 7.22; found C 84.72, H 5.45, N 7.30.

10,15,20-Tris(*p*-tolyl)-21,23-dithiaporphyrin (3): A solution of diol **7** (277 mg, 1.18 mmol) and 5,10-di(*p*-tolyl)-15,17-dihydro-16-thiatripyrrin **11** (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 **3**. The excess propionic acid was removed under vacuum and thorough washing with warm water gave the crude mixture. The crude product was purified by silica gel column chromatography with petroleum ether/dichloromethane (60:40) as eluent to afford the desired porphyrin as a purple solid (102 mg, 14%). M.p. > 300 °C. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2929, 2864, 1456, 956, 810. ^1H NMR ($CDCl_3$): δ = 2.71 (s, 9 H, CH_3), 7.60−7.64 (m, 6 H, *m*-tolyl), 8.10−8.15 (m, 6 H, *o*-tolyl), 8.71 (s, 2 H, β-pyrrole), 8.81 (d, *J* = 3.6 Hz, 1 H, β-pyrrole), 9.07 (d, *J* = 3.6 Hz, 1 H, β-pyrrole), 9.72 (d, *J* = 3.6 Hz, 2 H, β-thiophene), 9.82 (d, *J* = 3.6 Hz, 1 H, β-thiophene), 9.99 (d, *J* = 3.6 Hz, 1 H, β-thiophene), 10.74 (s, 1 H, *meso*) ppm. ^{13}C NMR ($CDCl_3$): δ = 21.7, 118.5, 123.0, 124.3, 127.3, 128.3, 128.5, 134.4, 134.8, 134.9, 135.0, 135.7, 135.9, 137.9, 141.9, 147.2, 148.4, 156.8, 157.2 ppm. ESMS: $C_{41}H_{30}N_2S_2$ calcd. av. mass 614.8, obsd. *m*/*z* = 615.1 $[M]^+$ (100%). $C_{41}H_{30}N_2S_2$: calcd. C 80.10, H 4.92, N 4.56, S 10.43; found C 80.03, H 4.98, N 4.51, S 10.55.

10,15,20-Tris(*p*-tolyl)-21,23-dioxaporphyrin (4): Condensation of the diol **8** (268 mg, 1.23 mmol) with 5,10-di(*p*-tolyl)-15,17-dihydro-16-oxatripyrrin **12** (500 mg, 1.23 mmol) in propionic acid (125 mL) under similar reaction conditions as mentioned for **3** gave a green solid identified as porphyrin **4** in 2% yield (15 mg). M.p. > 300 °C. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2931, 2868, 1452, 961, 820. ^1H NMR ($CDCl_3$): δ = 2.71 (s, 9 H, CH_3), 7.70 (d, *J* = 7.2 Hz, 6 H, *m*-tolyl), 8.18 (d, *J* = 7.2 Hz, 6 H, *o*-tolyl), 8.70 (s, 2 H, β-pyrrole), 8.89(d, *J* = 4.2 Hz, 1 H, β-pyrrole), 8.95 (d, *J* = 4.2 Hz, 1 H, β-pyrrole), 9.64 (d, *J* = 4.6 Hz, 2 H, β-furan), 9.70 (d, *J* = 4.6 Hz, 1 H, β-furan), 9.82 (d, *J* = 4.6 Hz, 1 H, β-furan), 10.16 (s, 1 H, *meso*) ppm. ESMS: $C_{41}H_{30}N_2O_2$ calcd. av. mass 582.7, obsd. *m*/*z* = 583.1 $[M]^+$ (100%). $C_{41}H_{30}N_2O_2$: calcd. C 84.51, H 5.19, N 4.81; found C 84.66, H 5.23, N 4.88.

10,15,20-Tris(*p*-tolyl)-21-oxa-23-thiaporphyrin (5): Samples of the diol **7** (288 mg, 1.23 mmol) and the 16-oxatripyrrin **12** (500 mg, 1.23 mmol) were dissolved in 125 mL of propionic acid and the reaction mixture was refluxed for 3 h. The excess propionic acid was removed under vacuum and the crude mixture was purified by silica gel column chromatography with CH_2Cl_2 as eluent. The desired porphyrin **5** was obtained as a purple solid (37 mg, 5%). The same porphyrin was also obtained by the condensation of the diol **16** (185 mg, 0.602 mmol) with the 16-thiatripyrrin **13** (200 mg, 0.602 mmol) under the same experimental conditions as mentioned above, but in lower yield (10 mg, 2.7%). M.p. > 300 °C. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2928, 2864, 1443, 962, 814. ^1H NMR ($CDCl_3$): δ = 2.72 (s, 9 H, CH_3), 7.61−7.67 (m, 6 H, *m*-tolyl), 8.07−8.13 (m, 6 H, *o*-tolyl), 8.47 (d, *J* = 4.4 Hz, 1 H, β-pyrrole), 8.60 (d, *J* = 4.8 Hz, 1 H, β-pyrrole), 8.74 (d, *J* = 4.8 Hz, 1 H, β-pyrrole), 9.01 (d, *J* = 4.4 Hz, 1 H, β-pyrrole), 9.36 (d, *J* = 4.8 Hz, 1 H, β-furan), 9.70 (d, *J* = 4.8 Hz, 1 H, β-furan), 9.73 (d, *J* = 4.8 Hz, 1 H, β-thiophene), 9.97 (d, *J* = 4.8 Hz, 1 H, β-thiophene), 10.62 (s, 1 H, *meso*) ppm. ESMS: $C_{41}H_{30}N_2OS$ calcd. av. mass 598.8, obsd. 599.2 $[M]^+$ (100%). $C_{41}H_{30}N_2OS$: calcd. C 82.24, H 5.05, N 4.68, S 5.36; found C 82.39, H 5.11, N 4.77, S 5.39.

10,15,20-Tris(*p*-tolyl)-23-oxa-21-thiaporphyrin (6): Condensation of the diol **8** (258 mg, 1.18 mmol) with the 16-thiatripyrrin **11** (500 mg, 1.18 mmol) in propionic acid (125 mL) under similar reaction conditions as mentioned for **5** gave the desired porphyrin **6** as a purple solid (50 mg, 7%). The same product was also synthesised by the condensation of the diol **15** (205 mg, 0.633 mmol) with the 16-oxatripyrrin **14** (200 mg, 0.633 mmol). This method gave porphyrin **6** in lower yield (11 mg, 3%). M.p. > 300 °C. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2930, 2860, 1441, 960, 816. ^1H NMR ($CDCl_3$): δ = 2.71 (s, 9 H, CH_3), 7.59−7.67 (m, 6 H, *m*-tolyl), 8.07−8.15 (m, 6 H, *o*-tolyl), 8.46 (d, *J* = 4.4 Hz, 1 H, β-pyrrole), 8.60 (d, *J* = 4.8 Hz, 1 H, β-pyrrole), 8.77 (d, *J* = 4.8 Hz, 1 H, β-pyrrole), 9.04 (d, *J* = 4.4 Hz, 1 H, β-pyrrole), 9.37 (d, *J* = 4.8 Hz, 1 H, β-furan), 9.72 (d, *J* = 4.8 Hz, 1 H, β-furan), 9.74 (d, *J* = 5.2 Hz, 1 H, β-thiophene), 9.77 (d, *J* = 5.2 Hz, 1 H, β-thiophene), 10.12 (s, 1 H, *meso*) ppm. ESMS: $C_{41}H_{30}N_2OS$ calcd av. mass 598.8, obsd. 599.1 $[M]^+$ (100%). $C_{41}H_{30}N_2OS$: calcd. C 82.24, H 5.05, N 4.68, S 5.36; found C 82.31, H 5.10, N 4.71, S 5.40.

5-Bromo-10,15,20-tris(*p*-tolyl)-21-oxaporphyrin (17): A solution of the oxaporphyrin **2** (20 mg, 0.0344 mmol) in chloroform (15 mL) in a 50 mL round-bottomed flask was treated with *N*-bromosuccinimide (9.16 mg, 0.0413 mmol) at room temperature for 15 min. The progress of the reaction was monitored by TLC and absorption

spectroscopy. After complete consumption of the porphyrin **2** (as confirmed by TLC) the reaction was stopped and the solvent was removed with a rotary evaporator under vacuum. The crude compound was subjected to silica gel column chromatography with petroleum ether/CH_2Cl_2 (30:70) as eluent and the pure bromoporphyrin **17** was afforded as a purple solid in 71% yield (17 mg). M.p. > 250 °C. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2936, 2858, 1462, 969, 807, 690. ^1H NMR ($CDCl_3$): δ = −2.82 (s, 1 H, NH), 2.70 (s, 9 H, CH_3), 7.52−7.56 (m, 6 H, *m*-tolyl), 8.02−8.05 (m, 6 H, *o*-tolyl), 8.50 (d, *J* = 4.4 Hz, 1 H, β-pyrrole), 8.57 (d, *J* = 4.8 Hz, 1 H, β-pyrrole), 8.68 (d, *J* = 4.4 Hz, 1 H, β-pyrrole), 8.84 (s, 2 H, β-pyrrole), 9.29 (d, *J* = 4.4 Hz, 1 H, β-pyrrole), 9.49 (d, *J* = 4.8 Hz, 1 H, β-furan), 10.04 (d, *J* = 4.4 Hz, 1 H, β-furan) ppm. ^{13}C NMR ($CDCl_3$): δ = 21.7, 29.9, 125.0, 127.5, 128.1, 128.5, 129.4, 132.1, 133.2, 134.4, 134.7, 135.9, 137.8, 138.1, 141.8, 145.2, 147.6, 151.5, 154.9, 155.6, 157.7 ppm. ESMS: $C_{41}H_{30}BrN_3O$ calcd. av. mass 660.6, obsd. *m*/*z* = 662.1 $[M]^+$ (100%). $C_{41}H_{30}BrN_3O$: C 74.55, H 4.58, N 6.39; found C 74.62, H 4.68, N 6.45.

10,15,20-Tris(*p*-tolyl)-5-trimethylsilylethynyl-21-oxaporphyrin (18): A mixture of the bromoporphyrin **17** (30 mg, 0.045 mmol), $[Pd_2(dba)_3]$ (12 mg, 0.014 mmol) and triphenylarsane (33 mg, 0.108 mmol) in toluene/triethylamine (20/4 mL) was stirred under N_2 for 10 min at room temperature. Trimethylsilylacetylene (13 μL, 0.090 mmol) was then added and stirring was continued for 2 h. After complete consumption of the porphyrin **17** (as confirmed by TLC and absorption spectroscopy) the reaction was stopped and the solvent was removed under reduced pressure. The crude mixture was purified by basic alumina column chromatography with petroleum ether/CH_2Cl_2 (40:60) as eluent. The desired porphyrin **18** was obtained as a deep-purple crystalline solid (18 mg, 58%). M.p. > 300 °C. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 2929, 2845, 2272, 1462, 956, 846, 807. ^1H NMR ($CDCl_3$): δ = −2.78 (s, 1 H, NH), 0.63 (s, 9 H, Si−CH_3) 2.75 (s, 9 H, CH_3), 7.33−7.7.43 (*m*, 6 H, *m*-tolyl), 7.61−7.77 (m, 6 H, *o*-tolyl), 8.20 (d, *J* = 4.2 Hz, 1 H, β-pyrrole), 8.42 (d, *J* = 4.6 Hz, 1 H, β-pyrrole), 8.50 (d, *J* = 4.2 Hz, 1 H, β-pyrrole), 8.63 (s, 2 H, β-pyrrole), 9.11(d, *J* = 4.6 Hz, 1 H, β-pyrrole), 9.52 (d, *J* = 4.6 Hz, 1 H, β-furan), 10.1 (d, *J* = 4.6 Hz, 1 H, β-furan) ppm. ESMS: $C_{46}H_{39}N_3OSi$ calcd. av. mass 677.9, obsd. *m*/*z* = 678.3 $[M]^+$ (100%). $C_{46}H_{39}N_3OSi$: C 81.45, H 5.80, N 6.20; found C 81.56, H 5.90, N 6.28.

5-Ethynyl-10,15,20-tris(*p*-tolyl)-21-oxaporphyrin (19): A solution of **18** (15 mg, 0.022 mmol) in THF/CH_3OH (10/3 mL) in a 100 mL, two-necked, round-bottomed flask, fitted with a reflux condenser was allowed to stir for 5 min under N_2. K_2CO_3 (21 mg, 0.155 mmol) was then added and the reaction mixture was refluxed for 5 h. The product formation was confirmed by TLC analysis. The solvent was removed under vacuum and the crude reaction mixture was purified by basic alumina chromatography with petroleum ether/CH_2Cl_2 (30:70) as eluent to afford the porphyrin **19** as a deep-purple solid (18 mg, 58%). M.p. > 300 °C. IR (KBr, cm^{-1}): $\tilde{\nu}$ = 3310, 2929, 2845, 2280, 1462, 956, 846, 807, 652. ^1H NMR ($CDCl_3$): δ = −2.80 (s, 1 H, NH), 2.23 (s, 1 H, CH_3), 7.35−7.7.40 (m, 6 H, *m*-tolyl), 7.63−7.76 (m, 6 H, *o*-tolyl), 8.23 (d, *J* = 4.2 Hz, 1 H, β-pyrrole), 8.45(d, *J* = 4.6 Hz, 1 H, β-pyrrole), 8.52 (d, *J* = 4.2 Hz, 1 H, β-pyrrole), 8.63 (s, 2 H, β-pyrrole), 9.14(d, *J* = 4.6 Hz, 1 H, β-pyrrole), 9.53 (d, *J* = 4.6 Hz, 1 H, β-furan), 10.1(d, *J* = 4.6 Hz, 1 H, β-furan) ppm. ESMS: $C_{43}H_{30}N_3O$ calcd. av. mass 605.7, obsd. *m*/*z* = 606.2 $[M]^+$ (100%). $C_{43}H_{30}N_3O$: calcd. C 85.27, H 5.00, N 6.94; found C 86.09, H 5.05, N 7.04.

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[1] [1a] D. P. Arnold, Y. Sakata, K-I. Sugiura, E. I. Worthington, *Chem. Commun.* **1998**, 2331−2332. [1b] D. P. Arnold, P. C. Healy, M. J. Hodgson, M. L. Williams, *J. Organomet. Chem.* **2000**, *607*, 41−50.

[2] [2a] F. R. Longo, E. J. Thorne, A. D. Adler, S. Dym, *J. Heterocycl. Chem.* **1975**, *12*, 1305−1309. [2b] S. Neya, H. Yodo, N. Funasaki, *J. Heterocycl. Chem.* **1993**, *30*, 549−550. [2c] S. Neya, N. Funasaki, *Tetrahedron Lett.* **2002**, *43*, 1057−1058.

[3] N. Yoshida, H. Shimidzu, A. Osuka, *Chem. Lett.* **1998**, 55−56.

[4] N. Agarwal, C-H. Hung, M. Ravikanth, *Eur. J. Org. Chem.* **2003**, 3730−3734.

[5] P. J. Chmielewski, L. Latos-Grazynski, M. M. Olmstead, A. L. Balch, *Chem. Eur. J.* **1997**, *3*, 268−278.

[6] [6a] W. W. Kalisch, M. O. Senge, *Angew. Chem. Int. Ed.* **1998**, *37*, 1107−1109. [6b] X. Feng, I. Bischoff, M. O. Senge, *J. Org. Chem.* **2001**, *28*, 8693−8700. [6c] d-F. Shi, R. T. Wheelhouse, *Tetrahedron Lett.* **2002**, *43*, 9341−9342.

[7] L. Latos-Grazynski, in *The Porphyrin Handbook* (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), Academic Press, New York, **2000**, vol. 2, pp. 361−416 and references cited therein.

[8] [8a] B. Sridevi, S. J. Narayanan, A. Srinivasan, M. V. Reddy, T. K. Chandrashekar, *J. Porphyrins Phthalocyanines* **1998**, *2*, 69−78. [8b] P-Y. Heo, C-H. Lee, *Bull. Korean Chem. Soc.* **1996**, *17*, 515−520.

[9] [9a] A. Ulman, J. Manassen, *J. Chem. Soc., Perkin Trans.* **1979**, 1066. [9b] Z. Gross, I. Saltsman, R. P. Pandian, C. M. Barzilay, *Tetrahedron Lett.* **1997**, *38*, 2383.

[10] [10a] S. G. DiMagno, V. S-Y. Lin, M. J. Therien, *J. Org. Chem.* **1993**, *58*, 5983−5993. [10b] S. G. DiMagno, V. S-Y. Lin, M. J. Therien, *J. Am. Chem. Soc.* **1993**, *115*, 12513. [10c] V. S-Y. Lin, S. G. DiMagno, M. J. Therien, *Science* **1994**, *264*, 1105−1111.

[11] M. J. Plater, S. Aiken, G. Bourhill, *Tetrahedron.* **2002**, *58*, 2405−2413.

[12] [12a] D. P. Arnold, *Synlett* **2000**, 296. [12b] D. P. Arnold, R. D. Hartnell, G. A. Heath, L. Newby, R. D. Webster, *Chem. Commun.* **2002**, 754−755. [12c] D. P. Arnold, L. J. Nitschinsk, *Tetrahedron* **2000**, *48*, 8781−8792. [12d] M. S. LeCours, C. M. Philips, C. J. de Paula, M. J. Therien, *J. Am. Chem. Soc.* **1996**, *118*, 8344−8354.

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