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Synthesis of Nanometer-sized Homo- and Heteroorganometallic Tripodaphyrins

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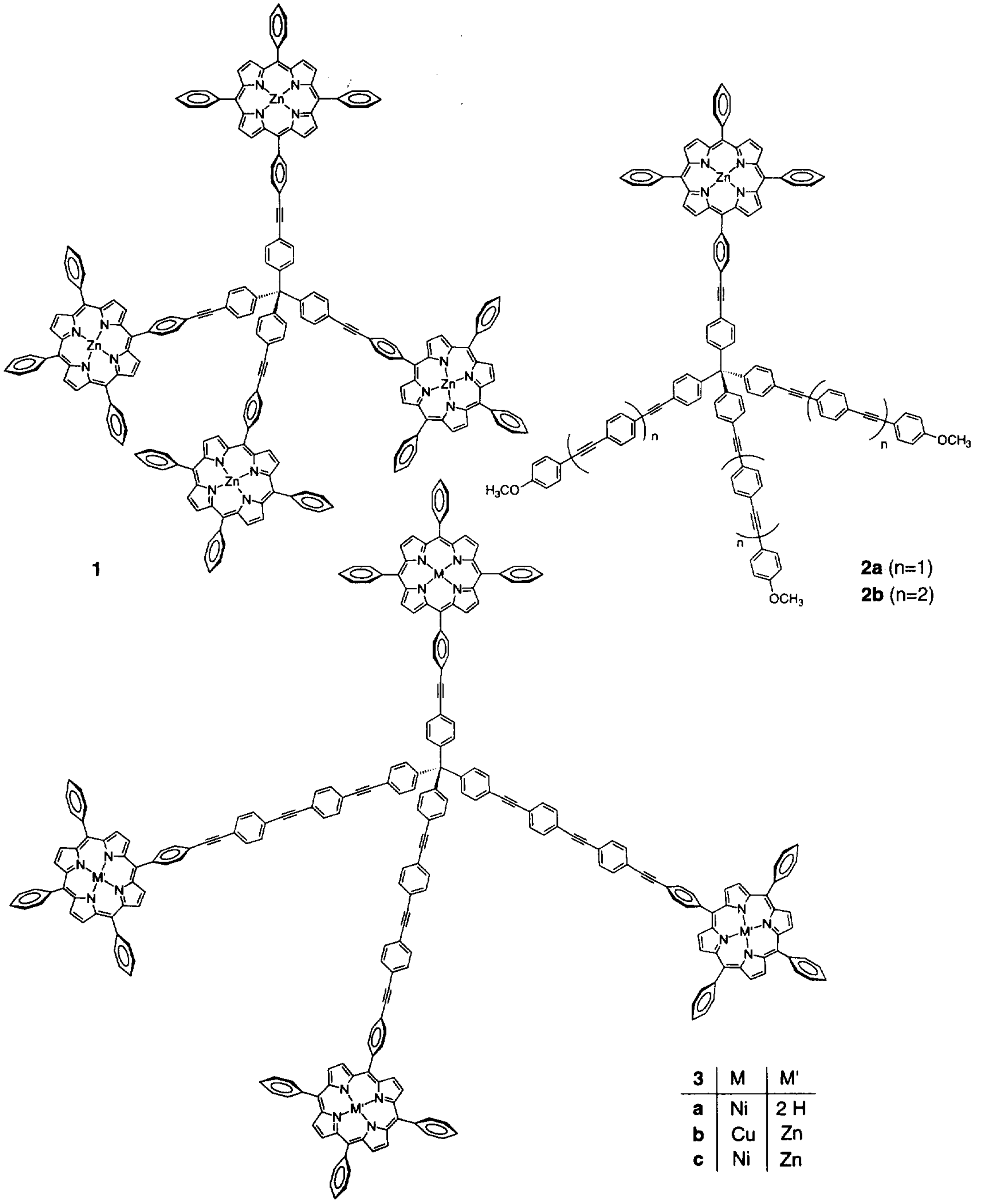
Abstract : Tripodaphyrins are tetrahedral or pyramidal assemblies in which a porphyrin macrocycle situated on the top of the molecule is "supported" by three "legs" consisting of linear arrays of covalently linked rigid constitutive elements. The edge-length at the "base" of the molecules which have been synthesized until now lies in the range from 3.2 to 6.5 nm. In some tripodaphyrins (**3a-c**) the chromophore situated on the top of the molecule differs on the complexed metal ion from the other three, which are located at the ends of the "legs". Owing to the dimensions of the molecules, no intramolecular interaction between the chromophores is observed, even in the presence of a paramagnetic Cu(II) chelate.

Introduction. Recently, we reported the synthesis of a new kind of porphyrin derivatives (named "tripodaphyrins"[1]) which owing to their molecular dimensions should be appropriate for nanofabrication experiments using commercially available scanning probe microscopes (SPM). The present work summarizes the experimental procedures used for the synthesis of these compounds. The different types of tripodaphyrins which have been synthesized hitherto in our laboratory are represented by formulae **1**, **2a,b**, and **3a-c**. In type **1**, the distance between the vertices of the tetrahedral molecule measure approximately 4.20 nm. Longer basal edge lengths have been attained with tripodaphyrins of types **2a,b** and **3a-c**, in which three "legs" of the molecules are elongated by means of phenylacetylene units. The longest distance between the vertices of the pyramidal (D_{3d}-symmetric) molecules thus obtained amounts to 6.52 nm in compounds **3a-c**. Moreover, derivative **3b** containing a paramagnetic metal ion has been synthesized as a probe for the lack of interaction between the porphyrin chromophores present in the same molecule.

Results. All tripodaphyrins described in the present work (Figure 1) have been synthesized from the same starting material, 5-(4-iodophenyl)-10,15,20-triphenylporphine (**4**), which was already known[2] (*cf.* Scheme 1). The strategy devised for the synthesis of tripodaphyrins is based on the use of tetrakis(4-iodophenyl) methane (**9a**)[3] as the core of the molecule. Substitution of ethynyl groups for all four iodine atoms is achieved on reaction of **9a** with trimethylsilylacetylene under Pd(II)-catalyzed conditions,[4] as outlined on Scheme 2 (on the *left*). Selective deprotection of only one ethynyl group is possible, thus yielding **9d**, which was used as starting material for the synthesis of tripodaphyrins **2a,b** and **3a-c** (Scheme 1). Tripodaphyrin **1**, on the other hand, was synthesized by Pd(0)-catalyzed reaction[5] of **9c** with the Zn(II) complex (**4a** in Scheme 1) of 5-(4-iodophenyl)-10,15,20-triphenylporphine (**4**). By the same procedure, **4a** as well as the corresponding Cu(II) and Ni(II) chelates (**4b** and **4c**, respectively) were treated with **9d** to yield, after cleavage of the trimethylsilyl protecting groups, **6a**-**c** (Scheme 1), which served as precursors of the pyramidal tripodaphyrins **2a**,**b** and **3a**-**c**. Elongation of the "legs" of the molecules was achieved using phenylacetylene units as spacers. Thus, 4-methoxyphenylacetylene (**10**)[6] was transformed into 1-iodo-4-[(4-methoxyphenyl)ethynyl]benzene (**11**) and 1-[(4-iodophenyl)ethynyl]-4-[(4-methoxyphenyl)ethynyl]benzene (**15**) as outlined in Scheme 2 (on the *right*).



1

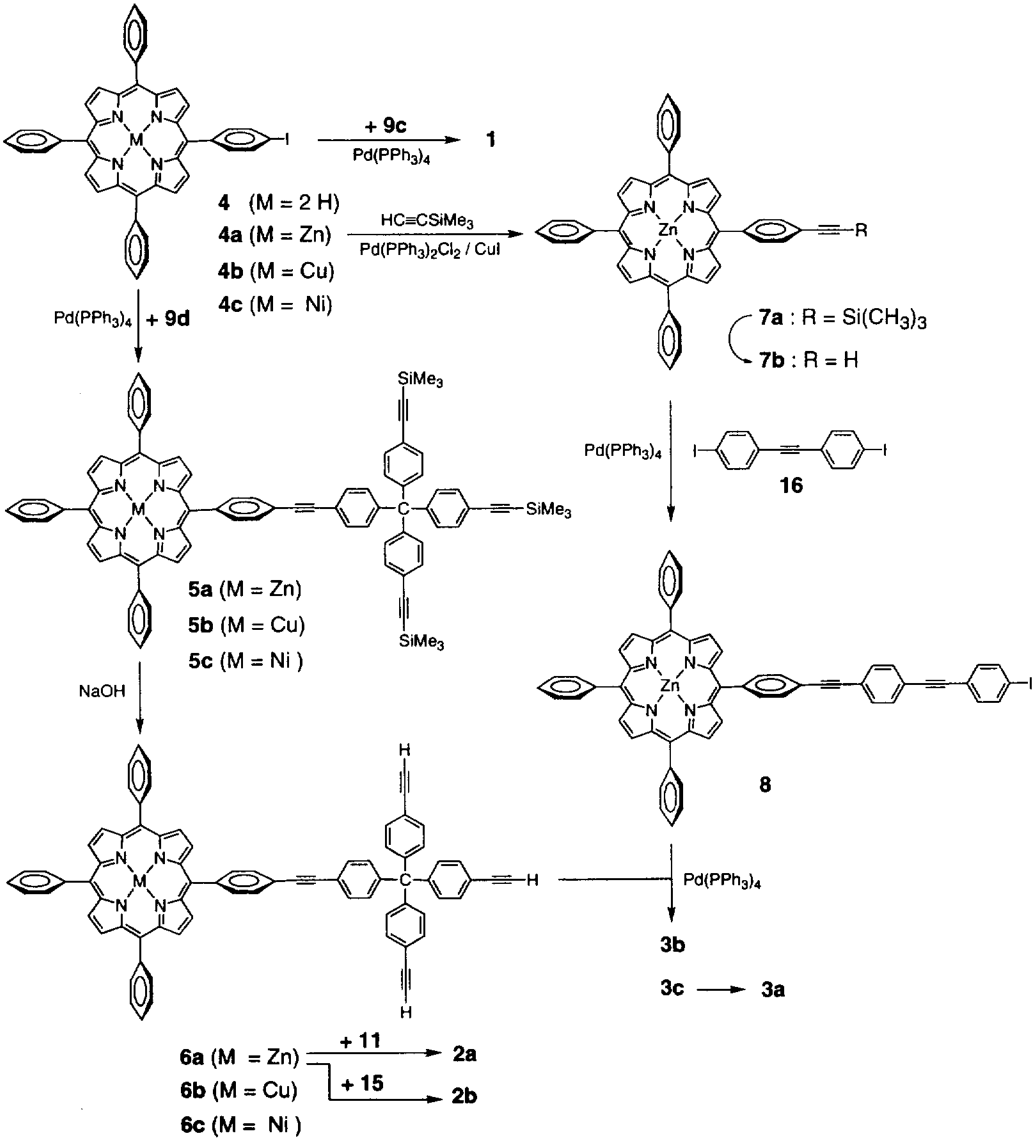
2a (n=1)
2b (n=2)

3	M	M'
a	Ni	2 H
b	Cu	Zn
c	Ni	Zn

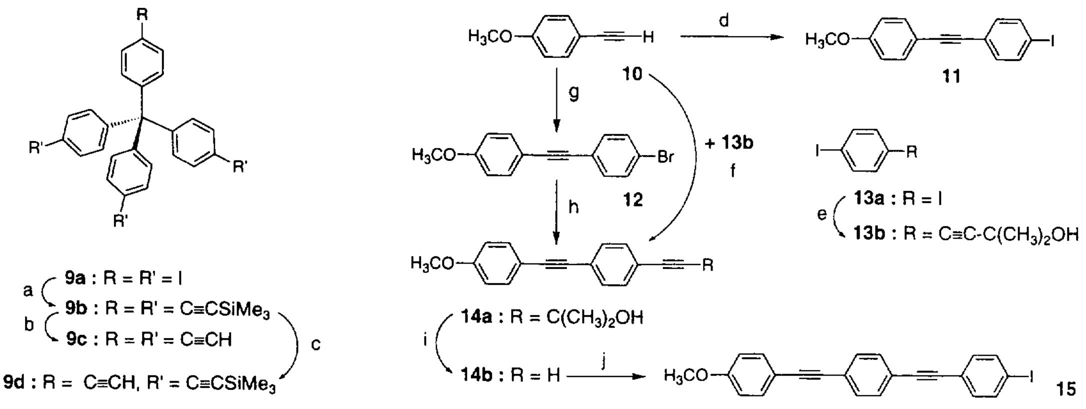
Figure 1. Tripodaphyrins synthesized from porphine derivative **4**.

As a precursor of **15**, **14a** was prepared by two alternative routes with essentially the same overall yield (*cf.* Experimental Section). Pd(0)-catalyzed reaction of **6a** with **11** or **15** afforded tripodaphyrins **2a** and **2b**, respectively (Scheme 1). On the other hand, 5-(4-ethynylphenyl)-10,15,20-triphenylporphine (**7b**) was treated with 4,4'-diiodotolane (**16**), which was synthesized from 4-iodoaniline as described in the Experimental Section,[7] to yield the zinc(II) porphyrin chelate **8**. Pd(0)-catalyzed reaction of the latter with **6b** and **6c** afforded tripodaphyrins **3b** and **3c**, respectively (*cf.* Scheme 1). As expected, the latter can be demetallated selectively by treatment with acid, yielding the corresponding monochelate **3a**.

Despite of their large molecular size, the tripodaphyrins described in the present work are fairly soluble in common aprotic organic solvents, such as dichloromethane, chloroform or benzene.



Scheme 1. Synthesis of tripodaphyrins (*cf.* Experimental Section)



Scheme 2. (*Left*) a) $HC{\equiv}CSiMe_3$, $Pd(PPh_3)_2Cl_2$, CuI, DMF/NEt_3, 35 °C, 15h (95%). b) 1N NaOH, THF, 20 °C, (93%). c) TBAF, $CHCl_3$ (30%). (*Right*) d) 1,4-diiodobenzene (3 eq.), $Pd(PPh_3)_4$, CuI in toluene / NEt_3, 40 °C, 15h (65%). e) 2-methyl-3-butyn-2-ol (0.9 eq.), same cat. and solv. as in d, 40 °C, 3h (63%). f) **13b**, same cat. and solv. as in d, 75 °C, 15h (95%). g) 1-bromo-4-iodobenzene (1 eq.), same cond. as in d (65%). h) 2-methyl-3-butyn-2-ol, same cat. and solv. as in d, 75 °C, 15h (97%). i) NaOH, toluene, reflux, 1.5h (91%). j) same cond. as in d, 3h (65%).

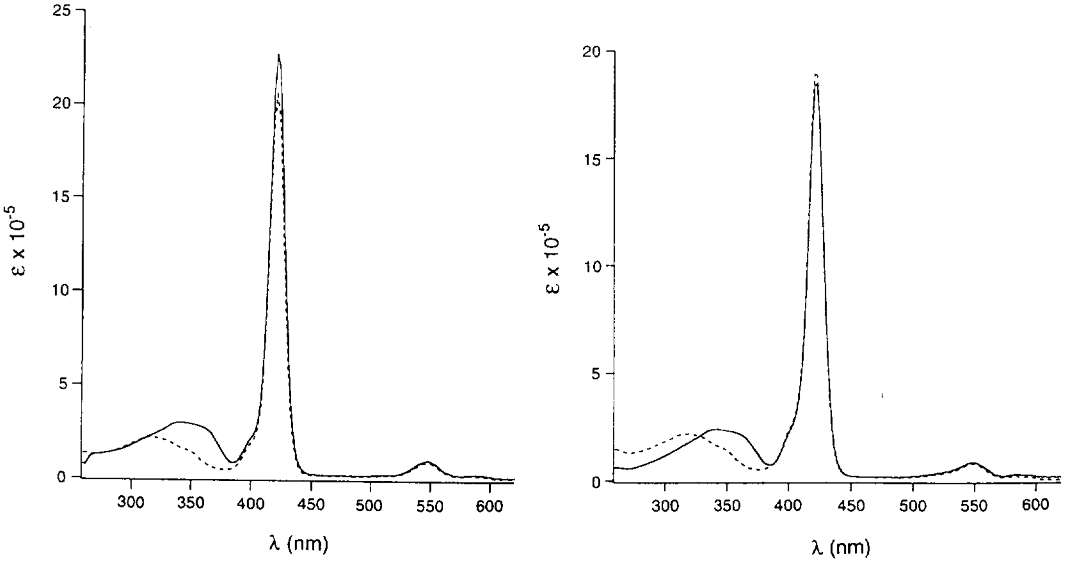


Figure 2. UV/VIS spectra in CH_2Cl_2 of **3b** and **3c** (———— on the left and right, respectively) and addition spectra, in a 1 : 3 ratio, of **6b** + **8** and **6c** + **8**, respectively (-------- on the left and right, respectively)

As in the case of tripodaphyrin **1**, reported earlier,[1] the UV/VIS spectra of **3a-c** are mainly a superposition of the spectra of the individual porphyrin components, except in the range of absorption of the phenylethynyl chromophores, in which a broad absorption maximum is shifted from 320 nm (in **8**) to 340 nm (in **3a-c**), probably due to the extension of π-electron delocalization in the "legs" of the latter (Figure 2). Interestingly, the quantum yields of fluorescence of tripodaphyrins **3b** and **3c** (Φ_f = 3.2 and 3.5%, respectively) are almost the same as that of (*meso*-tetraphenylporphinato) Zn(II).[8] Thus, although it is well known that paramagnetic Cu(II) porphyrins are d^9-metal chelates, the excited states of which are very short lived and non fluorescent,[9] intramolecular quenching of the fluorescence of the (porphinato)Zn(II) chromophores present in the same molecule does not take place neither *via* exciton coupling nor *via* electron transfer.[10] Actually, this result is not surprising, owing to the large separation between the chromophores (about 3.65 nm) and their mutual geometrical orientation. This is further confirmed by the ^1H NMR spectrum of the diamagnetic chelate **3c**, which is nearly the sum of the ^1H NMR spectra of its synthetic precursors **6c** and **8** (*cf.* Experimental Section).

EXPERIMENTAL

General. 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. Emission spectra: *Perkin-Elmer-MPF-4* fluorescence spectrophotometer. NMR: *Varian Gemini 200* (^1H: 200.00 MHz, ^{13}C: 50.30 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; FAB: in 2-nitrobenzyl alcohol with Ar at 8 kV. Tetraphenylmethane was purchased from *MTM Research Chemicals, Lancaster Synthesis Division* (F-67800 Bischheim); 1-bromo-4-iodobenzene, tetrakis(triphenylphosphine) palladium(0) and tetrabutylammonium fluoride (TBAF) from *Aldrich Chemie* (CH-9471 Buchs); 1,4-diiodobenzene, 4-iodoaniline, dimethylformamide (DMF), trifluoroacetic acid (TFA), tetrahydrofuran (THF), and other reagents from *Fluka Chemie AG* (CH-9471 Buchs).

Tripodaphyrin 1. *Method A*: air was removed from a soln. of **4a** (80 mg, 99 μmol) and **9c** (10 mg, 24 μmol) in 20 mL of DMF / NEt_3 (5:1) by blowing argon for 20 min. Then $Pd(PPh_3)_4$ (11 mg, 9.6 μmol) was added, and deaeration was continued for 10 min. Thereafter the mixture was heated at 40 °C for 15h. The solvent was removed under reduced pressure and the crude product was purified by CC ($CHCl_3$ / hexane 7:3) to yield 43.8 mg (58%) of **1**. *Method B*: the same product was obtained under the same conditions as in *Method A* by reaction of **9a** (13 mg, 16 μmol) with **7b** (67 mg, 95 μmol) in the presence of $Pd(PPh_3)_4$ (7.5 mg, 6.5 μmol), in 15 mL of DMF / NEt_3 (5:1). By this method 44.1 mg (89%) of **1** were obtained. UV/VIS (CH_2Cl_2) 300 (5.28), 422 (6.33), 548 (5.10), 588 (4.49); UV/VIS (benzene) : 300 (5.15), 426 (6.26), 550 (4.93), 590 (4.34). Φ_f = 0.04 relative to Zn(II) *meso*-tetraphenylporphine (Φ_f = 0.033 in benzene[8]). ^1H NMR (500.13 MHz) δ 7.47 and 7.73 (2 × apparent *d*, J = 8.4, 16H, H-phenylene on central C), 7.73-7.79 (*m*, 36H, m- and p-H-phenyl), 7.98 and 8.26 (2 × apparent *d*, J = 8.2, 16H, H-phenylene on porphine), 8.21-8.25 (*m*, 24H, o-H-phenyl), 8.96 (*s*, 16H, β-H on porphine), 8.98 and 9.00 (2 × *d*, J = 4.7, 16H, β-H on porphine). MALDI-MS: 3120.3 (calc. avg. mass for $C_{209}H_{124}N_{16}Zn_4$: 3120.91), 2344.5 (calc. for $M^+-C_{52}H_{31}N_4Zn$: 2343.7), 776.6 (calc. for $[C_{52}H_{31}N_4Zn]^+$: 777.22). ES$^+$-MS (in HCO_2H) : 1434 ($[MH_2]^{2+}$), 957 ($[MH_3]^{3+}$), 718 ($[MH_4]^{4+}$), 574 ($[MH_5]^{5+}$) (calc. for $C_{209}H_{132}N_{16}$: 2867).

Tripodaphyrin 2a. Air was removed from a soln. of **6a** (20.1 mg, 18.4 μmol) and **11** (19 mg, 57 μmol) in 7 mL of DMF / NEt_3 (5:1) by blowing argon for 20 min. Then $Pd(PPh_3)_4$ (8 mg, 6.9 μmol) was added, and deaeration was continued for 10 min. Thereafter the mixture was heated at 45 °C for 20h. The solvent was removed under reduced pressure and the residue was purified by CC ($CHCl_3$ / hexane 65:35) to yield 27.8 mg (88%) of **2a**. UV/VIS (CH_2Cl_2) : 334 (5.33), 421 (5.71), 548 (4.40), 590 (3.88). ^{1}H NMR (200.00 MHz) δ 3.83 (*s*, 9H, OCH_3), 6.89 and 7.48 (2 × apparent *d*, *J* = 8.7, 12H, H-phenylene-OCH_3), 7.29 (6H), 7.31 (2H), 7.51 (6H), and 7.63 (2H) (4 × apparent *d*, *J* = 8.4, H-phenylene on central C), 7.50 (*s*, 12H, H-phenylene in the "legs"), 7.73-7.80 (*m*, 9H, m- and p-H-phenyl), 7.93 (apparent *d*, *J* = 8.1, 2H, H-phenylene on porphine), 8.20-8.26 (*m*, 8H, o-H-phenyl and H-phenylene on porphine), 8.96 and 8.98 (2 × *s*, 2 × 4H, β-H on porphine). FAB-MS: 1711.6 (calc. avg. mass for $C_{122}H_{76}N_4O_3Zn$: 1711.36).

Tripodaphyrin 2b. As described for **2a**, from **6a** (21 mg, 19.2 μmol) and **15** (26 mg, 59.9 μmol). The crude product was purified by two successive CC ($CHCl_3$ / hexane 65:35) to yield 32.4 mg (84%) of **2b**. UV/VIS (CH_2Cl_2) : 346 (5.44), 421 (5.72), 548 (4.39), 590 (3.91). ^{1}H NMR (500.13 MHz) δ 3.83 (*s*, 9H, OCH_3), 6.89 and 7.47 (2 × apparent *d*, *J* = 8.9, 12H, H-phenylene-OCH_3), 7.28 (6H), 7.30 (2H), 7.50 (6H), and 7.62 (2H) (4 × apparent *d*, *J* = 8.6, H-phenylene on central C), 7.50 and 7.52 (2 × *s*, 2 × 12H, H-phenylene in the "legs"), 7.73-7.80 (*m*, 9H, m- and p-H-phenyl), 7.92 (apparent *d*, *J* = 8.3, 2H, H-phenylene on porphine), 8.20-8.24 (*m*, 8H, o-H-phenyl and H-phenylene on porphine), 8.95 and 8.97 (2 × *s*, 2 × 4H, β-H on porphine). FAB-MS: 2013.0 (calc. avg. mass for $C_{146}H_{88}N_4O_3Zn$: 2011.72).

Tripodaphyrin 3a. To a soln. of **3c** (10 mg, 2.7 μmol) in $CHCl_3$ (7.5 mL) was added TFA (2.5 mL) and the mixture was stirred at 20 °C for 4 h. Then the mixture was poured in sat. aq. Na_2CO_3 and the organic layer was separated, washed with water and dried (Na_2SO_4) before the solvent was evaporated. The residue was purified by CC ($CHCl_3$ / hexane 3:1) to yield 8.6 mg (90%) of **3a**. UV/VIS (CH_2Cl_2) : 342 (5.40), 419 (6.21), 452 (4.77), 516 (4.84), 550 (4.58), 592 (4.32), 648 (4.25). ^{1}H NMR (500.13 MHz) δ – 2.77 (*s*, 6H, NH), 7.29 (6H), 7.31 (2H), 7.53 (6H), and 7.61 (2H) (4 × apparent *d*, *J* = 8.4, H-phenylene on central C), 7.56 (*s*, 12H, H-phenylene in the "legs"), 7.61 and 7.68 (2 × apparent *d*, *J* = 8.3, 12H, H-phenylene in the "legs"), 7.65-7.71 (*m*, 9H, m- and p-H-phenyl on NiTPP), 7.72-7.79 (*m*, 27H, m- and p-H-phenyl on H_2TPP), 7.86 and 8.02 (2 × apparent *d*, *J* = 8.3, 4H, H-phenylene on NiTPP), 7.94 and 8.23 (2 × apparent *d*, *J* = 8.2, 12H, H-phenylene on H_2TPP), 8.00-8.04 (*m*, 6H, o-H-phenyl on NiTPP), 8.20-8.25 (*m*, 18H, o-H-phenyl on H_2TPP), 8.75 (s, 4H, β-H on NiTPP), 8.76 and 8.77 (2 × *d*, *J* = 5.1, 4H, β-H on NiTPP), 8.85 (*s*, 12H, β-H on H_2TPP), 8.86 and 8.88 (2 × *d*, *J* = 4.7, 12H, β-H on H_2TPP). MALDI-MS: 3523.3 (calc. avg. mass for $C_{257}H_{154}N_{16}Ni$: 3524.91).

Tripodaphyrin 3b. As described for **2a**, from **6b** (10 mg, 9.2 μmol) and **8** (29 mg, 28.9 μmol) in 11 mL of DMF / NEt_3 (5:1). The crude product was purified by two successive CC ($CHCl_3$ / hexane: gradient from 1:1 to 3:1) to yield 24.4 mg (72%) of **3b**. UV/VIS (CH_2Cl_2) : 340 (5.48), 420 (6.36), 547 (5.01), 588 (4.46); UV/VIS (benzene) : 340 (5.38), 424 (6.25), 549 (4.93), 589 (4.36). Φ_f = 0.032 referred to Zn(II) *meso*-tetraphenylporphine (Φ_f = 0.033 in benzene[8]). ^{1}H NMR (500.13 MHz) δ 7.29 and 7.52 (2 × apparent *d*, *J* = 8.3, 16H, H-phenylene on central C), 7.56 (*s*, 12H, H-phenylene in the "legs"), 7.61 and 7.68 (2 × apparent *d*, *J* = 8.3, 12H, H-phenylene in the "legs"), 7.73-7.80 (*m*, 27H, m- and p-H-phenyl on ZnTPP), 7.94 and 8.23 (2 × apparent *d*, *J* = 8.1, 12H, H-phenylene on ZnTPP), 8.21-8.25 (*m*, 18H, o-H-phenyl on ZnTPP), 8.96 (*s*, 12H, β-H on ZnTPP), 8.97 and 8.98 (2 × *d*, *J* = 4.7 Hz, 12H, β-H on ZnTPP); signals for H-phenyl, H-phenylene and β-H on CuTPP are either very broad or unperceptible. MALDI-MS: 3720.4 (calc. avg. mass for $C_{257}H_{148}CuN_{16}Zn_3$: 3719.80). ES$^+$-MS : 3719.9. FAB-MS : 3719.8. Atomic absorption spectrum: Zn / Cu = 3.1 ± 0.2.

Tripodaphyrin 3c. As described for **2a**, from **6c** (9.9 mg, 9.1 μmol) and **8** (28 mg, 27.9 μmol) in 9 mL of DMF / NEt_3 (5:1). The crude product was purified by two successive CC using gradient elution with $CHCl_3$ / hexane from 1:1 to 3:1 to yield 24.1 mg (71%) of **3c**. UV/VIS (CH_2Cl_2) : 340 (5.38), 421 (6.27), 548 (4.95), 588 (4.52); UV/VIS (benzene) : 338 (5.33), 425 (6.14), 550 (4.82), 590 nm (4.25). Φ_f = 0.035 referred to Zn(II) *meso*-tetraphenylporphine (Φ_f = 0.033 in benzene[8]). ^{1}H NMR (500.13 MHz) δ 7.29 (6H), 7.31 (2H),7.52 (6H), and 7.61 (2H) (4 × apparent *d*, *J* = 8.4, H-phenylene on central C), 7.56 (*s*, 12H, H-phenylene in the "legs"), 7.60 and 7.67 (2 × apparent *d*, *J* = 8.2, 12H, H-phenylene in the "legs"), 7.65-7.72 (9H) and 7.73-7.81 (27H) (2 × *m*, m- and p-H-phenyl on NiTPP and ZnTPP, respectively), 7.86 and 8.02 (2 × apparent *d*, *J* = 8.3, 4H, H-phenylene on NiTPP), 7.94 and 8.23 (2 × apparent *d*, *J* = 8.2, 12H, H-phenylene on ZnTPP), 8.00-8.04 (6H) and 8.21-8.25 (18H) (2 × *m*, o-H-phenyl on NiTPP and ZnTPP, respectively), 8.75 (4H) and 8.95 (12H) (2 × *s*, β-H on NiTPP and ZnTPP, respectively), 8.76 and 8.77 (2 × *d*, *J* = 5.0, 4H, β-H on NiTPP), 8.96 and 8.98 (2 × *d*, *J* = 4.7, 12H, β-H on ZnTPP). MALDI-MS: 3715.0 (calc. avg. mass for $C_{257}H_{148}N_{16}NiZn_3$: 3714.97). ES$^+$-MS : 3714.3. FAB-MS : 3715.5. Atomic absorption spectrum: Zn / Ni = 3.0 ± 0.2.

[5-(4-Iodophenyl)-10,15,20-triphenylporphinato(2-)]zinc(II) (4a). To a soln. of **4**[2] (0.222 g, 0.3 mmol) in 30 mL of $CHCl_3$ / MeOH (9:1) zinc acetate dihydrate (1.19 g, 5.4 mmol) was added, and the mixture was refluxed for 1 h. Thereafter the mixture was washed with water (3 × 15 mL), dried (Na_2SO_4) and the solvent was evaporated. The residue was purified by CC ($CHCl_3$ / hexane 7:3) to yield 0.237 g (98%) of **4a**. UV/VIS (CH_2Cl_2) 420 (5.70), 548 (4.36), 586 (3.88). ^{1}H NMR (200.00 MHz) δ 7.74-7.80 (*m*, 9H, m-H and p-H-phenyl), 7.97 and 8.11 (2 × apparent *d*, *J* = 8.4, 4H, H-phenylene), 8.20-8.25 (*m*, 6H, o-H-phenyl), 8.94 and 8.97 (2 × *d*, *J* = 4.7, 4H, β-H), 8.96 (*s*, 4H, β-H). FAB-MS : 804.1 (calc. avg. mass for $C_{44}H_{27}IN_4Zn$: 804.01).

[5-(4-Iodophenyl)-10,15,20-triphenylporphinato(2-)]Cu(II) (4b) was obtained in 98% yield (0.108 g), as described for **4a**, from **4** (0.102 g, 0.138 mmol) in 14 mL of $CHCl_3$ / AcOH (9:1) and copper acetate monohydrate (0.49 g, 2.45 mmol) after purification by CC ($CHCl_3$ / hexane 35:65). UV/VIS (CH_2Cl_2) 415 (5.70), 502 (3.61), 538 (4.33), 574 (3.47). FAB-MS : 802.4 (calc. avg. mass for $C_{44}H_{27}CuIN_4$: 802.18). HRMS calc. for $^{12}C_{44}{}^{1}H_{27}{}^{63}Cu^{127}I^{14}N_4$: 801.0576; found: 801.0560.

[5-(4-Iodophenyl)-10,15,20-triphenylporphinato(2–)]Ni(II) (4c) was obtained in 99% yield 0.129 g), as described for **4a**, from **4** (0.12 g, 0.162 mmol) in 16 mL of $CHCl_3$ / AcOH (9:1) and nickel acetate tetrahydrate (0.73 g, 2.92 mmol) after purification by CC ($CHCl_3$ / hexane 35:65). UV/VIS (CH_2Cl_2) 414 (5.41), 527 (4.24). ^{1}H NMR (200.00 MHz) δ 7.63-7.74 (*m*, 9H, m-H and p-H-phenyl), 7.76 (apparent *d*, *J* = 8.4, 2H, H-phenylene), 7.98-8.05 (*m*, 8H, H-phenylene and o-H-phenyl), 8.72 and 8.76 (2 × *d*, *J* = 4.9, 4H, β-H), 8.75 (*s*, 4H, β-H). FAB-MS : 797.5 (calc. avg. mass for $C_{44}H_{27}IN_4Ni$: 797.35).

[10,15,20-Triphenyl-5-[4-[[4-[tris[4-[(trimethylsilyl)ethynyl]phenyl]methyl]phenyl]ethynyl]phenyl]porphinato(2–)]Zn(II) (5a). Air was removed from a soln. of **4a** (35 mg, 43.5 μmol) and **9d** (28 mg, 44 μmol) in 10 mL of DMF / NEt_3 (5:1) by blowing argon for 20 min. Then $Pd(PPh_3)_4$ (17 mg, 0.015 mmol) was added, and deaeration was continued for 10 min. Thereafter the mixture was heated at 40 °C for 15h. The solvent was removed under reduced pressure and the crude product was purified by CC ($CHCl_3$ / hexane 1:4, then 1:1) to yield 45.8 mg (80%) of **5a**. UV/VIS (CH_2Cl_2) 272 (4.97), 421 (5.72), 548 (4.37), 588 (3.79). ^{1}H NMR (200.00 MHz) δ 0.26 (*s*, 27H, $SiMe_3$), 7.15 and 7.41 (2 × apparent *d*, *J* = 8.6, 12H, H-phenylene(ethynyl)Si), 7.20 and 7.57 (2 × apparent *d*, *J* = 8.6, 4H, H-phenylene on quat. C), 7.73-7.80 (*m*, 9H, m-H and p-H-phenyl), 7.92 (apparent *d*, *J* = 8.3, 2H, H-phenylene on porphine), 8.20-8.26 (*m*, 8H, o-H-phenyl and H-phenylene on porphine), 8.96 and 8.98 (2 × *s*, 2 × 4H, β-H on porphine). FAB-MS : 1310.0 (calc. avg. mass for $C_{86}H_{70}N_4Si_3Zn$: 1309.17).

[10,15,20-Triphenyl-5-[4-[[4-[tris[4-[(trimethylsilyl)ethynyl]phenyl]methyl]phenyl]ethynyl]phenyl]porphinato(2–)]Cu(II) (5b). As described for **5a**, from **4b** (30 mg, 37 μmol) and **9d** (24 mg, 38 μmol) in 8 mL of DMF / NEt_3 (5:1); CC ($CHCl_3$ / hexane 1:4 then 3:7): 31.7 mg (65%) of **5b**. UV/VIS

(CH_2Cl_2) 272 (5.04), 416 (5.74), 502 (3.75), 539 (4.41), 574 (3.68). ^{1}H NMR (CD_2Cl_2, 500.13 MHz) δ 0.24 (*s*, 27H, $SiMe_3$), 7.15 and 7.37 (2 × apparent *d*, *J* = 8.4, 12H, H-phenylene(ethynyl)Si), 7.20 (apparent *d*, *J* =7.9, 2H, H-phenylene on quat. C), 7.53 (br *m*, 13H, m- and p-H-phenyl, and H-phenylene on porphine); signals for β-H and o-H phenyl on porphine are either very broad or unperceptible. FAB-MS : 1307.08 (calc. avg. mass for $C_{86}H_{70}CuN_4Si_3$: 1307.34).

[10,15,20-Triphenyl-5-[4-[[4-[tris[4-[(trimethylsilyl)ethynyl]phenyl]methyl]phenyl]ethynyl]phenyl]porphinato(2–)]Ni(II) (5c). As described for **5a**, from **4c** (45 mg, 56 μmol) and **9d** (37 mg, 58 μmol) in 10 mL of DMF / NEt_3 (5:1); CC ($CHCl_3$ / hexane 1:3): 53.9 mg (73%) of **5c**. UV/VIS (CH_2Cl_2) 272 (5.05), 416 (5.45), 528 (4.38). ^{1}H NMR (200.00 MHz) δ 0.26 (*s*, 27H, $SiMe_3$), 7.13 and 7.40 (2 × apparent *d*, *J* = 8.5, 12H, H-phenylene(ethynyl)Si), 7.18 and 7.53 (2 × apparent *d*, *J* = 8.6, 4H, H-phenylene on quat. C), 7.64-7.73 (*m*, 9H, m- and p-H-phenyl), 7.84 (apparent *d*, *J* = 8.4, 2H, H-phenylene on porphine), 7.98-8.05 (*m*, 8H, o-H-phenyl and H-phenylene on porphine), 8.75 and 8.76 (2 × *s*, 2 × 4H, β-H on porphine). FAB-MS : 1303.2 (calc. avg. mass for $C_{86}H_{70}N_4NiSi_3$: 1302.51).

[10,15,20-Triphenyl-5-[4-[[4-[tris(4-ethynylphenyl)methyl]phenyl]ethynyl]phenyl]porphinato(2–)]Zn(II) (6a). To a soln. of **5a** (28 mg, 21.4 μmol) in THF (5 mL) was added aq. NaOH (1N, 4 mL) and the mixture was vigorously stirred at 20 °C for 3h. THF was evaporated and CH_2Cl_2 (10 mL) was added. The organic layer was separated, washed with water and dried (Na_2SO_4). The residue obtained after removal of the solvent was purified by CC ($CHCl_3$ / hexane 55:45): 23.3 mg (99%) of **6a**. UV/VIS (CH_2Cl_2) 421 (5.75), 549 (4.39), 588 (3.88). ^{1}H NMR (200.00 MHz) δ 3.10 (*s*, 3H, C≡CH), 7.21 and 7.46 (2 × apparent *d*, *J* = 8.4, 12H, H-phenylene-C≡CH), 7.21 and 7.60 (2 × apparent *d*, *J* = 8.4, 4H, H-phenylene on quat. C), 7.73-7.80 (*m*, 9H, m- and p-H-phenyl), 7.92 (apparent *d*, *J* = 8.0, 2H, H-phenylene on porphine), 8.20-8.26 (*m*, 8H, o-H-phenyl and H-phenylene on porphine), 8.97 and 8.98 (2 × *s*, 2 × 4H, β-H on porphine). FAB-MS: 1093.4 (calc. avg. mass for $C_{77}H_{46}N_4Zn$: 1092.62).

[10,15,20-Triphenyl-5-[4-[[4-[tris(4-ethynylphenyl)methyl]phenyl]ethynyl]phenyl]porphinato(2–)]Cu(II) (6b) was obtained in 98% yield (18.2 mg), as described for **6a**, from **5b** (22.2 mg, 17 μmol), after purification by CC ($CHCl_3$ / hexane 35:65). UV/VIS (CH_2Cl_2) 416 (5.74), 502 (3.59), 539 (4.37), 574 (3.61). ^{1}H NMR (500.13 MHz) δ 3.08 (*s*, 3H, C≡CH), 7.17 and 7.43 (2 × apparent *d*, *J* = 8.4, 12H, H-phenylene-C≡CH), 7.20 (apparent *d*, *J* = 8.2, 2H, H-phenylene on quat. C), 7.52 (br *m*, 13H, m- and p-H-phenyl, and H-phenylene on porphine); signals for o-H-phenyl and β-H on porphine are either very broad or unperceptible. FAB-MS : 1091.7 (calc. avg. mass for $C_{77}H_{46}CuN_4$: 1090.79).

[10,15,20-Triphenyl-5-[4-[[4-[tris(4-ethynylphenyl)methyl]phenyl]ethynyl]phenyl]porphinato(2–)]Ni(II) (6c) was obtained in 97% yield (42.6 mg), as described for **6a**, from **5c** (52.5 mg, 40.3 μmol) after purification by CC ($CHCl_3$ / hexane 2:3 then 1:1). UV/VIS (CH_2Cl_2) 416 (5.45), 528 (4.32). ^{1}H NMR (500.13 MHz) δ 3.08 (*s*, 3H, C≡CH), 7.18 and 7.43 (2 × apparent *d*, *J* = 8.7, 12H, H-phenylene-C≡CH), 7.22 and 7.55 (2 × apparent *d*, *J* = 8.6, 4H, H-phenylene on quat. C), 7.65-7.73 (*m*, 9H, m- and p-H-phenyl), 7.83 (apparent *d*, *J* = 8.4, 2H, H-phenylene on porphine), 7.98-8.03 (*m*, 8H, o-H-phenyl and H-phenylene on porphine), 8.74 and 8.76 (2 × *d*, *J* = 4.9, 4H, β-H on porphine), 8.75 (*s*, 4H, β-H on porphine). FAB-MS : 1087.1 (calc. avg. mass for $C_{77}H_{46}N_4Ni$: 1085.96).

[5-[4-(Trimethylsilylethynyl)phenyl]-10,15,20-triphenylporphinato]Zn(II) (7a). Air was removed by argon from a suspension of **4a** (0.18 g, 0.224 mmol) in 30 mL of DMF / NEt_3 (9:1). Then CuI (0.085 g, 0.045 mmol), $Pd(PPh_3)_2Cl_2$ (0.016 g, 0.023 mmol) and ethynyltrimethylsilane (95 μL, 0.672 mmol) were added, and the mixture was stirred at 35 °C for 15 h. The solvent was removed under reduced pressure and the residue was purified by CC ($CHCl_3$ / hexane 1:1) to yield 0.162 g (93%) of **7a**. UV/VIS (CH_2Cl_2) 420

(5.73), 548 (4.33), 586 (3.64). ^{1}H NMR (200.00 MHz) δ 0.39 (*s*, 9H, SiMe$_3$), 7.74-7.79 (*m*, 9H, m- and p-H-phenyl), 7.88 and 8.18 (2 × apparent *d*, *J* = 8.4, 4H, H-phenylene), 8.20-8.25 (*m*, 6H, o-H-phenyl), 8.92 and 8.97 (2 × *d*, *J* = 4.6, 4H, β-H), 8.96 (*s*, 4H, β-H). FAB-MS : 774.2 (calc. avg. mass for $C_{49}H_{36}N_4SiZn$: 774.32).

[5-(4-Ethynylphenyl)-10,15,20-triphenylporphinato]Zn(II) (7b). To a solution of **7a** (0.15 g, 0.194 mmol) in THF (15 mL), 10 mL of aq. NaOH (0.5 N) were added and the mixture was stirred vigorously at 20 °C for 2h. After evaporation of the THF, CH_2Cl_2 (30 mL) was added and the organic layer was separated. The aq. layer was extracted with CH_2Cl_2 and the combined org. phases were dried (Na_2SO_4). Pure **7b** (0.126 g, 92%) was obtained after removal of the solvent and purification of the residue by CC using gradient elution with $CHCl_3$ / hexane from 1:1 to 7:3. UV/VIS (CH_2Cl_2) 420 (5.71), 548 (4.32), 586 (3.63). ^{1}H NMR (200.00 MHz) δ 3.32 (*s*, 1H, C≡CH), 7.73-7.81 (*m*, 9H, m- and p-H-phenyl), 7.90 and 8.20 (2 × apparent *d*, *J* = 8.2, 4H, H-phenylene), 8.20-8.25 (*m*, 6H, o-H-phenyl), 8.93 and 8.97 (2 × *d*, *J* = 4.7, 4H, β-H), 8.96 (*s*, 4H, β-H). FAB-MS : 702.1 (calc. avg. mass for $C_{46}H_{28}N_4Zn$: 702.13).

[5-[4-[[4-[(4-Iodophenyl)ethynyl]phenyl]ethynyl]phenyl]-10,15,20-triphenylporphinato(2–)] Zn(II) (8). Air was removed from a soln. of **7b** (71 mg, 0.1 mmol) and **16** (130 mg, 0.3 mmol) in 18 mL of DMF / NEt_3 (5:1) blowing argon for 20 min. Then $Pd(PPh_3)_4$ (17 mg, 0.015 mmol) was added, and the argon stream was maintained for 10 min before the mixture was heated at 40 °C for 15h. The solvent was removed under reduced pressure and the residue was purified by CC using gradient elution with $CHCl_3$ / hexane from 3:7 to 1:1 to yield 72.4 mg (71%) of **8**. UV/VIS (CH_2Cl_2) 320 (4.81), 421 (5.75), 548 (4.40), 588 (3.84). ^{1}H NMR (500.13 MHz) δ 7.29 and 7.72 (2 × apparent *d*, *J* = 8.2, 4H, H-phenylene-I), 7.58 and 7.66 (2 × apparent *d*, *J* = 8.1, 4H, H-phenylene), 7.73-7.80 (*m*, 9H, m- and p-H-phenyl), 7.93 (apparent *d*, *J* = 8.0, 2H, H-phenylene on porphine), 8.21-8.24 (*m*, 8H, o-H-phenyl and H-phenylene on porphine), 8.95 (*s*, 4H, β-H on porphine), 8.96 and 8.98 (2 × *d*, *J* = 4.7, 4H, β-H on porphine). FAB-MS : 1005.3 (calc. avg. mass for $C_{60}H_{35}IN_4Zn$: 1004.25).

Tetrakis[4-(trimethylsilylethynyl)phenyl]methane (9b). Air was removed by argon from a suspension of **9a**^{3} (0.45 g, 0.55 mmol) in 80 mL of DMF / NEt_3 (9:1). Then CuI (0.021 g, 0.11 mmol), $Pd(PPh_3)_2Cl_2$ (0.077 g, 0.11 mmol) and ethynyltrimethylsilane (0.78 mL, 5.5 mmol) were added, and the mixture was stirred at 35 °C for 15 h. The solvent was removed under reduced pressure and the residue was purified by CC (CH_2Cl_2 / hexane 1:9) to yield 0.367 g (95%) of **9b**, mp 347-349 °C. ^{1}H NMR (200.00 MHz) δ 0.23 (*s*, 36H, SiMe$_3$), 7.04 (AA'BB', apparent *d*, *J* = 8.5, 8H, H-2), 7.33 (AA'BB', apparent *d*, *J* = 8.5, 8H, H-3); ^{13}C NMR (50.30 MHz) δ -0.1 (SiMe$_3$), 64.8 (central C), 94.8 (C≡*C*-SiMe$_3$), 104.7 (*C*≡C-SiMe$_3$), 121.3 (C-4), 130.7 and 131.4 (C-2 and C-3), 146.0 (C-1). Anal. Calcd for $C_{45}H_{52}Si_4$ (705.26): C, 76.64; H, 7.43. Found: C, 76.36; H, 7.62. FAB-MS: 705 (M$^+$).

Tetrakis(4-ethynylphenyl)methane (9c). To a soln. of **9b** (0.270 g, 0.383 mmol) in THF (35 mL) 15 mL of aq. NaOH (1N) were added and the mixture was stirred vigorously at 20 °C for 2h. After evaporation of the THF, CH_2Cl_2 (30 mL) was added and the organic layer was separated. The aq. layer was extracted with CH_2Cl_2 and the combined org. phases were dried (Na_2SO_4). The residue obtained after removal of the solvent was purified by CC (CH_2Cl_2 / hexane 1:9) to yield 0.149 g (93%) of **9c**, mp >360 °C. ^{1}H NMR (200.00 MHz) δ 3.06 (*s*, 4H, C≡CH), 7.12 (apparent *d*, *J* = 8.6, 8H, H-2), 7.39 (apparent *d*, *J* = 8.6, 8H, H-3); ^{13}C NMR (50.30 MHz) δ 64.9 (central C), 77.6 (C≡*C*H), 83.2 (*C*≡CH), 120.4 (C-4), 130.8 and 131.7 (C-2 and C-3), 146.2 (C-1). Anal. Calcd for $C_{33}H_{20}$ (416.53): C, 95.16; H, 4.84. Found: C, 94.94; H, 5.10. EI-MS: 416 (M$^+$, 21%), 315 ([M-$C_6H_4C_2H$]$^+$, 64%), 213 (89%), 101 ([$C_6H_4C_2H$]$^+$, 53%), 75 (100%).

(4-Ethynylphenyl)-tris[4-(trimethylsilylethynyl)phenyl]methane (9d). To a soln. of **9b** (0.24 g, 0.34 mmol) in dry $CHCl_3$ (150 mL), TBAF (1M in THF, 0.17 mL) was added, and the mixture was refluxed for 15 min. The oily residue obtained after evaporation of the solvent was subjected to CC (CH_2Cl_2 / hexane 4 : 96). From the first fraction most of unchanged **9b** was recovered, a second fraction consisted of a mixture of **9d** and unchanged **9b**. This fraction was subjected again to CC to give **9d** in 90% purity (determined by ^1H NMR). Pure **9d** (0.065 g : 30%) could be obtained from a third separation by CC. ^1H-NMR (500.13 MHz) δ 0.23 (*s*, 27H, $SiMe_3$), 3.06 (*s*, 1H, C≡CH), 7.06 (apparent *d*, *J* = 8.7, 6H, H-2), 7.08 (apparent *d*, *J* = 8.6, 2H, H-2'), 7.34 (apparent *d*, *J* = 8.7, 6H, H-3), 7.36 (apparent *d*, *J* = 8.6, 2H, H-3'); ^{13}C NMR (125.76 MHz) δ -0.1 ($SiMe_3$), 64.7 (central C), 77.5 (C≡*C*H), 83.2 (*C*≡CH), 94.8 (C≡*C*-$SiMe_3$), 104.5 (*C*≡C-$SiMe_3$), 120.1 (C-4'), 121.2 (C-4), 130.7 and 131.4 (C-2 and C-3), 130.8 and 131.5 (C-2' and C-3'), 145.9 (C-1), 146.3 (C-1'). Anal. Calcd for $C_{42}H_{44}Si_3$ (633.08): C, 79.69; H, 7.01. Found: C, 79.40; H, 7.19. FAB-MS: 633 (M^+).

1-Iodo-4-[(4-methoxyphenyl)ethynyl]benzene (11). Air was removed by argon from a soln. of 4-methoxyphenylacetylene[6] (0.102 g, 0.77 mmol) and 1,4-diiodobenzene (0.765 g, 2.32 mmol) in 12 mL of toluene / NEt_3 (5:1). Then CuI (0.009 g, 0.047 mmol) and $Pd(PPh_3)_4$ (0.027 g, 0.023 mmol) were added, and the mixture was stirred at 40 °C for 15h. After evaporation of the solvent, the residue was purified by CC (CH_2Cl_2 / hexane 1:4) to yield 0.168 g (65%) of **11**. Mp 184 °C. ^1H NMR (200.00 MHz) δ 3.84 (*s*, 3H, OCH_3), 6.89 (AA'BB', apparent *d*, *J* = 8.9, 2H, H-3'), 7.24 (AA'BB', apparent *d*, *J* = 8.6, 2H, H-3), 7.47 (AA'BB', apparent *d*, *J* = 8.9, 2H, H-2'), 7.68 (AA'BB', apparent *d*, *J* = 8.6, 2H, H-2). ^{13}C NMR (50.30 MHz) δ 55.3 (OCH_3), 87.2 and 90.9 (C≡C), 93.6 (C-1), 114.1 (C-3'), 115.0 (C-1'), 123.2 (C-4), 132.9 (C-3), 133.1 (C-2'), 137.5 (C-2), 159.9 (C-4'). Anal. Calcd for $C_{15}H_{11}IO$ (334.16): C, 53.92; H, 3.32; I, 37.98. Found: C, 54.09; H, 3.44; I, 37.81. EI-MS: 334 (M^+, 47%), 319 ($[M-CH_3]^+$, 15%), 32 (100%).

1-Bromo-4-[(4-methoxyphenyl)ethynyl]benzene (12) was obtained in 65% yield (0.142 g), as described for **11**, from 4-methoxyphenylacetylene[6] (0.1 g, 0.76 mmol) and 1-bromo-4-iodobenzene (0.215 g, 0.76 mmol) after purification by CC (CH_2Cl_2 / hexane 1:4). Mp 150-152 °C. ^1H NMR (200.00 MHz) δ 3.84 (*s*, 3H, OCH_3), 6.89 (AA'BB', apparent *d*, *J* = 8.9, 2H, H-3'), 7.37 (AA'BB', apparent *d*, *J* = 8.7, 2H, H-3), 7.47 (AA'BB', apparent *d*, *J* = 8.9, 2H, H-2'), 7.48 (AA'BB', apparent *d*, *J* = 8.7, 2H, H-2); ^{13}C NMR (50.30 MHz) δ 55.3 (OCH_3), 87.0 and 90.6 (C≡C), 114.1 (C-3'), 115.0 (C-1'), 122.0 and 122.6 (C-1 and C-4), 131.5 (C-2), 132.8 (C-3), 133.1 (C-2'), 159.8 (C-4'). Anal. Calcd for $C_{15}H_{11}BrO$ (287.16): C, 62.74; H, 3.86. Found: C, 63.03; H, 3.94. EI-MS: 286 / 288 (^{79}Br / ^{81}Br).

[4-(4-Iodophenyl)-2-methyl-3-butyn-2-ol (13b). Air was removed by argon from a soln. of 1,4-diiodobenzene (**13a**) (1 g, 3.03 mmol) in 30 mL of toluene / NEt_3 (5:1). Thereon CuI (0.031 g, 0.163 mmol), $Pd(PPh_3)_4$ (0.095 g, 0.082 mmol) and 2-methyl-3-butyn-2-ol (0.23 g, 2.73 mmol) were added, and the mixture was stirred at 40 °C for 3h. After evaporation of the solvent, the residue was purified by CC (CH_2Cl_2 / hexane 7:3, then CH_2Cl_2) to yield 0.495 g (63%) of **13b**, mp 86.5-87 °C (lit.[11] 87-88 °C).

4-[4-[(4-Methoxyphenyl)ethynyl]phenyl]-2-methyl-3-butyn-2-ol (14a). *Method A:* Air was removed by argon from a soln. of **12** (0.11 g, 0.38 mmol) in 14 mL of toluene / NEt_3 (5:1). Then CuI (0.005 g, 0.026 mmol), $Pd(PPh_3)_2Cl_2$ (0.009 g, 0.013 mmol) and 2-methyl-3-butyn-2-ol (75 µl, 0.77 mmol) were added, and the mixture was stirred at 75 °C for 15h. After evaporation of the solvent, the residue was purified by CC (CH_2Cl_2) to yield (97%) of **14a**. *Method B:* the same product was obtained in 95% yield (0.108 g) under the same conditions as in *Method A* by reaction of **10** (0.09 g, 0.68 mmol) with **13b** (0.16 g, 0.56 mmol) in the presence of CuI (0.007 g, 0.036 mmol) and $Pd(PPh_3)_4$ (0.02 g, 0.017 mmol). Mp 153.5-154 °C. ^1H NMR (200.00 MHz) δ 1.63 (*s*, 6H, CH_3), 2.11 (*s*, 1H, OH), 3.83 (*s*, 3H, OCH_3), 6.88 (AA'BB', apparent *d*, *J* = 8.9, 2H, H-3'), 7.38 (AA'BB', apparent *d*, *J* = 8.4, 2H, H-2), 7.45 (AA'BB', apparent *d*, *J* = 8.4, 2H, H-3), 7.47 (AA'BB', apparent *d*, *J* = 8.9, 2H, H-2'); ^{13}C NMR (50.30 MHz) δ 31.5 (CH_3), 55.3 (OCH_3), 65.7 (C-OH), 81.9, 87.8, 91.2 and 95.4 (C≡C), 114.1 (C-3'), 115.2 (C-1'), 122.2 (C-4), 123.6 (C-1), 131.3 (C-2), 131.6 (C-3), 133.1 (C-2'), 159.8 (C-4'). Anal. Calcd for $C_{20}H_{18}O_2$ (290.37): C, 82.73; H, 6.25. Found: C, 82.59; H, 6.18. EI-MS: 290 (M^+, 100%), 275 ($[M\text{-}CH_3]^+$, 72%).

1-Ethynyl-4-[(4-methoxyphenyl)ethynyl]benzene (14b). To a soln. of **14a** (0.15 g, 0.52 mmol) in toluene (12 mL) was added solid NaOH (0.052 g). The mixture was heated under reflux for 1.5 h. After cooling the remaining NaOH was filtered off and the solvent was evaporated. The crude product was purified by CC (CH_2Cl_2 / hexane 1:3) to yield 0.109 g (91%) of **14b**. Mp 163.5-165.5 °C. ^{1}H NMR (200.00 MHz) δ 3.18 (*s*, 1H, C≡CH), 3.84 (*s*, 3H, OCH_3), 6.89 (AA'BB', apparent *d*, *J* = 8.9, 2H, H-3'), 7.47 (*s*, 4H, H-2 and H-3), 7.48 (AA'BB', apparent *d*, *J* = 8.9, 2H, H-2'); ^{13}C NMR (50.30 MHz) δ 55.3 (OCH_3), 78.7 (C≡*C*H), 83.4 (*C*≡CH), 87.6 and 91.5 (C≡C), 114.1 (C-3'), 115.0 (C-1'), 121.5 (C-1), 124.2 (C-4), 131.3 (C-3), 132.0 (C-2), 133.1 (C-2'), 159.9 (C-4'). Anal. Calcd for $C_{17}H_{12}O$ (232.28): C, 87.90; H, 5.21. Found: C, 87.61; H, 5.41. EI-MS: 232 (M^+, 100%), 217 ($[M\text{-}CH_3]^+$, 41%).

1-[(4-Iodophenyl)ethynyl]-4-[(4-methoxyphenyl)ethynyl]benzene (15). Air was removed by argon from a soln. of **14b** (0.097 g, 0.42 mmol) and 1,4-diiodobenzene (0.415 g, 1.26 mmol) in 16 mL of toluene / NEt_3 (5:1). Then CuI (0.005 g, 0.026 mmol) and $Pd(PPh_3)_4$ (0.015 g, 0.013 mmol) were added, and the mixture was stirred at 40 °C for 3h. A voluminous precipitate separated, which was collected by filtration and dissolved in hot toluene. The solution was quickly filtered through a short column of silica gel and allowed to stand at 0 °C. Crystalline **15** (0.117 g, 65%) of mp 278-280 °C was thus obtained. ^{1}H NMR (CD_2Cl_2, 200.00 MHz) δ 3.83 (*s*, 3H, OCH_3), 6.91 (AA'BB', apparent *d*, *J* = 8.9, 2H, H-3"), 7.28 (AA'BB', apparent *d*, *J* = 8.5, 2H, H-2'), 7.48 (AA'BB', apparent *d*, *J* = 8.9, 2H, H-2"), 7.51 (*s*, 4H, H-2 and H-3), 7.73 (AA'BB', apparent *d*, *J* = 8.5, 2H, H-3'). Anal. Calcd for $C_{23}H_{15}IO$ (434.28): C, 63.61; H, 3.48. Found: C, 63.85; H, 3.56. EI-MS: 434 (M^+, 14%), 419 ($[M\text{-}CH_3]^+$, 3%), 32 (100%).

1,1'-(1,2-Ethynediyl)bis(4-iodobenzene) = 4,4'-diiodotolane (16). A soln. of 4-[(4-iodophenyl)ethynyl]aniline (0.565 g, 1.77 mmol), which was prepared as described below, in 100 mL of $CHCl_3$ / AcOH (3:7) was cooled to 0 °C before isoamylnitrite (2.07 g in 8 mL $CHCl_3$) was added dropwise under stirring. Thereon, stirring was continued for 20 min before 10 mL of aq. KI (5.8 g) was added. The solution was left to attain room temp. and then heated at 40 °C for 2h. After cooling, CH_2Cl_2, water and sodium thiosulfate were added until decolorization of the mixture was complete. The org. layer was separated, washed with aq. Na_2CO_3 and dried (Na_2SO_4).The crude product obtained after evaporation of the solvent was purified by recrystallization from $CHCl_3$ / hexane to yield 0.398 g (52%) of **16**, mp 251-252 °C (lit.[12] 237-238 °C). ^{1}H NMR (200.00 MHz) 7.24 (AA'BB', apparent *d*, *J* = 8.7, 4H, H-2 and H-2'), 7.70 (AA'BB', apparent *d*, *J* = 8.7, 4H, H-3 and H-3'). Anal. Calcd for $C_{14}H_8I_2$ (430.03): C, 39.10; H, 1.88. Found: C, 39.25; H, 1.92. EI-MS: 430 (M^+, 100%), 303 ($[M\text{-}I]^+$, 8%), 176 ($[M\text{-}2\ I]^+$, 70%).

4-Ethynylaniline. After removal of air by argon from a soln. of 4-iodoaniline (2.41 g, 11 mmol) in triethylamine (50 mL), CuI (0.042 g, 0.022 mmol), $Pd(PPh_3)_2Cl_2$ (0.155 g, 0.22 mmol) and 2-methyl-3-butyn-2-ol (1.3 ml, 13.4 mmol) were added and thereon the mixture was stirred at 40 °C for 3h. The precipitate which separated was filtered off and washed with ether. The filtrate was evaporated to dryness and the residue was purified by CC (CH_2Cl_2 / AcOEt 9:1) to yield 1.49 g (77%) of [4-(4-aminophenyl)]-2-methyl-3-butyn-2-ol, which was dissolved in isopropanol (25 mL) and treated with solid KOH (1.4 g). The mixture was heated under reflux for 2.5 h and then evaporated to dryness. The obtained residue was purified by CC (CH_2Cl_2) to yield 0.739 g (74%) of the title compound, mp 101.5-103 °C (lit.[13] 99.5-101 °C).

4-[(4-Iodophenyl)ethynyl]aniline was obtained, as described for **11**, from 4-ethynylaniline (0.12 g, 1.02 mmol) and 1,4-diiodobenzene (1.01 g, 3.06 mmol) after stirring for 3h. The crude product was purified by CC (CH_2Cl_2 / hexane 1:1) to yield 0.286 g (87%) of the title compound, mp 180.5-181.5 °C. ^{1}H NMR (200.00 MHz) δ 3.83 (br *s*, 2H, NH_2), 6.63 (AA'BB', apparent *d*, *J* = 8.7, 2H, H-2), 7.21 (AA'BB', apparent *d*, *J* = 8.6, 2H, H-2'), 7.32 (AA'BB', apparent *d*, *J* = 8.7, 2H, H-3), 7.65 (AA'BB', apparent *d*, *J* = 8.6, 2H, H-3'). ^{13}C NMR (50.30 MHz) δ 86.5 and 91.7 (C≡C), 93.2 (C-4'), 112.3 (C-4), 114.8 (C-2), 123.6 (C-1'), 132.9 and 133.0 (C-2' and C-3), 137.4 (C-3'), 146.9 (C-1). Anal. Calcd for $C_{14}H_{10}IN$ (319.15): C, 52.69; H, 3.16; N, 4.39; I, 39.76. Found: C, 52.45; H, 3.25; N, 4.50; I, 39.52. EI-MS: 319 (M^+, 100%).

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