Synthesis of C_1- and C_{3v}-Symmetric Porphyrin Trimers Based on Triphenylmethane Cores

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Summary. This work describes the synthesis of a new class of tripodaphyrin derivatives with a triphenylmethane core. Both C_1- and C_{3v}-symmetric tetrahedral large molecules with covalently linked rigid elements were obtained.

Keywords. Porphyrines; Alkynes; Nanostructures; Chirality; Tripodaphyrin.

Introduction

The design and construction of novel porphyrin architectures with well-defined geometries is an area of increasing current interest [1]. Multi-porphyrins macrorings have attracted enormous interest because porphyrins provide rigid frameworks with relatively easy synthesis approaches [2]. Their biological importance, as it was found that the antenna chlorophylls in photosynthetic bacteria are arranged into macrorings to absorb and transfer solar energy with great efficiency, makes them one of the attracting research targets. In preceding papers [3, 4] we described the synthesis of tripodaphyrins, a new class of porphyrine derivatives. Tripodaphyrins are pyramidal assemblies in which a porphyrin macrocycle, situated on the top of the molecule, is "supported" by three "legs" consisting of linear arrays of cova-

lently linked rigid constitutives elements. Our principal aims of applications of tripodaphyrins are both studies of these molecules as light-harversting systems arrays and molecular-based information storage. Indeed, one can envisage that multiple bits of information could be stored through the positioning of (±)-chiral tripodaphyrins by means of scanning probe microscopy (STM/AFM). In the present work, we describe the full synthetic details of C_1- and C_{3v}-symmetric tripodaphyrin derivatives.

Results and Discussion

As a starting point for the design of a C_{3v}-symmetric tripodaphyrin derivative, we choose readily available 4,4′,4″-methylidynetrisphenol [5] skeleton **1**. Its reaction with a threefold excess of trifluoromethanesulfonyl chloride afforded the expected compound **2** in 80% yield. Substitution of all three triflate groups by ethynyl groups was achieved in 95% yield on reaction of **2** with triisopropylsilylacetylene under Pd(0)-catalyzed conditions using copper iodide (Scheme 1). Thereafter, cleavage of both trialkylsilyl protecting groups gave the core molecule **4** (70%), which was reacted with [5-(4-iodophenyl)-10,15,20-triphenylporphinato(2-)]zinc [4] to afford the desired C_{3v}-symmetric porphyrin trimer **6** in 49% yield.

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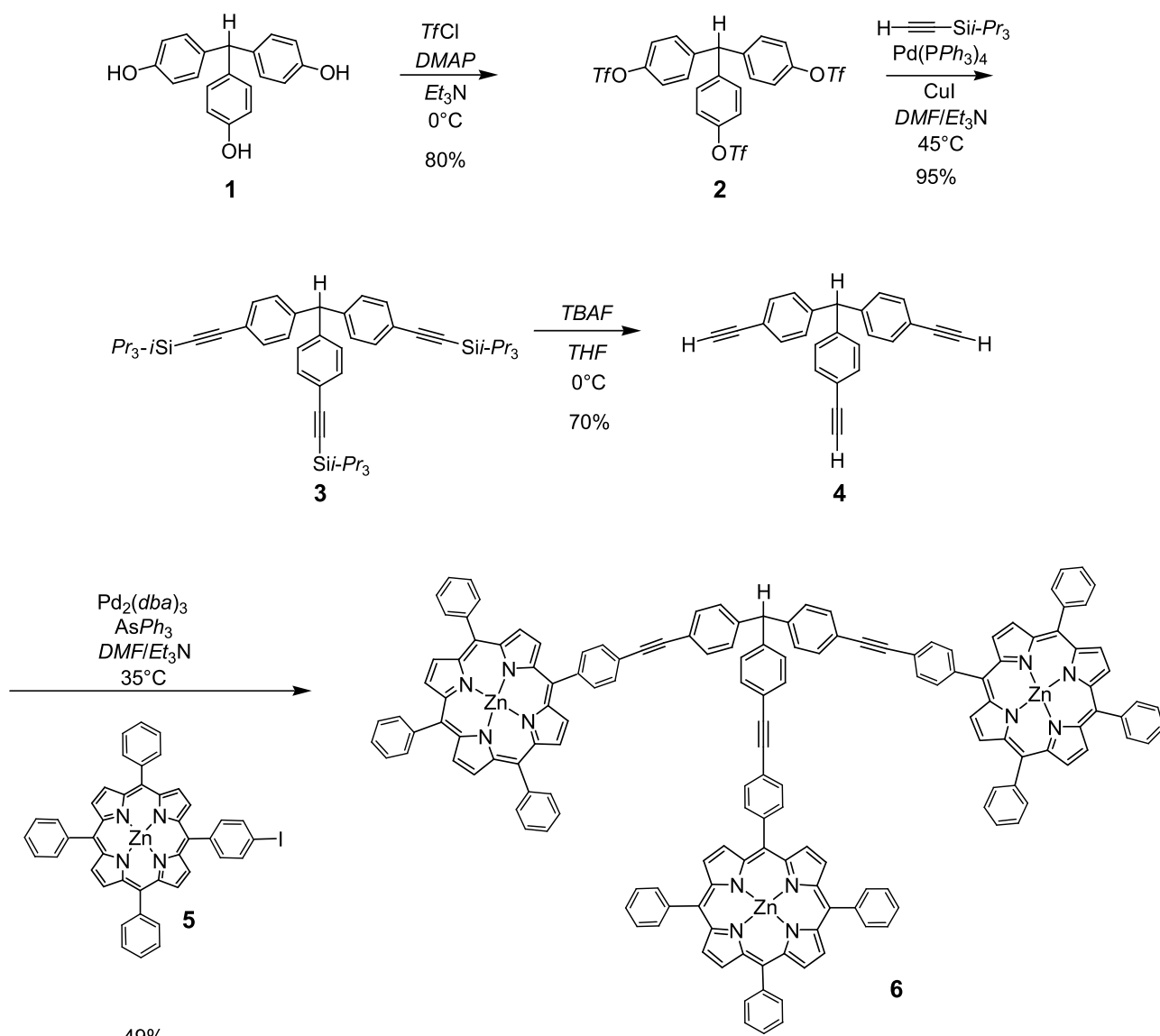
Scheme 1

The strategy devised for the synthesis of a (±)-chiral tripodaphyrin derivative (C_1-symmetry) was based upon the use of pure [6] tris(4-iodophenyl)-methane (**8**), which was prepared in 89% yield starting from **7**. Then, successive replacement of the iodine atoms of triphenylmethane **8** by *Sonogashira* coupling reactions with ethynyltrimethylsilane and compound **10** [8] was possible yielding **9** (41%) and **11** (40%). Thus, a (±)-chiral triphenylmethane core was obtained (Scheme 2).

As a precursor of the (±)-chiral tripodaphyrin derivative, compound **13** was prepared in 88% yield by coupling **11** and [5-(4-ethynylphenyl)-10,15,20-triphenylporphinato(2-)]zinc (**12**) [4] using triphenyl-

arsine as a ligand of the palladium catalyst instead of triphenylphosphine [7]. The porphyrin trimer **16** with three ''arms'' of different lengths (C_1-symmetry) was synthesized after cleavage of both trialkyl-silyl protecting groups in 85% yield and coupling with tetraphenylporphyrine **15** elongated with an iodotolane [4] unit (18%) (Scheme 3).

In conclusion, we developed a synthesis to obtain a new class of tripodaphyrins derivatives designed for nanofabrication. On one hand, we synthesized a C_{3v}-symmetric triphenylmethane in which three porphyrin macrocycles are attached to each phenyl ring. On the other hand, by using successive substitution of the three iodine atoms of tris(4-iodophenyl)methane,
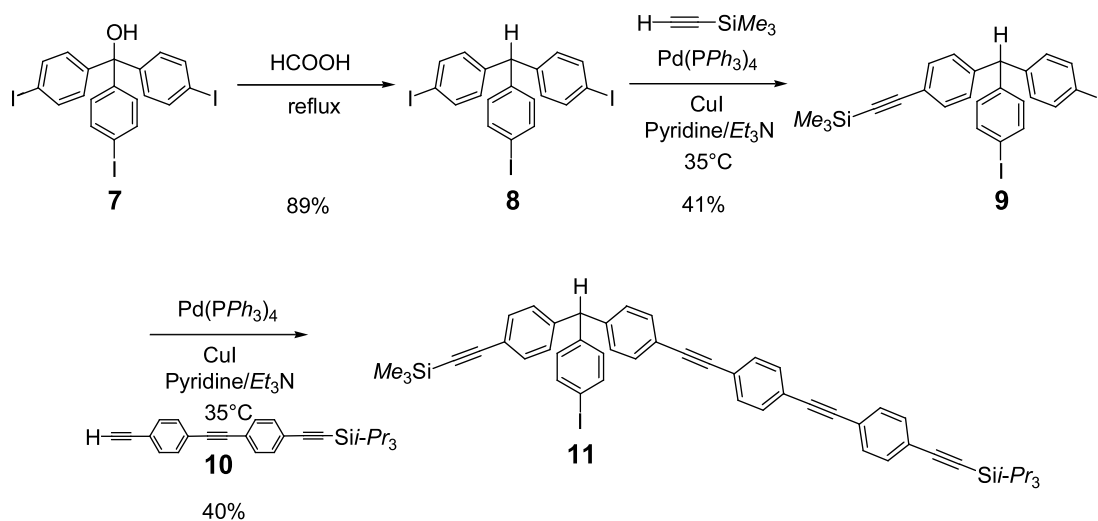
Scheme 2

a trimer with three "arms" of different length was also obtained.

Experimental

All air- or water-sensitive reactions were carried out under Ar. Solvents were generally dried and distilled prior to use. Reactions were monitored by thin-layer chromatography on E. Merck silica gel 60F$_{254}$ (0.2 mm) precoated aluminum foils. Column chromatography (CC): E. Merck silica gel 60 (230–400 mesh). Melting points (m.p.) 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} in nm (log ε in mol^{-1} dm^3 cm^{-1}). NMR: Varian Gemini 200 (^{1}H: 200.00 MHz; ^{13}C: 50.30 MHz), Bruker-AM 360 (^{1}H: 360.14 MHz), or Bruker Avance DRX 500 (^{1}H: 500.13 MHz; ^{13}C: 125.76 MHz); ^{1}H and ^{13}C chemical shifts (δ) are given in ppm relative to *TMS* as internal standard, *J* values in Hz. Mass spectra: Vacuum Generators Micromass 7070E instrument equipped with a data system DS 11–250, FAB (fast atom bombardment): in 2-nitrobenzyl alcohol with Ar at 8 kV. Elemental analysis (C, H, N) were conducted by Ciba Specialities Mikrolabor, Marly, Switzerland, their results were found to be in good agreement ($\pm0.2\%$) with the calculated values. Tetrakis(triphenylphosphine)palladium, tris(dibenzylideneacetone)dipalladium (Pd$_2$dba$_3$), triphenylarsine and tetrabutylammonium fluoride (*TBAF*) were purchased from Aldrich; dimethylformamide (*DMF*), tetrahydrofuran (*THF*), trimethylsilylacetylene (*TMSA*), triisopropylsilylacetylene, and other reagents from Fluka.

Trifluoromethanesulfonic acid methylidynetri-4,1-phenylene ester (**2**) [10]
Trifluoromethanesulfonyl chloride (0.178 cm^3, 1.68 mmol) was slowly added under an Ar atmosphere to a stirring mix-

ture of 149 mg 4,4′,4″-methylidynetrisphenol [5] (0.51 mmol), 0.348 cm^3 *Et*$_3$N (2.5 mmol), and 6.2 mg *DMAP* (0.051 mmol) in 4.3 cm^3 dry acetone at 0°C. After being stirred for 3 h at 0°C, the solvent was removed under reduced pressure and the crude product was purified by CC (CH$_2$Cl$_2$/*n*-hexane = 1/4) to yield 280 mg (80%) **2**. M.p.: 82°C; ^{1}H NMR (200.00 MHz, CDCl$_3$): $\delta = 5.64$ (*s*, 1H, CH), 7.15 and 7.25 (AA′XX′, 2 × apparent *d*, $J = 8.9$ Hz, 12H, H-2, H-3) ppm; ^{13}C NMR (50.30 MHz, CDCl$_3$): $\delta = 54.7$ (CH), 118.7 (*q*, $J = 321$ Hz, CF$_3$), 121.7 (C-2), 131.0 (C-3), 142.5 (C-4), 148.5 (C-1) ppm; FAB-MS: m/z (%) = 687 ([M − H]$^+$, 19), 555 (25), 463 (100).

[Methylidynetris(4,1-phenylene-2,1-ethynediyl)] tris(triisopropylsilane) (**3**, C$_{52}$H$_{76}$Si$_3$)
Air was removed from a soln. of 82.5 mg **2** (0.12 mmol) in 7 cm^3 *DMF*/*Et*$_3$N (5:1) by blowing Ar for 20 min. Then 41.7 mg Pd(P*Ph*$_3$)$_4$ (0.036 mmol), 13.8 mg CuI (0.072 mmol), and 0.134 mm^3 ethynyltriisopropylsilane (0.6 mmol) were added, and deaeration was continued for 10 min. Thereafter, the mixture was heated at 45°C for 18 h. The solvent was removed under reduced pressure and the crude product was purified by CC (*n*-hexane) to yield 89.6 mg (95%) **3**. M.p.: 167°C; ^{1}H NMR (200.00 MHz, CDCl$_3$): $\delta = 1.12$ (*m*, 63H, Si*i*-*Pr*$_3$), 5.49 (*s*, 1H, CH), 6.99 and 7.39 (AA′XX′, 2 × apparent *d*, $J = 8.2$ Hz, 12H, H-2, H-3) ppm; ^{13}C NMR (50.30 MHz, CDCl$_3$): $\delta = 11.3$ (SiCH), 18.7 (CH(CH$_3$)$_2$), 56.3 (CH), 90.6 (*C*≡C-Si*i*-*Pr*$_3$), 106.8 (*C*≡C-Si*i*-*Pr*$_3$), 121.9 (C-1), 129.2 (C-3), 132.1 (C-2), 143.3 (C-4) ppm; FAB-MS: m/z (%) = 786 (M, 57), 742 (100).

Tris(4-ethynylphenyl)methane (**4**, C$_{25}$H$_{16}$)
To a solution of 23.7 mg **3** (30.2 μmol) in 8 cm^3 *THF*, 18 mm^3 *TBAF* (1 *M* in *THF*, 18 μmol) were added at 0°C, and the mixture was stirred at 0°C for 10 min. A few grains of CaCl$_2$ were added and the solvent was evaporated. The crude product was purified by CC (gradient from *n*-hexane to CHCl$_3$/*n*-hexane = 9/1) to yield 6.7 mg (70%) of **4**. ^{1}H NMR
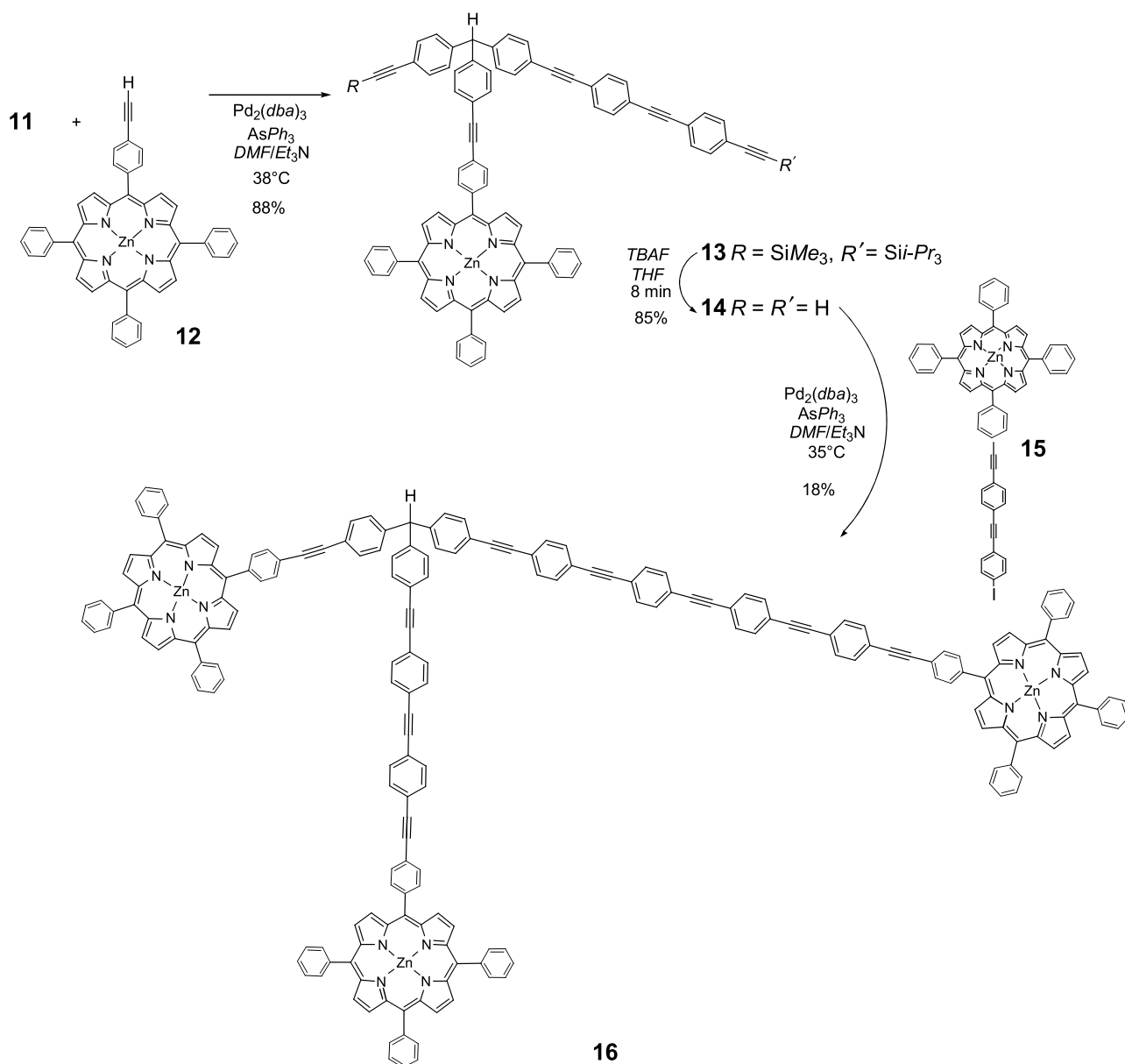
Scheme 3

(360.14 MHz, CDCl$_3$): $\delta = 3.05$ (*s*, 3H, C≡CH), 5.52 (*s*, 1H, CH), 7.02 and 7.42 (AA'XX', 2 × apparent *d*, *J* = 8.1 Hz, 12H, H-2, H-3) ppm; ^{13}C NMR (50.30 MHz, CDCl$_3$): $\delta = 56.3$ (CH), 77.3 (C≡*C*–H), 83.3 (*C*≡C–H), 120.5 (C-4), 129.3 (C-2), 132.3 (C-3), 143.6 (C-1) ppm; FAB-MS: *m/z* (%) = 317 (M$^+$, 31), 215 (100).

C$_{3v}$-Symmetric Triporphyrin (**6**, C$_{157}$H$_{94}$N$_{12}$Zn$_3$)

Air was removed from a soln. of 2.2 mg **4** (7 μmol) and 22.7 mg [5-(4-iodophenyl)-10,15,20-triphenylporphinato (2-)]zinc (**5**) [4] (28.2 μmol) in 4.8 cm^3 *DMF/Et$_3$N* (5/1) by blowing Ar for 20 min. Then 0.79 mg Pd$_2$(*dba*)$_3$ (0.86 μmol) and 2.11 mg As*Ph*$_3$ (6.89 μmol) were added, and deaeration was continued for 10 min. Thereafter, the mixture was heated at 35°C for 6 h. At that time, the same amount of Pd$_2$(*dba*)$_3$ and As*Ph*$_3$ was again added and the stirring continued for 3 h. The solvent was removed under reduced pressure and the crude product was purified by two successive CC (CHCl$_3$/*n*-hexane: gradient from 3/2 to 3/1) to yield 8.1 mg (49%) **6**. UV/VIS (CH$_2$Cl$_2$): λ_{max} (log ε) = 298 (4.94), 420 (6.10), 548 (4.69), 578 (3.96), 586 (4.14), 594 (3.69) nm (mol^{-1} dm^3 cm^{-1}); ^{1}H NMR (360.14 MHz, CDCl$_3$): $\delta = 5.72$ (*s*, 1H, CH), 7.28 and 7.70 (AA'XX', 2 × apparent *d*, *J* = 8.4 Hz, 12H, H-phenylene), 7.72–7.81 (*m*, 27H, *m*- and *p*-H-phenyl), 7.96 (apparent *d*, *J* = 8.0 Hz, 6H, H-phenylene on porphyrin), 8.19–8.26 (*m*, 24H, *o*-H-phenyl and H-phenylene on porphyrin), 8.95 (*s*, 12H, β-H on porphyrin ouside), 8.98 (*s*, 12H, β-H on porphyrin inside) ppm; ES$^+$-MS (in CHCl$_3$/

HCOOH): $m/z = 1078.0$ ([M-3Zn + 8H]$^{2+}$), 719.2 ([M-3Zn + 9H]$^{3+}$) (calc. avg. mass for $C_{157}H_{94}N_{12}Zn_3$: 2344.69).

Tris(4-iodophenyl)methane (8) [6]

A soln. of 162.4 mg tris(4-iodophenyl)methanol (0.25 mmol) was refluxed in 98% HCOOH for 22 h. Thereafter, the soln. was diluted with CH_2Cl_2 and water. The mixture was neutralized with solid NaHCO$_3$, extracted three times with CH_2Cl_2, dried (Na$_2$SO$_4$), and evaporated. The crude product was purified by CC (CH_2Cl_2/n-hexane = 1/19) to yield 140.4 mg (89%) 8. ^{1}H NMR (200.00 MHz, CDCl$_3$): $\delta = 5.35$ (s, 1H, CH), 6.80 and 7.61 (AA′XX′, $2 \times$ apparent d, $J = 8.2$ Hz, 12H, H-phenylene) ppm; ^{13}C NMR (50.30 MHz, CDCl$_3$): $\delta = 55.4$ (CH), 92.3 (C-4), 131.2 (C-2), 137.6 (C-3), 142.3 (C-1) ppm.

[[4-[[Bis-(4-iodophenyl)]methyl]phenyl]ethynyl]-trimethylsilane (9, $C_{24}H_{22}I_2Si$)

Air was removed from a soln. of 130.3 mg tris(4-iodophenyl)methane (8) [6] (0.21 mmol) in 7.4 cm^3 pyridine/Et_3N (1/1) by blowing Ar for 20 min. Then, 8.3 mg Pd(PPh_3)$_4$ (7.2 μmol), 4.4 mg CuI (23 μmol), and 26 mm^3 TMSA (0.187 mmol) were added, and the mixture was stirred at 35°C for 2 h. The solvent was removed under reduced pressure and the residue was purified by CC (CH_2Cl_2/n-hexane = 1/19) to yield 45.4 mg (41%) 9. ^{1}H NMR (360.14 MHz, CDCl$_3$): $\delta = 0.24$ (s, 9H, SiMe$_3$), 5.39 (s, 1H, CH), 6.79 and 7.60 (AA′XX′, $2 \times$ apparent d, $J = 8.6$ Hz, 8H, H-iodophenyl), 6.97 and 7.38 (AA′XX′, $2 \times$ apparent d, $J = 8.2$ Hz, 4H, H-phenylene) ppm; ^{13}C NMR (50.30 MHz, CDCl$_3$): $\delta = -0.05$ (SiMe$_3$), 55.6 (central CH), 92.2 (C-4′), 94.5 (C≡C-SiMe$_3$), 104.6 (C≡C-SiMe$_3$), 121.6 (C-1), 129.1 (C-3), 131.3 (C-2′), 132.1 (C-2), 137.6 (C-3′), 142.5 (C1′), 143.0 (C-4) ppm; FAB-MS: m/z (%) = 592 (M$^+$, 24), 591 ([M − H]$^+$, 46), 577 ([M − CH$_3$]$^+$, 69), 419 ([M − H − I − 3CH$_3$]$^+$, 95), 389 (100).

[[4-[[(4-Iodophenyl)-[4-[[4-[[4-[(triisopropylsilyl)ethynyl]phenyl]ethynyl]phenyl]ethynyl]phenyl]]methyl]phenyl]-ethynyl]trimethylsilane (11, $C_{51}H_{51}ISi_2$)

Air was removed from a soln. of 32 mg 9 (54 μmol) and 18.8 mg [[4-[(4-ethynylphenyl)ethynyl]phenyl]ethynyl]triisopropylsilane (10) [8] (49 μmol) in 3 cm^3 pyridine/Et_3N (1/1) by blowing Ar for 20 min. Then, 3 mg Pd(PPh_3)$_4$ (2.6 μmol) and 2.2 mg CuI (12 μmol) were added, and the mixture was stirred at 35°C for 2 h. The solvent was removed under reduced pressure and the residue was purified by CC (gradient from n-hexane to CH_2Cl_2/n-hexane = 2/23) to yield 16.7 mg (40%) 11. M.p.: 73°C; ^{1}H NMR (360.14 MHz, CDCl$_3$): $\delta = 0.24$ (s, 9H, SiMe$_3$), 1.13 (m, 21H, Sii-Pr$_3$), 5.47 (s, 1H, CH), 6.82 and 7.61 (AA′XX′, $2 \times$ apparent d, $J = 8.5$ Hz, 4H, H-iodophenyl), 7.00 and 7.39 (AA′XX′, $2 \times$ apparent d, $J = 8.3$ Hz, 4H, H-2, H-3), 7.03 and 7.44 (AA′XX′, $2 \times$ apparent d, $J = 8.0$ Hz, 4H, H-2′, H-3′), 7.45 (m, 4H, H-2‴, H-3‴), 7.49 (m, 4H, H-2″, H-3″) ppm; ^{13}C NMR (50.30 MHz, CDCl$_3$): $\delta = -0.05$ (SiMe$_3$), 11.3 (SiCH), 18.7 (CH(CH$_3$)$_2$), 56.0 (central CH), 89.2, 90.9, 91.0, 91.1 (C≡C), 92.2 (C-4 iodophenyl), 93.0 (C≡C-Sii-Pr$_3$), 94.4 (C≡C−SiMe$_3$), 104.7 (C≡C−SiMe$_3$), 106.6 (C≡C−Sii-Pr$_3$), 121.4, 121.6 (C-1, C-4‴), 122.8 (C-1″,

C-4″), 123.2, 123.5 (C-4′, C-1‴), 129.2, 129.4 (C-3, C-2′), 131.4 (C-2 iodophenyl), 131.5, 131.6, 131.8 (C-3′, C2″, C-3″, C-2‴), 132.0, 132.1 (C-2, C-3″), 137.6 (C-3 iodophenyl), 142.6 (C-1 iodophenyl), 143.2, 143.3 (C-4, C-1′) ppm; FAB-MS: m/z (%) = 847 (M$^+$, 100), 803 (53).

[10,15,20-Triphenyl-5-[4-[[4-[[4-[[4-[(triisopropylsilyl)ethynyl]phenyl]ethynyl]phenyl]ethynyl]-phenyl]-[4-[(trimethylsilyl)ethynyl]phenyl]methyl]phenyl]ethynyl]phenyl]porphinato(2-)]zinc (13, $C_{97}H_{78}N_4Si_2Zn$)

Air was removed from a soln. of 6.0 mg 11 (7.1 μmol) and 20 mg [5-(4-ethynylphenyl)-10,15,20-triphenylporphinato(2-)]zinc 12 [4] (28.5 μmol) in 2.4 cm^3 of DMF/Et_3N (5/1) by blowing Ar for 20 min. Then 0.41 mg Pd$_2$(dba)$_3$ (0.45 μmol) and 1.09 mg AsPh_3 (3.56 μmol) were added, and deaeration was continued for 10 min. Thereafter, the mixture was heated at 40°C for 4 h. At that time, the same amount of Pd$_2$(dba)$_3$ and AsPh_3 was again added and the stirring continued for 3 h. The solvent was removed under reduced pressure and the crude product was purified by CC (CHCl$_3$/ n-hexane: gradient from 2/3 to 11/9) to yield 8.9 mg (88%) 13. UV/VIS (CH$_2$Cl$_2$): λ_{max} (log ε) = 336 (4.86), 360 (4.72), 422 (5.68), 548 (4.34), 588 (3.84) nm (mol^{-1} dm^3 cm^{-1}); ^{1}H NMR (500.13 MHz, CDCl$_3$): $\delta = 0.26$ (s, 9H, SiMe$_3$), 1.13 (s, 21H, Sii-Pr$_3$), 5.60 (s, 1H, CH), 7.09 and 7.45 (AA′XX′, $2 \times$ apparent d, $J = 8.3$ Hz, 4H, H-trimethylsilylethynylphenyl), 7.12 and 7.50 (AA′XX′, $2 \times$ apparent d, $J = 8.3$ Hz, 4H, H-phenylene-CH in big "leg"), 7.15 and 7.61 (AA′XX′, $2 \times$ apparent d, $J = 8.2$ Hz, 4H, H-phenylene-CH in porphyrin "leg"), 7.46 (m, 4H, H-triisopropylsilylethynylphenyl), 7.51 (m, 4H, H-central phenylene), 7.73–7.80 (m, 9H, m- and p-H-phenyl), 7.92 (apparent d, $J = 8.2$ Hz, 2H, H-phenylene on porphyrin), 8.21–8.23 (m, 8H, o-H-phenyl and H-phenylene on porphyrin), 8.96 (m, 8H, β-H on porphyrin) ppm; FAB-MS: m/z (%) = 1420.9 (calc. avg. mass for $C_{97}H_{78}N_4Si_2Zn$: 1421.26).

[5-[4-[[4-[(4-Ethynylphenyl)-[4-[[4-[(4-ethynylphenyl)ethynyl]phenyl]ethynyl]phenyl]methyl]phenyl]ethynyl]-phenyl]-10,15,20-triphenylporphinato(2-)]zinc (14, $C_{85}H_{50}N_4Zn$)

Compound 14 was obtained in 85% yield (6.4 mg), as described for 4, from 8.9 mg 13 (6.3 μmol) for 8 min, after purification by CC (CHCl$_3$/n-hexane = 11/9). UV/VIS (CH$_2$Cl$_2$): λ_{max} (log ε) = 334 (4.79), 354 (4.62), 420 (5.62), 548 (4.19), 590 (3.47) nm (mol^{-1} dm^3 cm^{-1}); ^{1}H NMR (360.14 MHz, CDCl$_3$): $\delta = 3.09$ (s, 1H, C≡CH), 3.18 (s, 1H, C≡CH in big "leg"), 5.61 (s, 1H, CH), 7.12 and 7.48 (AA′XX′, $2 \times$ apparent d, $J = 8.3$ Hz, 4H, H-phenylene-CH), 7.13 and 7.50 (AA′XX′, $2 \times$ apparent d, $J = 8.3$ Hz, 4H, H-phenylene-CH), 7.16 and 7.62 (AA′XX′, $2 \times$ apparent d, $J = 8.3$ Hz, 4H, H-phenylene-CH in porphyrin "leg"), 7.48 (m, 4H, H-phenylene in big "leg"), 7.51 (m, 4H, H-central phenylene in big "leg"), 7.72–7.80 (m, 9H, m- and p-H-phenyl), 7.92 (apparent d, $J = 8.3$ Hz, 2H, H-phenylene on porphyrin), 8.20–8.23 (m, 8H, o-H-phenyl and H-phenylene on porphyrin), 8.96 (m, 8H, β-H on porphyrin) ppm; FAB-MS: m/z (%) = 1193.1 (calc. avg. mass for $C_{85}H_{50}N_4Zn$: 1192.74).

C₁-Symmetric Triporphyrin (**16**, $C_{205}H_{118}N_{12}Zn_3$)

Air was removed from a soln. of 11 mg **14** (9.2 μmol) and 28.4 mg [5-[4-[[4-[(4-iodophenyl)ethynyl]phenyl]ethynyl]-phenyl]-10,15,20-triphenylporphinato(2-)]zinc (**15**) [4] (28.2 μmol) in 6.4 cm³ *DMF/Et₃*N (5:1) by blowing Ar for 20 min. Then 2.08 mg Pd₂(*dba*)₃ (2.28 μmol) and 5.5 mg As*Ph₃* (18 μmol) were added, and deaeration was continued for 10 min. Thereafter, the mixture was heated at 40°C for 4 h. At that time, the same amount of Pd₂(*dba*)₃ and As*Ph₃* was again added and the stirring continued for 3 h. The solvent was removed under reduced pressure and the crude product was purified after two successive CC (CHCl₃/*n*-hexane: gradient from 1/1 to 3/1) to yield 4.8 mg (18%) **16**. UV/VIS (CH₂Cl₂): λ_{max} (log ε) = 354 (5.15), 420 (6.06), 548 (4.69), 586 (4.14) nm (mol⁻¹ dm³ cm⁻¹); ¹H NMR (500.13 MHz, CDCl₃): δ = 5.65 (*s*, 1H, CH), 7.18 and 7.54 (2 × AA′XX′, 4 × apparent *d*, *J* = 8.3 Hz, 8H, H-phenylene on central CH in medium and big "legs"), 7.20 and 7.65 (AA′XX′, 2 × apparent *d*, *J* = 8.0 Hz, 4H, H-phenylene on central CH in small "leg"), 7.52–7.57 (*m*, 16H, H-phenylene in medium and big "legs"), 7.61 and 7.68 (2 × AA′XX′, 4 × apparent *d*, *J* = 8.0 Hz, 8H, H-phenylene on porphyrin in medium and big "legs"), 7.73–7.81 (*m*, 27H, *m*- and *p*-H-phenyl), 7.94 (*m*, 6H, H-phenylene on porphyrin), 8.23 (*m*, 24H, *o*-H-phenyl and H-phenylene on porphyrin), 8.96 (*s*, 12H, β-H on porphyrin outside), 8.97 (*m*, 12H, β-H on porphyrin inside) ppm; ES⁺-MS (in CHCl₃/ HCOOH): m/z (%) = 1378.7 ([M − 3Zn + 8H]²⁺), 919.3 ([M − 3Zn + 9H]³⁺) (calc. avg. mass for $C_{205}H_{118}N_{12}Zn_3$: 2945.41).

Acknowledgements

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[6] The synthesis described in the Experimental Section yields tris(4-iodophenyl)methane in higher purity than the procedure reported in Ref. [9] in which direct iodination of triphenylmethane leads in fact to tris(4-iodophenyl)methanol as the major product and a mixture containing tris(4-iodophenyl)methane

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