A Rapid Synthesis of New Benzene-centered Porphyrin Trimers

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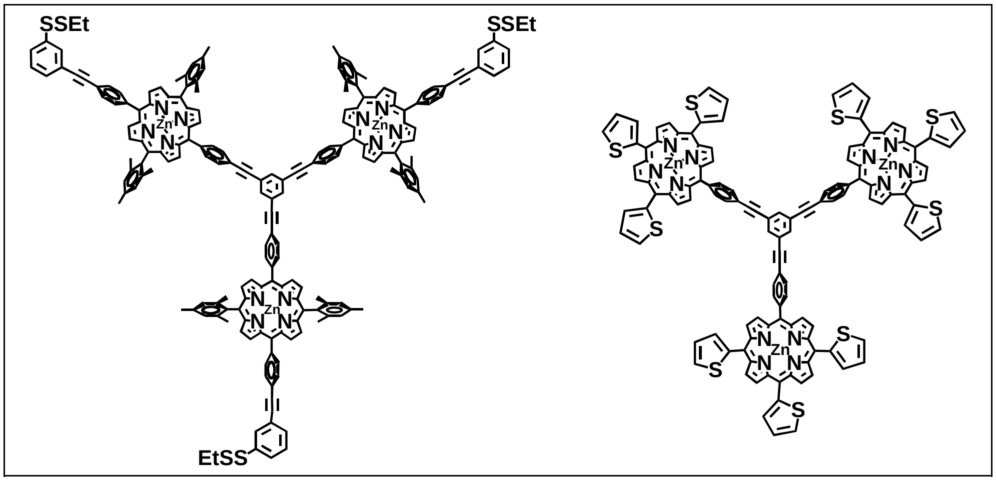

In connection with our study of the capability of forming ordered self-assembled monolayers on gold substrates, we described the full details concerning the rapid synthesis of two rigid, star-shaped *D3*-symmetric arrays with a benzene core attached to three identical metalloporphyrins containing either ethyldisulfide functions or thienyl groups.

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INTRODUCTION

With the increasing demand for the ability to sculpt matter into precise functioning devices of nanoscale dimensions, the molecular level design of functional materials is an overarching theme in much of the synthetic materials literature [1]. Molecular engineering of porphyrin has become of great interest for use in molecular electronics [2a,b], nonlinear optics [2c], information storage [2d,e], molecular sensors [2f,g], electrochromic devices [2h]. Thus, the synthesis of multiporphyrin arrays is an area of active interest [3]. The formation of self-assembled monolayers occurs readily upon exposure of thiol-derivatized porphyrins to a gold substrate. A variety of porphyrin-containing compounds bearing free thiols [4-6], *S*-acetylthio esters [5-10] or disulfides [10,11] have been prepared. In a previous paper, we reported the synthesis of some porphyrin trimers bearing *meta*-thioanisole units at the apical positions like compound **1a** [12]. In connection with our study of the capability of forming ordered self-assembled monolayers on gold substrates, we have synthesized porphyrin trimers containing either ethyldisulfide functions or thienyl groups. The aim of this paper is to provide full details concerning the synthesis leading to compounds **1b** and **2** (Figure I).

RESULTS AND DISCUSSION

In order to obtain a porphyrin trimer with ethyldisulfide functions **1b**, we synthesized the precursor **5b** *via* cross-coupling methodology. Starting from 3-iodoaniline (Scheme I), a one-pot reaction [13] afforded 3-iodobenzenethiol **3b**. This compound was cleanly reacted with *N*-ethylthio-phtalimide [14] to lead to the disulfide derivative **3c**. Its reaction with trimethylsilylacetylene using palladium(II) as a catalyst afforded, after cleavage of the trimethylsilyl protecting groups, ethyl-(3-ethynylphenyl)disulfide **4b** which was used in a coupling reaction with porphyrin **5a** [12] (Scheme II). Reaction of 1,3,5-triethynylbenzene with **5b** in the presence of triphenylarsine as the ligand of the palladium catalyst [12] led to the porphyrin trimer **1b**.

To synthesize the porphyrin trimer **2**, the precursor **7c** was needed. We first tried to react 4-iodobenzaldehyde, 2-thiophenecarboxaldehyde and pyrrole with a catalytic amount of trifluoroacetic acid [15] for 1 hour at 20°C. But, only an inseparable mixture of iodinated compounds was obtained after treatment with DDQ. An inseparable mixture was also obtained by reaction of dipyrromethane **6**, prepared by condensation of pyrrole and 2-thiophene-carboxaldehyde, with 1 equivalent of 4-iodobenzaldehyde under boron trifluoride ethyl etherate catalysis [15] for 30 min at 20°C. Then, 4-acetamidobenzaldehyde was used

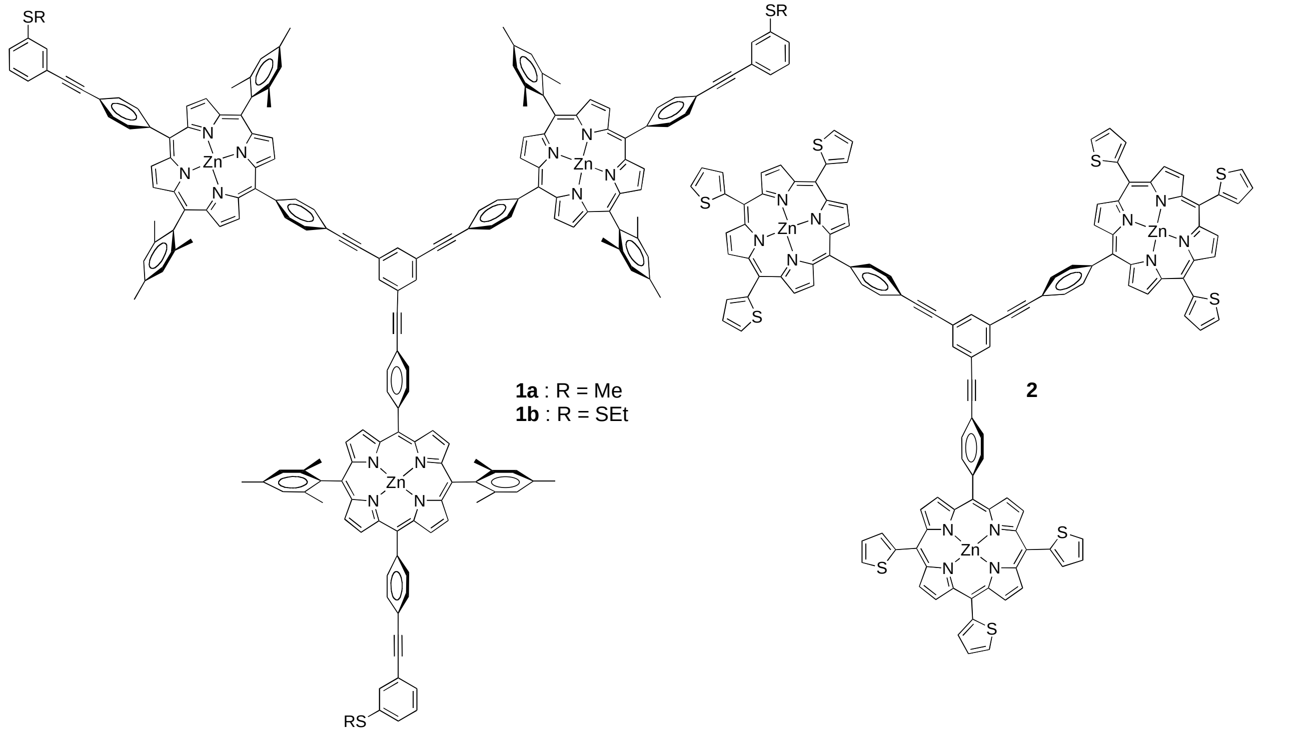
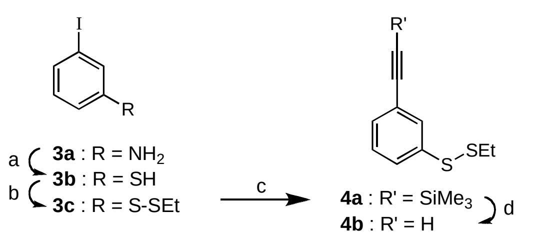


Figure 1

instead of 4-iodobenzaldehyde in a reaction with 2-thiophenecarboxaldehyde and pyrrole using either trifluoracetic acid or boron trifluoride ethyl etherate as a catalyst. But, these reactions failed. Finally, by using a substituent scrambling [16] strategy (Scheme III), the porphyrin **7a** was synthesized after condensation of dipyrromethane **6** and 4-acetamidobenzaldehyde under boron trifluoride ethyl etherate catalysis.

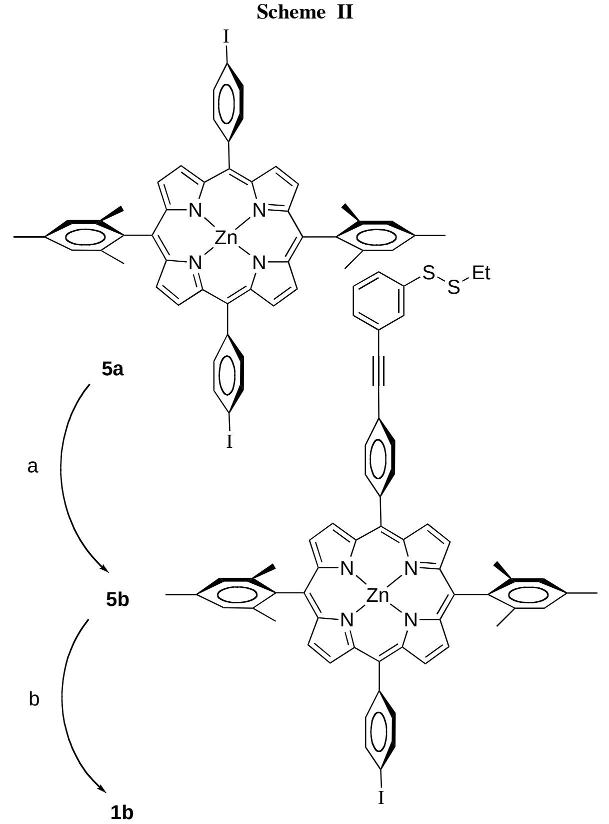
Hydrolysis of **7a** with 20 % aqueous hydrochloric acid afforded amine **7b** (Scheme IV). Thus, the amino group was reacted with isoamylnitrite and then potassium iodide to lead to a mixture of 4-iodophenylporphine **7c** and deiodinated compound. The porphyrin **7c** was transformed in 94 % yield into the corresponding zinc chelate **7d** under standard conditions with zinc acetate and thereafter

Scheme 1



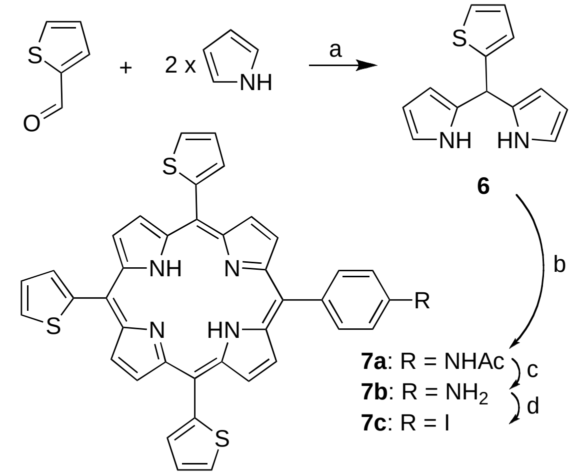
Reagents, conditions and yields. (a) $NaNO_2$, HCl, 0°C; C_2H_5CSSK, H_2O, 40°C, 30 min; KOH, EtOH, reflux, 6h; H_2SO_4 then PPh_3, MeOH, 20°C, 15h (21%); (b) *N*-(ethylthio)phtalimide, benzene, reflux, 15h (100%); (c) HC≡$CSiMe_3$ (excess), $Pd(PPh_3)_2Cl_2$, CuI, Toluene, Et_3N, 40°C, 4h (84%); (d) TBAF on silica gel, $CHCl_3$, 20°C, 7 min (86%).

Scheme II



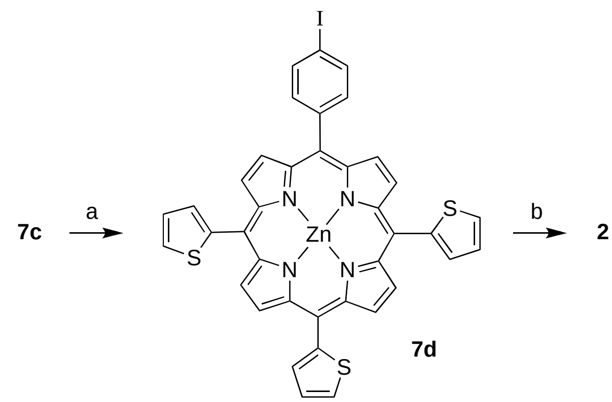
Reagents, conditions and yields. (a) 4b, Pd_2dba_3, $AsPh_3$, CuI, DMF, Et_3N, 75°C, 3h (22%); (b) 1,3,5-triethynylbenzene, Pd_2dba_3, $AsPh_3$, DMF, Et_3N, 50°C, 4h (24%).

Scheme III



Reagents, conditions and yields. (a) $BF_3.O(Et)_2$, 20°C, 20 min; (b) 4-acetamidobenzaldehyde, $BF_3.O(Et)_2$, $CHCl_3$, 20°C, 1h then DDQ, 20°C, 1h (7%); (c) HCl 20%, reflux, 5h (65%); (d) isoamylnitrite, $CHCl_3$, CH_3COOH, 0°C, 15 min then KI, 0°C to 45°C, 30 min (38%).

Scheme IV



Reagents, conditions and yields. (a) $Zn(OAc)_2$, $CHCl_3$, MeOH, reflux, 1h (94%); (b) 1,3,5-triethynylbenzene, $Pd(PPh_3)_4$, DMF, Et_3N, 45°C, 16h (84%).

reacted with 1,3,5-triethynylbenzene in the presence of palladium(0) as a catalyst to give the porphyrin trimer **2**. However, it is noteworthy to specify that porphyrins **7c** and **7d** were obtained pure with difficulty due to the presence of the corresponding deiodinated porphyrins.

In conclusion, new star-shaped D_3-symmetric arrays containing sulfur atoms were synthesized. Their capability of forming ordered self-assembled monolayers on gold surface are beyond the scope of this paper and will be described later.

EXPERIMENTAL

General Data. All air- or water-sensitive reactions were carried out under argon. Solvents were generally dried and distilled prior to use. Reactions were monitored by thin-layer chromatography (TLC) on *E. Merck* silica gel $60F_{254}$ (0.2 mm) precoated aluminium foils. Column chromatography (CC): *E. Merck* silica gel *60* (230-400 mesh). Melting points (mp) were determined with a hot stage apparatus (*Thermovar, C. Reichert AG*, Vienna) equipped with a digital thermometer. UV/VIS spectra were recorded on a *Hewlett-Packard-8452A* diode-array spectrophotometer; λ_{max} (log ε) in nm. NMR: *Varian Gemini 200* (^1H, 200.00 MHz; ^{13}C: 50.30 MHz), Bruker-AM 360 (^1H, 360.14 MHz), or *Bruker Avance DRX 500* (^1H: 500.13 MHz, ^{13}C: 125.76 MHz) in $CDCl_3$ solutions unless otherwise stated; ^1H and ^{13}C chemical shifts (δ) are given in ppm relative to Me_4Si as internal standard, *J* values in Hz. Mass spectra: *Vacuum Generators Micromass 7070E* instrument equipped with a data system *DS 11-250*, EI (electron ionization): acceleration voltage 70 eV, CI (chemical ionization) with methane as ionization gas, FAB (fast atom bombardment): in 2-nitrobenzyl alcohol with Ar at 8 kV; *FT/ICR* mass spectrometer *Bruker 4.7T BioAPEX II*, ES^+ (electrospray ionization, positive mode). Tetrakis(triphenylphosphine)palladium, tris(dibenzylideneacetone)dipalladium (Pd_2dba_3), triphenylarsine and tetrabutylammonium fluoride (TBAF) were purchased from *Aldrich Chemie* (CH-9471 Buchs); dimethylformamide (DMF), tetrahydrofuran (THF), trimethylsilylacetylene (TMSA), and other reagents from *Fluka Chemie AG* (CH-9471 Buchs). Experiments using DMF, $AsPh_3$ or Pd_2dba_3 should be done with caution. Indeed, DMF is a potential cancer hazard and may cause liver and kidney damage. This substance has caused adverse reproductive and fetal effects in animals. Concerning Pd_2dba_3, it may cause cardiac disturbances, central nervous system effects and kidney damage. Finally, for $AsPh_3$, the toxicological properties of this material have not been fully investigated but it is very toxic to aquatic organisms and may cause long-term adverse effects in the aquatic environment.

Triporphyrin (1b). Air was removed from a soln. of **5b** (8.5 mg, 7.8 mmol) and 1,3,5-triethynylbenzene [12] (0.295 mg, 1.96 mmol) in 4 mL of DMF/Et_3N (5:1) by blowing argon for 20 min. Then Pd_2dba_3 (0.54 mg, 0.59 mmol) and $AsPh_3$ (1.44 mg, 4.7 mmol) were added, and deaeration was continued for 10 min. Thereafter, the mixture was heated at 50°C for 4 h. The solvent was removed under reduced pressure and the crude product was purified by two successive CC ($CHCl_3$/hexane: gradient from 1:1 to 7:3) to yield 1.4 mg (24%) of **1b**. UV/VIS (CH_2Cl_2) 292 (5.18), 424 (6.11), 550 (4.85), 590 (4.28). ^1H NMR (360.14 MHz) δ 1.38 (*t*, *J* = 7.3, 9H, CH_3CH_2), 1.85 (*s*, 36H, *o*-CH_3 mesityl), 2.64 (*s*, 18H, *p*-CH_3 mesityl), 2.84 (*q*, *J* = 7.3, 6H, CH_3CH_2), 7.30 (*s*, 12H, H-mesityl), 7.38 (*t*, *J* = 7.8, 3H, H-5 ethyldisulfanylphenyl), 7.52 (*d*, *J* = 7.7, 3H, H-6 ethyldisulfanylphenyl), 7.56 (*d*, *J* = 7.7, 3H, H-4 ethyldisulfanylphenyl), 7.86 (*m*, 3H, H-2 ethyldisulfanylphenyl), 7.93 and 8.25 (AA'XX', 2 x apparent *d*, *J* = 8.0, 12H, H-outside phenylene on porphine), 8.02 and 8.31 (AA'XX', 2 x apparent *d*, *J* = 8.3, 12H, H-inside phenylene on porphine), 8.03 (*s*, 3H, H-benzenetriyl), 8.81 and 8.90 (2 x *d*, *J* = 4.7, 12H, β–H on porphine outside), 8.83 and 8.95 (2 x *d*, *J* = 4.6, 12H, β–H on porphine inside). ES^+-MS *m/z*: (in $CHCl_3$/MeOH/ HCOOH) 1410.0 ($[M-3Zn+8H]^{2+}$), 940.2 ($[M-3Zn+9H]^{3+}$) (calc. avg. mass for $C_{192}H_{144}N_{12}S_6Zn_3$: 3007.83).

Triporphyrin (2). Air was removed from a soln. of **7d** (5.9 mg, 7.2 mmol; determined by ^{1}H-NMR from an inseparable mixture with the deiodinated corresponding compound) and 1,3,5-triethynylbenzene (0.297 mg, 2.0 mmol) in 2 mL of DMF/Et_3N (5:1) by blowing argon for 20 min. Then $Pd(PPh_3)_4$ (1.6 mg, 1.4 mmol) was added, and deaeration was continued for 10 min. Thereafter, the mixture was heated at 45°C for 16 h. The solvent was removed under reduced pressure and the crude product was purified by CC ($CHCl_3$/hexane: gradient from 4:1 to 17:3) to yield 3.7 mg (84%) of **2**. UV/VIS (CH_2Cl_2) 298 (4.95), 426 (6.02), 554 (4.76), 592 (4.19), 598 (4.16). ^{1}H NMR (500.13 MHz) δ 7.51 (*dd*, *J* = 5.4, 3.4, 3H, H-4 thienyl), 7.52 (*dd*, *J* = 5.4, 3.4, 6H, H-4 thienyl), 7.85 (*dd*, *J* = 5.4, 1.3, 3H, H-5 thienyl), 7.86 (*dd*, *J* = 5.4, 1.3, 6H, H-5 thienyl), 7.93 (*dd*, *J* = 3.4, 1.3, 3H, H-3 thienyl), 7.94 (*dd*, *J* = 3.4, 1.3, 6H, H-3 thienyl), 8.04 and 8.28 (AA'XX', 2 x apparent *d*, *J* = 8.3, 12H, H-phenylene), 8.05 (*s*, 3H, H-benzenetriyl), 9.00 and 9.20 (2 x *d*, *J* = 4.7, 12H, β-H on porphine inside), 9.16 and 9.18 (2 x *d*, *J* = 4.7, 12H, β–H on porphine outside). ES$^+$-MS *m/z* : (in $CHCl_3$/ HCOOH) 2043.5 ($[M-3Zn+7H]^+$), 1022.4 ($[M-3Zn+8H]^{2+}$), 681.7 ($[M-3Zn+9H]^{3+}$); (in $CHCl_3$/MeOH) 1116.5 ($[M+2H]^{2+}$), 744.3 ($[M+3H]^{3+}$) (calc. avg. mass for $C_{126}H_{66}N_{12}S_9Zn_3$: 2232.67).

3-Iodobenzenethiol (3b). 4-Iodoaniline (5.0 g, 22.8 mmol) was added to a mixture of concd. HCl (4.6 mL) and crushed ice (4.6 g). After cooling to 0°C, a cold soln. of sodium nitrite (1.67 g, 24.2 mmol) in water (4 mL) was added, the temperature being kept below 4°C. The cold diazonium soln. was then slowly added to a mixture of potassium ethyl xanthate (4.26 g, 26.6 mmol) in water (5.5 mL) at 40°C. The mixture was stirred at this temperature for 30 min, then cooled to 20°C. It was extracted with Et_2O, the combined organic layers were washed with 10% aq. NaOH, then with water and dried (Na_2SO_4). The solvent was removed under reduced pressure. The residue was dissolved in 95% ethanol and solid KOH (8 g) was added. The mixture was refluxed for 6 h then EtOH was evaporated and water was added. The aq. layer was washed with Et_2O, then acidified with 60 mL H_2SO_4 (6 *N*) and extracted with CH_2Cl_2. After drying (Na_2SO_4), the solvent was evaporated. The residue was poured into a soln. of triphenylphosphine (3.0 g, 11.4 mmol) in MeOH (66 mL) and water (15 mL). After stirring at 20°C under argon for 15 h, the mixture was extracted with CH_2Cl_2 and the combined organic layers were dried (Na_2SO_4). The solvent was removed under reduced pressure and the crude product was purified by CC (hexane) to yield 1.74 g (32%) of **3b** as an oil. ^{1}H NMR (200.00 MHz) δ 3.44 (*s*, 1H, SH), 6.94 (*t*, *J* = 7.8, 1H, H-5), 7.21 (*dt*, *J* = 7.8, 1.7, 1H, H-6), 7.47 (*dt*, *J* = 7.8, 1.7, 1H, H-4), 7.62 (*t*, *J* = 1.7, 1H, H-2). ^{13}C NMR (50.30 MHz) δ 94.6 (C-3), 128.3 (C-6), 130.4 (C-5), 133.2 (C-1), 134.6 (C-4), 137.4 (C-2). Anal. Calcd for C_6H_5IS (236.07): C, 30.53; H, 2.13. Found: C, 30.80; H, 1.97. EI-MS: 236 (M^+, 100 %), 109 ($[M-I]^+$, 97 %).

Ethyl-(3-iodophenyl)disulfide (3c). A soln. of **3b** (500 mg, 2.12 mmol) and *N*-(ethylthio)phtalimide [14] (658 mg, 3.18 mmol) in benzene (25 mL) was refluxed under argon for 15 h. After cooling to 5°C, phthalimide was removed by filtration, the filtrate was evaporated under reduced pressure and the residue was purified by CC (CH_2Cl_2/hexane 1:9) to yield 621 mg (99%) of **3c** as an oil. ^{1}H NMR (200.00 MHz) δ 1.32 (*t*, *J* = 7.3, 3H, CH_3), 2.76 (*q*, *J* = 7.3, 2H, CH_2), 7.04 (*t*, *J* = 7.8, 1H, H-5), 7.49 (*ddd*, *J* = 7.8, 1.8, 1.2, 1H, H-6), 7.54 (*dt*, *J* = 7.8, 1.2, 1H, H-4), 7.89 (*t*, *J* = 1.8, 1H, H-2). ^{13}C NMR (50.30 MHz) δ 14.2 (CH_3), 32.7 (CH_2), 94.7 (C-3), 126.1 (C-6), 130.3 (C-5), 135.2, 135.4 (C-2, C-4), 140.1 (C-1). Anal. Calcd for $C_8H_9IS_2$ (296.18): C, 32.44; H, 3.06. Found: C, 32.30; H, 3.27. EI-MS: 296 (M^+, 100 %), 108 ($[M-I-SEt]^+$, 43 %).

[(3-Ethyldisulfanylphenyl)ethynyl]trimethylsilane (4a). Air was removed from a solution of **3c** (318 mg, 1.07 mmol) in 15 mL of toluene/Et_3N (5:1) by blowing argon for 30 min. Then $Pd(PPh_3)_2Cl_2$ (17.5 mg, 0.025 mmol), CuI (9.5 mg, 0.05 mmol) and TMSA (0.15 mL, 10.8 mmol) were added. Thereafter the mixture was stirred at 40°C for 4 h. The solvent was removed under reduced pressure and the crude product was purified by CC (gradient from hexane to CH_2Cl_2/hexane 1:19) to yield 240 mg (84%) of **4a** as a pale yellow oil. ^{1}H NMR (200.00 MHz) δ 0.26 (*s*, 9H, $SiMe_3$), 1.31 (*t*, *J* = 7.3, 3H, CH_3), 2.75 (*q*, *J* = 7.3, 2H, CH_2), 7.24 (*t*, *J* = 7.3, 1H, H-5), 7.32 (*ddd*, *J* = 7.6, 1.8, 1.4, 1H, H-6), 7.49 (*ddd*, *J* = 7.3, 1.8, 1.4, 1H, H-4), 7.64 (*m*, 1H, H-2). ^{13}C NMR (50.30 MHz) δ 0.4 ($SiMe_3$), 14.6 (CH_3), 33.2 (CH_2), 95.3 (C≡*C*-Si), 104.8 (*C*≡C-Si), 124.4 (C-1), 127.8 (C-4), 129.2 (C-5), 130.7 and 130.9 (C-2, C-6), 138.5 (C-3). Anal. Calcd for $C_{13}H_{18}S_2Si$ (266.49): C, 58.59; H, 6.81. Found: C, 58.48; H, 6.97. EI-MS: 266 (M^+, 83 %), 251 ($[M-CH_3]^+$, 100 %), 222 (31 %), 190 (39 %).

Ethyl-(3-ethynylphenyl)disulfide (4b). To TBAF on silica gel (345 mg, 0.38 mmol) under an atmosphere of argon was added a solution of **4a** (95 mg, 0.36 mmol) in 5.5 mL of $CHCl_3$. The mixture was stirred at 20°C for 7 min. A few grains of $CaCl_2$ were added and the solution was filtered through a column of silica gel (CH_2Cl_2/ hexane 1:9) to yield 60 mg (87%) of **4b** as a pale yellow oil. ^{1}H NMR (360.14 MHz) δ 1.31 (*t*, *J* = 7.4, 3H, CH_3), 2.75 (*q*, *J* = 7.4, 2H, CH_2), 3.10 (*s*, 1H, C≡CH), 7.27 (*t*, *J* = 7.7, 1H, H-5), 7.33 (*ddd*, *J* = 7.7, 1.9, 1.4, 1H, H-4), 7.51 (*ddd*, *J* = 7.7, 1.9, 1.4, 1H, H-6), 7.66 (*t*, *J* = 1.9, 1H, H-2). ^{13}C NMR (50.30 MHz) δ 14.1 (CH_3), 32.7 (CH_2), 77.8 (C≡*C*-H), 82.9 (*C*≡C-H), 122.9 (C-3), 127.4 (C-6), 128.7 (C-5), 130.2 and 130.3 (C-2, C-4), 138.1 (C-1). Anal. Calcd for $C_{10}H_{10}S_2$ (194.31): C, 61.81; H, 5.19. Found: C, 62.12; H, 4.96. CI-MS: 194 (MH^+, 15 %).

[5-[4-[[3-(Ethyldisulfanyl)phenyl]ethynyl]phenyl]-15-(4-iodophenyl)-10,20-bis(mesityl)porphinato(2-)]zinc (5b). Air was removed from a soln. of **5a** [12] (77 mg, 75.9 mmol) and **4b** (19 mg, 98.3 mmol) in 13 mL of DMF/Et_3N (5:1) by blowing argon for 20 min. Then $Pd_2(dba)_3$ (5.2 mg, 5.7 mmol), $AsPh_3$ (14 mg, 45.7 mmol) and CuI (2.2 mg, 11.6 mmol) were added, and deaeration was continued for 10 min. Thereafter, the mixture was heated at 75°C for 3 h. The solvent was removed under reduced pressure and the crude product was purified by CC (CH_2Cl_2/hexane: gradient from 2:23 to 1:4) to yield 17.7 mg (22%) of **5b**. UV/VIS (CH_2Cl_2) 292 (4.53), 421 (5.65), 549 (4.33), 589 (3.75). ^{1}H NMR (360.14 MHz) δ 1.37 (*t*, *J* = 7.3, 3H, CH_2CH_3), 1.82 (*s*, 12H, *o*-CH_3 mesityl), 2.63 (*s*, 6H, *p*-CH_3 mesityl), 2.82 (*q*, *J* = 7.3, 2H, CH_2CH_3), 7.28 (*s*, 4H, H-mesityl), 7.38 (*t*, *J* = 7.8, 1H, H-5 ethyldisulfanylphenyl), 7.51 (*dt*, *J* = 7.8, 1.0, 1H, H-6 ethyldisulfanylphenyl), 7.55 (*ddd*, *J* = 7.8, 1.9, 1.0, 1H, H-4 ethyldisulfanylphenyl), 7.85 (*t*, *J* = 1.9, 1H, H-2 ethyldisulfanylphenyl), 7.92 and 8.23 (AA'XX', 2 x apparent *d*, *J* = 8.3, 4H, H-ethynylphenyl), 7.96 and 8.07 (AA'XX', 2 x apparent *d*, *J* = 8.1, 4H, H-iodophenyl), 8.78 and 8.86 (2 x *d*, *J* = 4.7, 4H, β–H on porphine H-12, H-13, H-17, H-18), 8.79 and 8.89 (2 x *d*, *J* = 4.7, 4H, β–H on porphine H-2, H-3, H-7, H-8). FAB-MS : 1081.2 (calc. avg. mass for $C_{60}H_{47}IN_4S_2Zn$: 1080.46).

***meso*-(Thien-2-yl)dipyrromethane (6).** A soln. of 2-thiophenecarboxaldehyde (0.93 mL, 10 mmol) and pyrrole (28 mL, 404 mmol) was degassed for 30 min with argon. Then, $BF_3.O(Et)_2$ (0.37 mL, 3.0 mmol) was injected. The mixture was stirred for 30 min at 20°C, then diluted with CH_2Cl_2 and immediately washed with 0.1 *N* aq. NaOH (~50 mL). The organic layer was washed with water and dried (Na_2SO_4). Evaporation of the solvent under reduced pressure resulted in a brown oil. Unreacted pyrrole was removed by vacuum distillation at 20°C, yielding a tacky solid with light brown splotches. This solid was washed with 500 mL of hexane and collected by filtration. The crude product was purified by CC (CH_2Cl_2/hexane/Et_3N 10:10:0.1) to yield 1.39 g (61%) of **6** as a white solid. Mp 112-113°C. ^{1}H NMR (360.14 MHz) δ 5.75 (*s*, 1H, *meso*-H), 6.04 (*m*, 2H, H-3 pyrrole), 6.16 (*dd*, *J* = 6.1, 2.8, 2H, H-4 pyrrole), 6.70 (*m*, 2H, H-5 pyrrole), 6.89 (*m*, 1H, H-3'), 6.95 (*dd*, *J* = 5.0, 3.7, 1H, H-4'), 7.21 (*dd*, *J* = 5.0, 1.2, 1H, H-5'), 7.98 (*s*, 2H, NH). ^{13}C NMR (50.30 MHz) δ 39.1, 107.0, 108.5, 117.4, 124.6, 125.5, 126.7, 131.9, 145.6. Anal. Calcd for $C_{13}H_{12}N_2S$ (228.31): C, 68.39; H, 5.30; N, 12.27. Found: C, 68.68; H, 5.01; N, 12.01. EI-MS: 228 (M^+, 100 %), 173 (49 %).

***N*-[4-[10,15,20-Tris(thien-2-yl)-porphin-5-yl]phenyl]-acetamide (7a).** A soln. of **6** (80.2 mg, 0.35 mmol) and 4-acetamidobenzaldehyde (57.6 mg, 0.35 mmol) in 35 mL $CHCl_3$ was purged with argon for 30 min, then $BF_3.O(Et)_2$ (14.9 mL, 0.12 mmol) was added. The solution was stirred for 1 h at 20°C then DDQ (60.8 mg, 0.27 mmol) was added. The mixture was stirred at 20°C for an additional 1 h and then 0.5 mL Et_3N were added. The solvent was evaporated and the residue was purified by CC (CH_2Cl_2/AcOEt 9:1) to yield 8.7 mg (7%) of **7a**. UV/VIS (CH_2Cl_2) 308 (4.22), 424 (5.43), 522 (4.18), 560 (3.98), 596 (3.86). ^{1}H NMR (360.14 MHz) δ -2.67 (*s*, 2H, NH porphine), 2.37 (*s*, 3H, CH_3), 7.50 (*dd*, *J* = 5.5, 3.5, 2H, H-4 thienyl), 7.51 (*dd*, *J* = 5.2, 3.7, 1H, H-4 thienyl), 7.85 (*m*, 3H, H-5 thienyl), 7.89 and 8.15 (AA'XX', 2 x apparent *d*, *J* = 8.5, 4H, H-phenylene), 7.91 (*m*, 3H, H-3 thienyl), 8.92 (*d*, *J* = 4.8, 2H, β–H on porphine), 9.00-9.08 (*m*, 7H, β–H on porphine and N*H*Ac). FAB-MS : 690.3 (calc. avg. mass for $C_{40}H_{27}N_5OS_3$: 689.87).

4-[10,15,20-Tris(thien-2-yl)-porphin-5-yl]benzenamine (7b). A suspension of **7a** (28.3 mg, 41.0 mmol) was refluxed for 5 h in 20% HCl (16 mL). The solution was cooled and neutralized by adding 10% KOH solution. The neutralized solution was extracted 3 times with $CHCl_3$. The combined organic layers were dried ($MgSO_4$), the solvent evaporated and the residue was purified by CC ($CHCl_3$) to yield 17.2 mg (65%) of **7b**. UV/VIS (CH_2Cl_2) 308 (4.18), 426 (5.44), 524 (4.16), 560 (3.98), 592 (3.77), 598 (3.77). ^{1}H NMR (360.14 MHz) δ -2.64 (*s*, 2H, NH), 4.05 (*s*, 2H, NH_2), 7.07 and 7.98 (AA'XX', 2 x apparent *d*, *J* = 8.5, 4H, H-phenylene), 7.50 (*dd*, *J* = 5.3, 3.5, 3H, H-4 thienyl), 7.85 (*dd*, *J* = 5.3, 1.1, 3H, H-5 thienyl), 7.92 (*dd*, *J* = 3.5, 1.1, 3H, H-3 thienyl), 8.92 (*d*, *J* = 4.4, 2H, β–H on porphine), 9.00-9.05 (*m*, 6H, β–H on porphine). FAB-MS : 648.3 (calc. avg. mass for $C_{38}H_{25}N_5S_3$: 647.83).

5-(4-Iodophenyl)-10,15,20-tris(thien-2-yl)porphine (7c). To a solution cooled to 0-5°C of **7b** (11.8 mg, 18.2 mmol) in 4 mL $CHCl_3$/CH_3COOH (2:5) were added dropwise with stirring 27.4 mL (0.20 mmol) isoamylnitrite in 0.19 mL $CHCl_3$. After 15 min, a solution of 77 mg (0.464 mmol) KI in 0.15 mL water was added at once. The mixture was allowed to warm up to 20°C and then was heated to 45°C for 30 min. It was cooled, diluted with water and extracted with $CHCl_3$. The combined organic layers were washed with saturated Na_2CO_3 solution and saturated aq. $Na_2S_2O_3$ and dried over $MgSO_4$. After removal of solvent, the crude product was purified by CC (CH_2Cl_2/hexane 7:13) to yield to 8.9 mg of a mixture of **7c** (5.3 mg, 38%; determined by ^{1}H-NMR) and the corresponding deiodinated compound (3.6 mg; determined by ^{1}H-NMR). Purification of a small amount of the mixture by using a Lobar® (310-25) Lichroprep Si60 (40-63 mm) Merck, provided pure **7c** for analysis. UV/VIS (CH_2Cl_2) 308 (4.19), 424 (5.55), 520 (4.20), 560 (3.89), 592 (3.73), 598 (3.73). ^{1}H NMR (360.14 MHz) δ -2.70 (*s*, 2H, NH), 7.51 (*dd*, *J* = 5.2, 3.3, 3H, H-4 thienyl), 7.86 (*dd*, *J* = 5.2, 1.1, 3H, H-5 thienyl), 7.92 (*dd*, *J* = 3.3, 1.1, 3H, H-3 thienyl), 7.93 and 8.10 (AA'XX', 2 x apparent *d*, *J* = 8.4, 4H, H-phenylene), 8.80 (*d*, *J* = 4.8, 2H, β–H on porphine), 9.00-9.08 (*m*, 6H, β–H on porphine). FAB-MS : 759.5 (calc. avg. mass for $C_{38}H_{23}IN_4S_3$: 758.71).

[5-(4-Iodophenyl)-10,15,20-tris(thien-2-yl)porphinato(2-)]-zinc (7d). To a soln. of 11.4 mg of a mixture made up **7c** (6.8 mg, 9.0 mmol; determined by ^{1}H-NMR) and the corresponding deiodinated compound (4.6 mg; determined by ^{1}H-NMR) in 1.6 mL of $CHCl_3$/MeOH (9:1), zinc acetate monohydrate (90 mg, 0.45 mmol) was added and the mixture was refluxed for 1 h. Thereafter, the solvent was removed and the residue was purified by CC ($CHCl_3$/hexane 3:2) to yield 11.6 mg of a mixture of **7d** (6.9 mg, 94%; determined by ^{1}H-NMR) and the corresponding deiodinated compound (4.7 mg; determined by ^{1}H-NMR). A small amount of pure **7c** was used to provide pure **7d** for analysis. UV/VIS (CH_2Cl_2) 312 (3.92), 352 (3.84), 424 (5.54), 554 (4.24), 590 (3.68), 596 (3.70). ^{1}H NMR (360.14 MHz) δ 7.49 (*dd*, *J* = 5.1, 3.3, 3H, H-4 thienyl), 7.83 (*m*, 3H, H-5 thienyl), 7.89 (*m*, 3H, H-3 thienyl), 7.92 and 8.08 (AA'XX', 2 x apparent *d*, *J* = 8.1, 4H, H-phenylene), 8.87 and 9.10 (2 x *d*, *J* = 4.1, 4H, β–H on porphine), 9.11 (*s*, 4H, β–H on porphine). FAB-MS : 822.3 (calc. avg. mass for $C_{38}H_{21}IN_4S_3Zn$: 822.08).

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