Modular Synthesis of Benzene-Centered Porphyrin Trimers and a Dendritic Porphyrin Hexamer[†]

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Rigid, star-shaped D_3-symmetric arrays have been synthesized in which three porphyrin macrocycles are attached to the 1, 3, and 5 positions each of a benzene core through linkers consisting of collinear repetitive phenylethynyl units. Using the same methodology, a dendridic porphyrin hexamer having an external diameter of ca. 10 nm has been also obtained. By successive substitution of the three benzene positions, both a porphyrin trimer, the three linkers of which are of different length, and a starlike porphyrin, in which the complexed metal ions are different from each other, have been synthesized. The latter is the first example of a prochiral arrangement of metal ions in a D_3-symmetric ligand. To investigate their capability of forming ordered self-assembled monolayers on gold substrates, some of the porphyrin trimers and the dendritic porphyrin hexamer described in this work bear *meta*-thioanisole units at the apical positions. Analogously to similar multiporphyrin systems described in the literature, in which, however, the chromophores were arranged collinearly, the interaction between the chromophores of the multiporphyrin arrays described in this work is negligible, in the ground state, while effective energy transfer takes place in the singlet excited state.

Introduction

Owing to their ready accessibility,[1] large molecular size,[2] and rigid planar geometry as well as their electronic properties and their ability to complex almost any kind of metal ions, porphyrins are irreplaceable building blocks for the syntheses of both straight-chain and branched extended molecular systems designed to perform a great diversity of functions as, for instance, enzyme-mimetic catalysts,[3−5] optical switches,[6] molecular photonic wires,[7−10] molecular optoelectronic gates,[11] and light harvesting arrays.[12−19] On the other hand, the prospective application potential of branched, monodisperse, sequence-specific oligomers of polycyclic aromatic macromolecular systems for the construction of nanostructures has been emphasized recently in a comprehensive review article[20] as well as by Müllen's work on polyphenylene dendrimers.[21,22] As a matter of fact, the use of dendrimers in molecular recognition and self-assembling systems is attracting increasing attention in supramolecular chemistry.[23] Moreover, metal−donor atom interactions in dendrimers containing complexed metal ions increase still more the possibilities for their practical applications in diverse areas including material science and mimicking of the essential features used by living systems in energy-transfer processes.[24]

With this in mind, the syntheses of a series of benzene-centered porphyrin trimers as well as of a dendritic porphyrin hexamer, all of them possessing D_{3h} symmetry, have been carried out in the present work by means of the building block approach developped by Lindsey et al.[25] for covalent assembly of multiporphyrin arrays and

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[†] Dedicated to Prof. A. Ian Scott of the Texas A & M University on the occasion of his 70th birthday.

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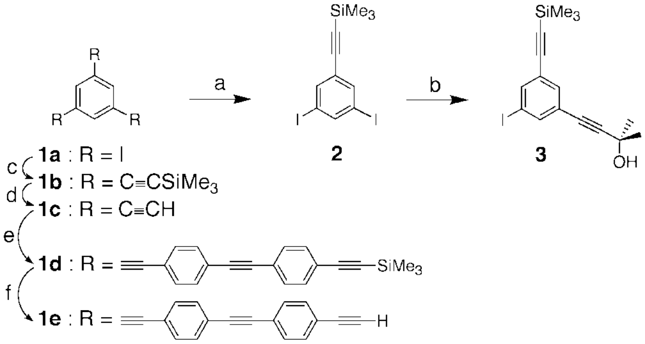
Scheme 1[a]



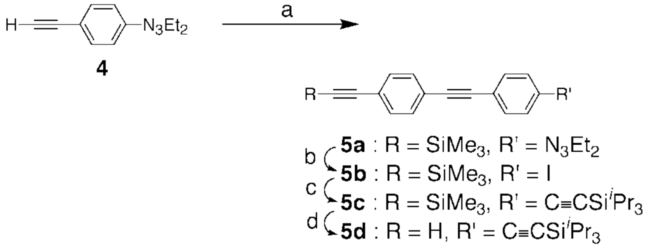
[a] Key: (a) $HC{\equiv}CSiMe_3$ (1 equiv), $Pd(PPh_3)_4$, CuI, pyridine/Et_3N, 35 °C, 2 h (51%); (b) 2-methyl-3-butyn-2-ol, same catalyst and solvent as in a, 40 °C, 4 h (65%); (c) $HC{\equiv}CSiMe_3$ (excess), $Pd(PPh_3)Cl_2$, CuI, Et_3N, 20 °C, 3 h (99%); (d) 1 N NaOH, THF (87%); (e) **5b**, $Pd(PPh_3)_4$, CuI, toluene/Et_3N, 45 °C, 12 h (70%); (f) TBAF, THF (69%).

adapted in our laboratory for the synthesis of "tripodaphyrins".[26,27] The porphyrin oligomers described in this work belong to a class of porphine derivatives designated as *stellular* (star-shaped) porphyrins.[5] In contrast to a likewise benzene-centered but C_{3h}-symmetric porphyrin trimer, the synthesis of which has been reported recently,[19] compounds **10**, **11**, **14**, **17**, and **19** are less conformatively flexible, thus enabling a better through-bond electronic interaction between the attached porphyrin macrocycles (cf. ref 14). Some examples of rigid, porphine-centered, starlike porphyrin arrays possessing D_{4h} symmetry have been reported earlier by Wennerström et al.[12] and Lindsey et al.[13] as well.

Results

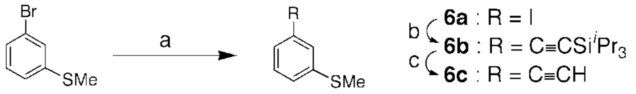
Synthesis of Poly(phenylacetylene) Linkers. The core of all multiporphyrin arrays described in this work has been constructed using 1,3,5-triiodobenzene (**1a**)[28] as starting material (Scheme 1). Its reaction with (trimethylsilyl)acetylene using palladium(II) as a catalyst[29] affords, after cleavage of the trimethylsilyl protecting groups, 1,3,5-triethynylbenzene (**1c**),[30] which was used for the synthesis of the porphyrin trimers **10b**−**d** and **11a**,**b**. On the other hand, **1e**, as the larger core of the porphyrin trimers **10e** and **11c**, was obtained by palladium(0)-catalyzed reaction[31] of **1c** with 4-iodo-4′-[(trimethylsilyl)ethynyl]tolane (**5b**),[32] which was prepared in a two-step sequence from 3,3-diethyl-1-(4-ethynylphenyl)-1-triazene (**4**)[33] (Scheme 2). Alternatively, successive replacement of the iodine atoms of **1a** by ethynyl groups is possible, thus yielding the corresponding monoethynyl and diethynyl derivatives (**2** and **3**, respectively). In the latter, two different protecting groups of the terminal ethyne-C-atoms were used to enable the stepwise synthesis of star-shaped porphyrins with different apical macrocycles (**17a**−**c**). Likewise, **2** was used as a building block for the synthesis of the dendritic porphyrin hexamer **19**. Finally, reaction of **2** with 4-[(triisopropylsilyl)-ethynyl]-4′-ethynyltolane (**5d**), which was prepared from **5b** via 4-[(trimethylsilyl)ethynyl]-4′-[(triisopropylsilyl)-ethynyl]tolane (**5c**) by selective cleavage of the trimethylsilyl protecting group of the latter (Scheme 2), yielded the suitable linker **12** for the synthesis of a star-shaped porphyrin trimer **14**, in which the three linkers are of different length.

Scheme 2[a]



[a] Key: (a) (4-iodophenyl)ethynyltrimethylsilane, $Pd(PPh_3)_4$, CuI, toluene/Et_3N, 35 °C, 12 h (81%); (b) CH_3I, 130 °C, 12 h (90%); (c) $HC{\equiv}CSi\text{-}i\text{-}Pr_3$, $Pd(PPh_3)_2Cl_2$, CuI, Et_3N, 45 °C, 12 h (99%); (d) 1 N NaOH, THF (86%).

Scheme 3[a]



[a] Key: (a) *tert*-BuLi, Et_2O, −75 °C; I_2, −75 °C → −20 °C (91%); (b) $HC{\equiv}CSi\text{-}i\text{-}Pr_3$, $Pd(PPh_3)_2Cl_2$, CuI, toluene/Et_3N, 20 °C, 2 h (98%); (c) TBAF, THF (99%).

Synthesis of *meso*-Tetraarylporphyrin Building Blocks. The synthesis of the metal chelates **9b**,**c** of 5-(4-iodophenyl)-10,15,20-triphenylporphine **9a** has been previously described.[26,27] As the solubility in organic solvents of multiporphyrin arrays synthesized therefrom attained a practical limit with compound **10e** ($\sim10^{-4}$ mol/L in $CHCl_3$), the porphyrin derivative **7** (Scheme 4) was used as precursor of a new series of multiporphyrin arrays, including the dendritic porphyrin hexamer **19**, in which the ortho substituents at the phenyl rings prevent cofacial aggregation of the macrocycles, thus improving their solubility (cf. ref 16). Moreover, elongation of one of the *p*-iodophenyl substituents of **7** with a *meta*-ethynylthioanisole unit (cf. Scheme 3) yielded a *meso*-tetraarylporphine intermediate **8a**, which not only led to more soluble final products but also endowed them with functional groups, which interact strongly with gold covered substrates, so that highly ordered self-assembled monolayers (SAM) may be formed on such substrates by spontaneous adsorption from solution (cf. ref 34). Substitution of the iodine atoms of **8a** and **9c** by ethynyl

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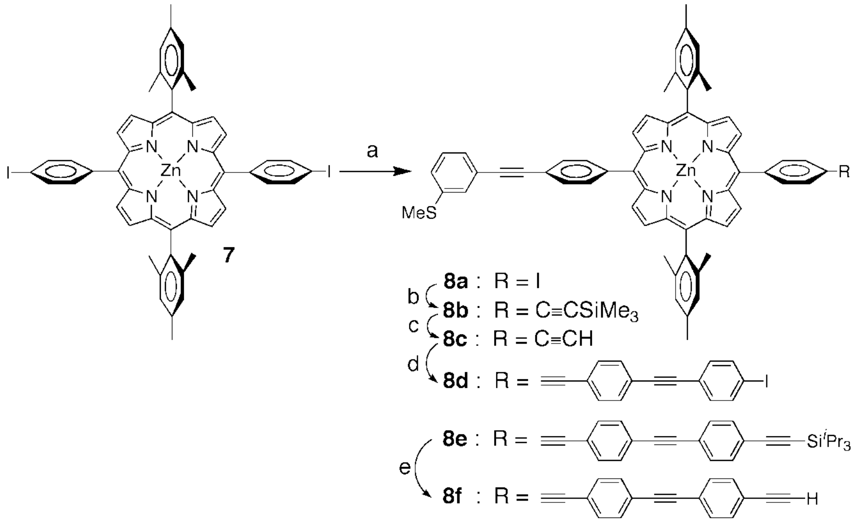
Scheme 4[a]



[a] Key: (a) **6c**, Pd_2dba_3, $AsPh_3$, DMF/Et_3N, 45 °C, 3 h (41%); (b) HC≡CSiMe$_3$, same conditions as in a (79%); (c) 1 N NaOH, THF (87%); (d) 4,4′-diiodotolane, $Pd(PPh_3)_4$, DMF/Et_3N, 45 °C, 18 h (89%); (e) TBAF, THF (53%).

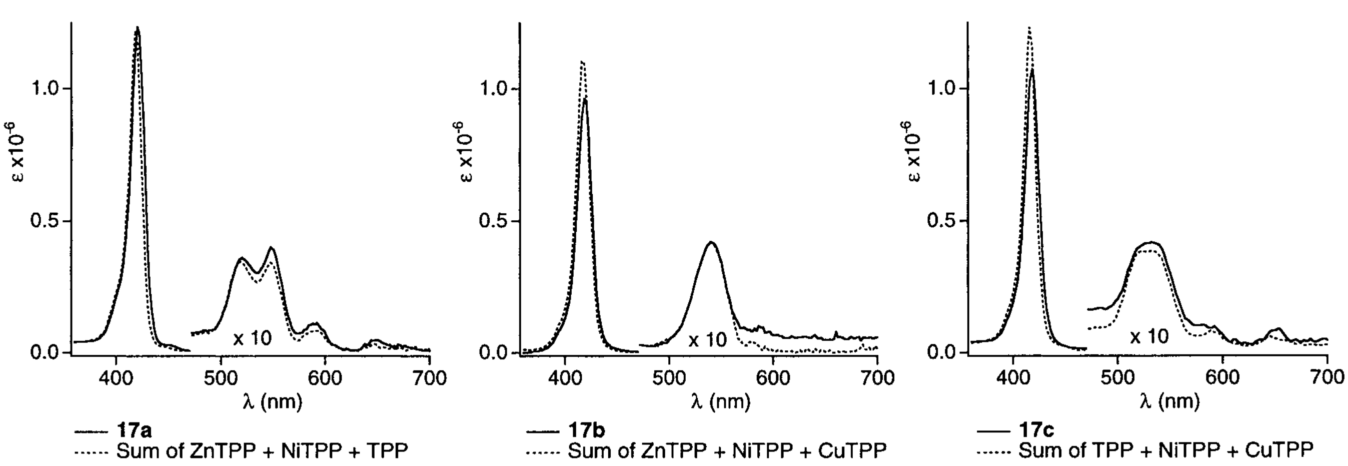


Figure 1. Absorption spectra of **17a**–**c** (solid lines). Composite spectra in the range of absorption of the porphyrin chromophores were generated by adding the spectra of the individual TPP chromophores (dotted lines). Spectra were measured in benzene at room temperature.

groups was achieved by reaction with (trimethylsilyl)acetylene and subsequent cleavage of the terminal trimethylsilyl group (cf. ref 27). Elongation of the ethynylphenyl group through reaction with 4,4′-diiodotolane led finally to the corresponding intermediates **8d** and **9d**,[27] respectively (Schemes 4 and 5, respectively). Derivative **8f** was directly obtained from **8a** by reaction with **5d** and following deprotection of the terminal ethyne group.

Synthesis of Multiporphyrin Arrays. Reaction of 1,3,5-triethynylbenzene (**1c**) with **9c** and **9d** in the presence of $Pd(PPh_3)_4$ led to D_3-symmetric porphyrin trimers **10c** and **10d**, respectively (Scheme 5). The latter was also obtained by reacting the larger D_3-symmetric core **1e** with the tetraphenylporphyrin derivative **9c**. The yield of this reaction was perceptibly improved from 18% up to 61%, however, using triphenylarsine instead of triphenylphosphine as the ligand of the palladium catalyst (cf. ref 35). The same procedure was used for the synthesis of the largest compound in this series (i.e., **10e**), which was obtained by reaction **9d** with **1e**. Analogously, the more soluble porphyrin trimers **11a**–**c** were prepared using **8a** and **8d** instead of **9c** and **9d**, respectively, as the building blocks. The alternative synthetic approach, in which the reactive ethynyl groups are located on the porphyrin moieties and the iodine atoms in the core was discarded because it led to the formation of butadiyne-linked porphyrin dimers as byproducts, which were very difficult to separate from the desired D_3-symmetric trimers.

The porphyrin trimer with three linkers of different lengths (**14**) was synthesized from the iodobenzene derivative **12** by successive reaction with **8c** and, after cleavage of both trialkylsilyl protecting groups, with an excess (2.5 mol) of the iodophenylporphyrin derivative **8d** (Scheme 6). On the other hand, selective cleavage of the trimethylsilyl and 2-hydroxylpropyl protecting group of **15a**, which was prepared from **3** (cf. Experimental Section), followed by reaction with the nickel and copper chelates of **9a**, respectively, led to a porphyrin trimer (**17b**), in which the complexed metal ions are different from each other. By the same strategy, other combinations of porphyrin metal chelates and metal-free porphy-

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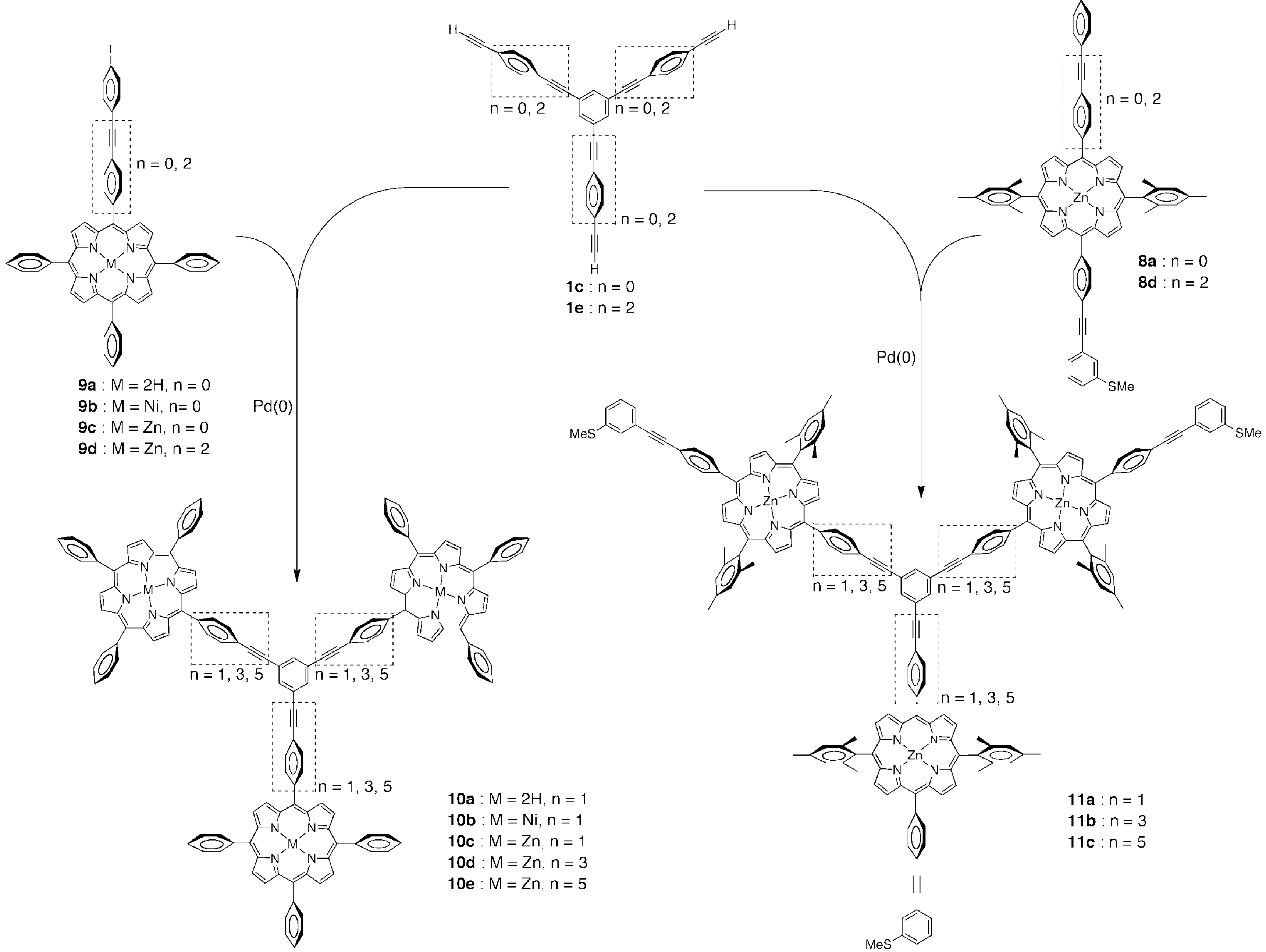
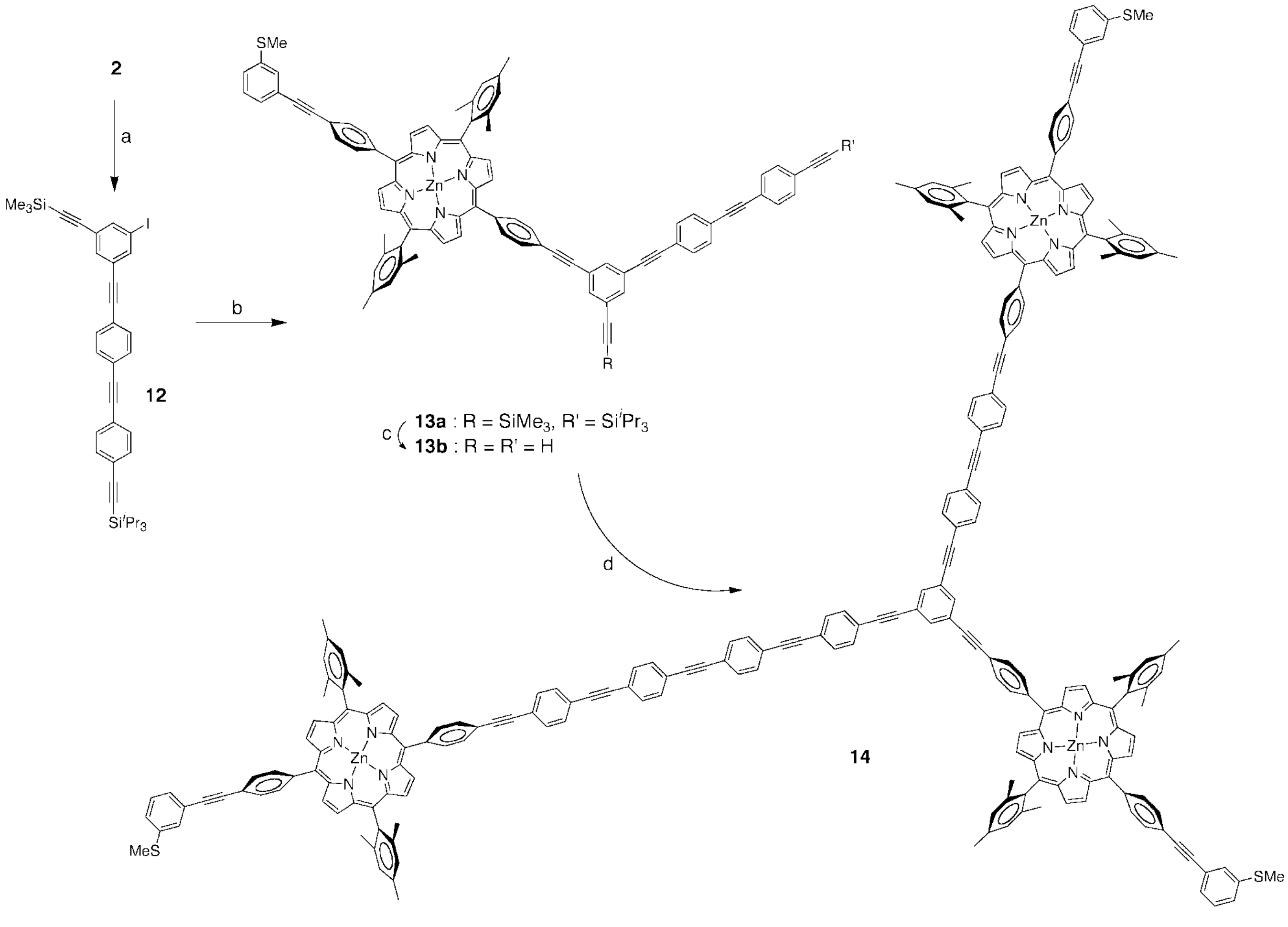
Scheme 5. Synthesis of Porphyrin Trimers (Cf. Experimental Section)



Scheme 6[a]



[a] Key: (a) **5d**, Pd(PPh$_3$)$_4$, CuI, pyridine/Et$_3$N, 35 °C, 2 h (61%); (b) **8c**, Pd(PPh$_3$)$_4$, DMF/Et$_3$N, 45 °C, 20 h (81%); (c) TBAF, THF (95%); (d) **8d**, same conditions as in b (67%).

rin ligands could be obtained (Scheme 7). Finally, reaction of diiodobenzene derivative **2** with 3 equivalents of **8c** led to a porphyrin dimer **18a**, which after cleavage of the trimethylsilyl protecting group, was reacted with an excess of 4,4′-diiodotolane to give the bifurcated porphyrin dimer **18c**. The latter was reacted with 1,3,5-triethynylbenzene (**1c**) in the presence of tris(dibenzylideneacetone)dipalladium (Pd$_2$dba$_3$) and triphenylarsine to yield the dendritic porphyrin hexamer **19** possessing an external diameter of ca. 10 nm (Scheme 8).

Discussion

Although the primary goal of the present work is the synthesis of nanometer-sized multiporphyrin arrays, which may be visualized by commercially available scanning probe microscopes (cf. refs 26 and 27), rather than the study of their photodynamic properties, some features of the energy absorption and emission of the corresponding chromophores deserve to be commented here briefly. Thus, the ground-state absorption of the multiporphyrin arrays is a sum of the absorption spectra of the individual chromophores both in the range of absorption of the porphyrin moieties (Figure 1) and the *p*-phenylene ethynylene linkers (Figure 2), suggesting that electronic coupling between the chromophores is weak. This is particularly manifest in the case of compound **14**, the absorption maxima of which correspond to those of its isomer **11b** although the distance between the chromophores is different in both arrays (Figure 2). Actually, a lack of interaction between the individual chromophores of the arrays described in this work is not surprising, since their linkers are attached to the meta positions of the benzene core (cf. ref 36). In contrast, λ_{max} in the range of absorption of the linkers theirselves shifts to longer wavelengths on increasing the number of *p*-phenylene ethynylene units (Figure 2). On the other hand, efficient singlet excited-state energy transfer is observed between the chromophores in the heteroorganometallic derivatives **17a**−**c** with concomitant diminution of emitted light (cf. Table 1). Particularly interesting in this connection is compound **17a**, in which the emission of the Zn-tetraphenylporphine (Zn-TPP) chromophore is almost completely quenched, while 74% of the emission of the tetraphenylporphine (TPP) chromophore is still present (Figure 3). Efficient transfer of singlet excited-state energy from the Zn porphyrin to the free-base porphyrin chromophore has been observed previously both through-bond via the linkers (Dexter-type mechanism)[17,37,38] and by the Förster mechanism[39] in dimeric and trimeric porphyrin arrays, in which Zn TPP and free-base TPP chromophores are arranged collinearly. Whether in the case of **17a** the loss of excitation

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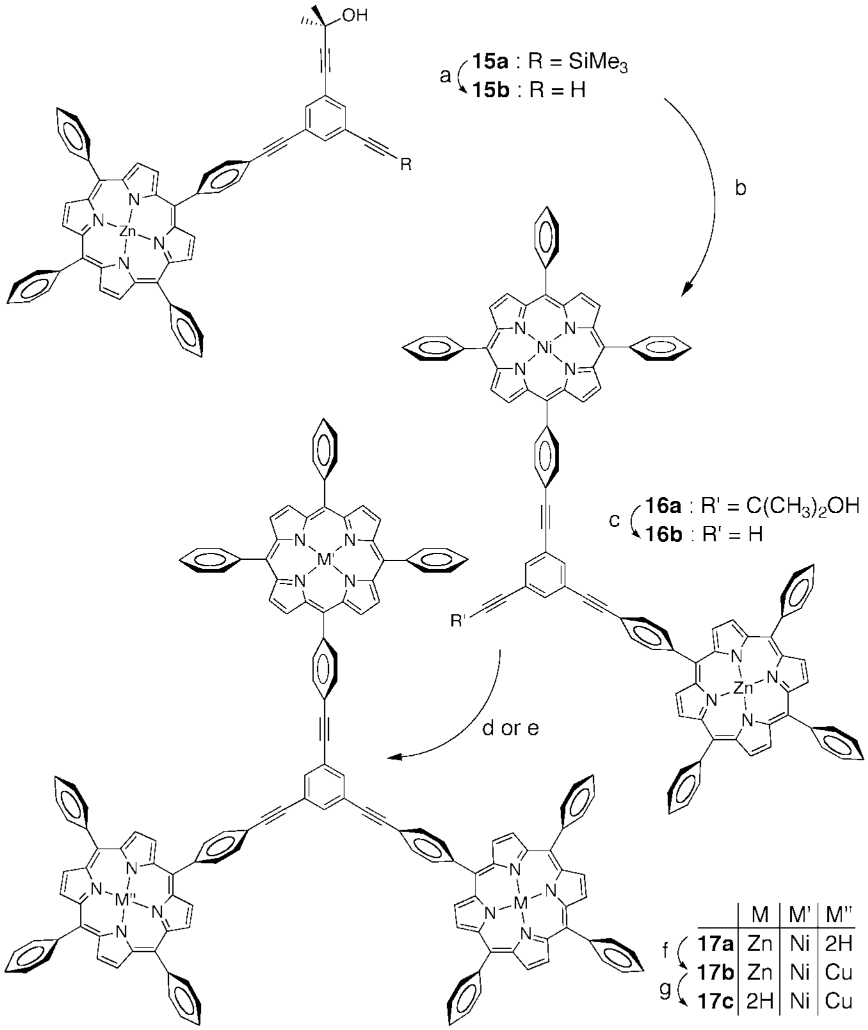
Scheme 7[a]



[a] Key: (a) TBAF, THF (94%); (b) **9b**, Pd(PPh$_3$)$_4$, DMF/Et$_3$N, 45 °C, 20 h (86%); (c) KOH, *i*-PrOH/toluene, reflux, 2 h (89%); (d) **9a**, same conditions as in b (82% of **17a**); (e) copper chelate of **9a**, same conditions as in b (62% of **17b**); (f) (CH$_3$CO$_2$)$_2$Cu·H$_2$O, CHCl$_3$/MeOH, 20 °C, 15 min (94%); (g) TFA, CHCl$_3$, 20 °C, 2 h (97%).

energy of the Zn TPP chromophore takes place by preferential transfer of the latter to the (nonfluorescent) Ni TPP chromophore or through the free-base porphyrin macrocycle is presently under investigation. Nevertheless, the photodynamic behavior of the multiporphyrin arrays described in the present work contrasts with that of similarly structured tripodaphyrins, in which no singlet excited-state energy transfer between Zn TPP and Ni TPP or Cu TPP chromophores could be observed.[27]

Experimental Section

General Methods. 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 aluminum foils. Column chromatography (CC): E. Merck silica gel 60 (230–400 mesh). UV/VIS λ_{max} (log ϵ) and emission spectra (EMS) λ_{em} are reported in nm. ^{1}H

Table 1. Quantum Yields of Fluorescence[a]

	quantum yields (Φ_f)	
compd	free base porph[b]	Zn porph[b]
ZnTPP		0.033[40]
TPP	0.11[41]	
10a	0.095	
10c		0.039
10d		0.040
17a	0.082	0.004
17b		0.0025
17c	0.046	

[a] Emission spectra were measured from 570 to 800 nm. [b] The quantum yields of emission were determined with λ_{ex} 550 nm; the emission intensity was integrated from λ_{em} 570 to 800 nm. The integrated areas of the free base porphyrin (TPP) and of the Zn TPP emission in heterometallic arrays were measured for the 690–800 nm and 570–620 nm range, respectively, and have been normalized to the emission of the corresponding monomers, allowing for the absorbance ratios at λ_{max} 550 nm of the different chromophores present in the molecule. It was assumed that the TPP and Zn TPP emissions have the same spectral profile in the arrays as in the corresponding porphyrin monomers. Quantum yields of TPP emission determined with λ_{ex} 648 nm, where only the free base porphyrin absorbs, gave the same results.

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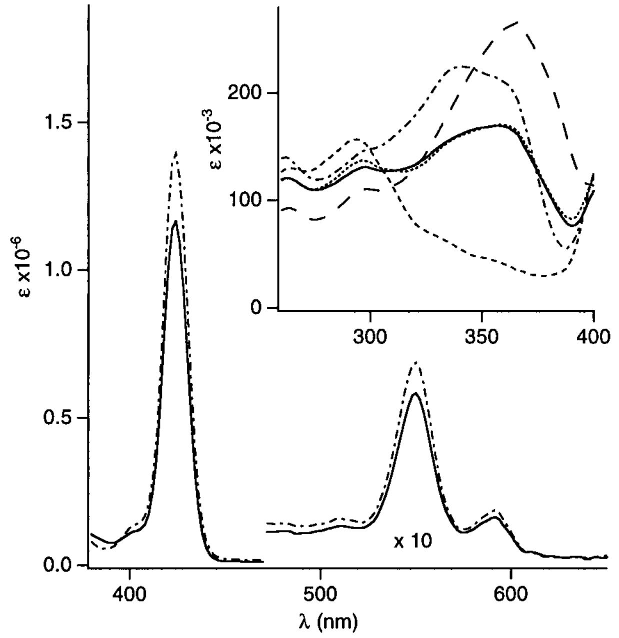

Figure 2. Absorption spectrum of **14** (—). For comparison, the absorption spectrum of the isomeric D_{3h} symmetric trimer **11b** is shown (–·–). Inset: composite spectrum (···) in the range of absorption of the *p*-phenylene ethynylene linkers generated by adding the absorption of each linker obtained from the spectra of **11a** (- - -), **11b** (–·–), **11c** (— —). Spectra were measured in benzene at room temperature.

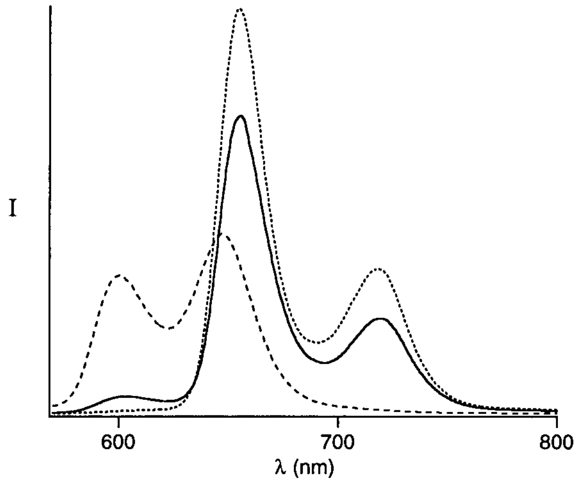

Figure 3. Emission spectrum of **17a** (—) in benzene at room temperature (λ_{ex} 550 nm). For comparison, the emission spectra observed from equimolar solutions of the porphyrin monomers Zn TPP (- - -) and TPP (···) are shown.

and ^{13}C NMR spectra were recorded in $CDCl_3$. Chemical shifts (δ) are given in ppm relative to Me_4Si as internal standard, *J* values in Hz. Tetrakis(triphenylphosphine)palladium, tris(dibenzylideneacetone)dipalladium (Pd_2dba_3), triphenylarsine, and tetrabutylammonium fluoride (TBAF) were purchased from Aldrich Chemie (CH-9471 Buchs); 1-bromo-3-(methylthio)benzene from MTM Research Chemicals, Lancaster Synthesis Division (F-67800 Bischheim); dimethylformamide (DMF), trifluoroacetic acid (TFA), tetrahydrofuran (THF), (trimethylsilyl)acetylene (TMSA), 2-methyl-3-butyn-2-ol, and other reagents from Fluka Chemie AG (CH-9471 Buchs).

(1,3,5-Benzenetriyltri-2,1-ethynediyl)tris(trimethylsilane) (1b). Air was removed from a solution of 1,3,5-triiodobenzene (**1a**)[28] (140 mg, 0.307 mmol) in Et_3N (12 mL) by blowing argon for 30 min. Then, $Pd(PPh_3)_2Cl_2$ (26 mg, 0.037 mmol), CuI (14 mg, 0.074 mmol), and TMSA (0.425 mL, 3.07 mmol) were added. Thereafter, the mixture was stirred at 20 °C for 3 h. The solvent was removed under reduced pressure, and the crude product was purified by CC (hexane) to yield 112 mg (99%) of **1b**: mp 79−80 °C; ^{1}H NMR (200.00 MHz) δ 0.23 (s, 27H), 7.49 (s, 3H). ^{13}C NMR (50.30 MHz) δ −0.2, 95.6, 103.2, 123.6, 134.9; EI-MS 366 (M^+, 30), 351 ($[M - CH_3]^+$, 100), 168 (40). Anal. Calcd for $C_{21}H_{30}Si_3$ (366.73): C, 68.78; H, 8.25. Found: C, 68.59; H, 8.43.

1,3,5-Triethynylbenzene (1c). To a solution of **1b** (456 mg, 1.24 mmol) in THF (5 mL) was added 3 mL of aqueous NaOH (1 N), and the mixture was stirred vigorously at 20 °C for 2 h. After evaporation of the THF, CH_2Cl_2 was added, and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2, and the combined organic phases were dried (Na_2SO_4). The residue obtained after removal of the solvent was purified by CC (hexane) to yield 163 mg (87%) of **1c**: mp 104.5−105 °C (lit.[30a] mp 105−107 °C, lit.[30b] mp 102−103 °C).

[1,3,5-Benzenetriyltris(2,1-ethynediyl-4,1-phenylene-2,1-ethynediyl-4,1-phenylene-2,1-ethynediyl)]tris(trimethylsilane) (1d). Air was removed from a solution of **1c** (4.83 mg, 32.1 μmol) and **5b** (39.4 mg, 98.4 μmol) in 3 mL of toluene/Et_3N (5:1) by blowing argon for 30 min. Then, $Pd(PPh_3)_4$ (6.4 mg, 5.5 μmol) and CuI (2.0 mg, 10.5 μmol) were added, and the mixture was heated at 45 °C for 12 h. The solvent was removed under reduced pressure, and the crude product was purified by CC (CH_2Cl_2/hexane: gradient from 1:9 to 1:4) to yield 21.9 mg (70%) of **1d**: mp 252 °C; ^{1}H NMR (200.00 MHz) δ 0.27 (s, 27H), 7.47 (m, 12H), 7.52 (m, 12H), 7.67 (s, 3H); ^{13}C NMR (50.30 MHz) δ −0.1, 89.6, 90.3, 90.9, 91.1, 96.5, 104.5, 122.7, 123.0, 123.2, 123.9, 131.4, 131.7, 131.9, 134.2; FAB-MS 966 (M^+). Anal. Calcd for $C_{69}H_{54}Si_3$ (967.44): C, 85.66; H, 5.63. Found: C, 85.35; H, 5.94.

1,3,5-Tris[[4-[(4-ethynylphenyl)ethynyl]phenyl]ethynyl]benzene (1e). To a solution of **1d** (44.9 mg, 46.4 μmol) in 6.3 mL of THF was added TBAF (1 M in THF, 0.14 mL, 0.14 mmol), and the mixture was stirred for 45 min at 20 °C. A few grains of $CaCl_2$ were added to remove any excess fluoride (cf. ref 42) and the solvent was evaporated. The crude product was purified by CC (CH_2Cl_2/hexane 1:4) to yield 24 mg (69%) of **1e** as a white solid: mp > 360 °C; ^{1}H NMR (200.00 MHz) δ 3.19 (s, 3H), 7.49 (m, 12H), 7.53 (m, 12H), 7.67 (s, 3H); ^{13}C NMR (50.30 MHz) δ 79.09, 83.2, 89.6, 90.3, 90.9, 122.1, 122.8, 123.2, 123.4, 123.9, 131.5, 131.7, 132.1, 134.2; FAB-MS 750 (M^+). Anal. Calcd for $C_{60}H_{30}$ (750.89): C, 95.97; H, 4.03. Found: C, 95.57; H, 4.33.

[(3,5-Diiodophenyl)ethynyl]trimethylsilane (2). Air was removed from a solution of **1a** (205 mg, 0.45 mmol) in 16 mL of pyridine/Et_3N (1:1) by blowing argon for 20 min. Then, $Pd(PPh_3)_4$ (16 mg, 0.014 mmol), CuI (5.3 mg, 0.028 mmol), and TMSA (62 μL, 0.45 mmol) were added, and the mixture was stirred at 35 °C for 2 h. The solvent was evaporated under reduced pressure, and then hexane was added to the residue. The insoluble part was removed by filtration, the solvent was evaporated, and the residue was purified by CC (hexane) to yield 98 mg (51%) of **2** as a colorless oil: ^{1}H NMR (200.00 MHz) δ 0.23 (s, 9H), 7.76 (d, $J = 1.6$, 2H), 7.99 (t, $J = 1.6$, 1H); ^{13}C NMR (50.30 MHz) δ −0.3, 93.9, 97.5, 101.3, 126.7, 139.7, 145.1; EI-MS 426 (M^+, 24), 411 ($[M - CH_3]^+$, 63), 284 ($[M - I]^+$, 9), 157 ($[M - 2I]^+$, 100). Anal. Calcd for $C_{11}H_{12}I_2Si$ (426.11): C, 31.00; H, 2.84. Found: C, 30.70; H, 3.01.

4-[5-Iodo-3-[(trimethylsilyl)ethynyl]phenyl]-2-methyl-3-butyn-2-ol (3). Air was removed from a solution of **2** (50 mg, 0.117 mmol) in 6 mL of pyridine/Et_3N (5:1) by blowing argon for 20 min. Then, $Pd(PPh_3)_4$ (4.1 mg, 3.6 μmol), CuI (1.4 mg, 7.4 μmol), and 2-methyl-3-butyn-2-ol (11.4 μL, 0.117 mmol) were added, and deaeration was continued for 10 min. Thereafter, the mixture was heated at 40 °C for 4 h. The

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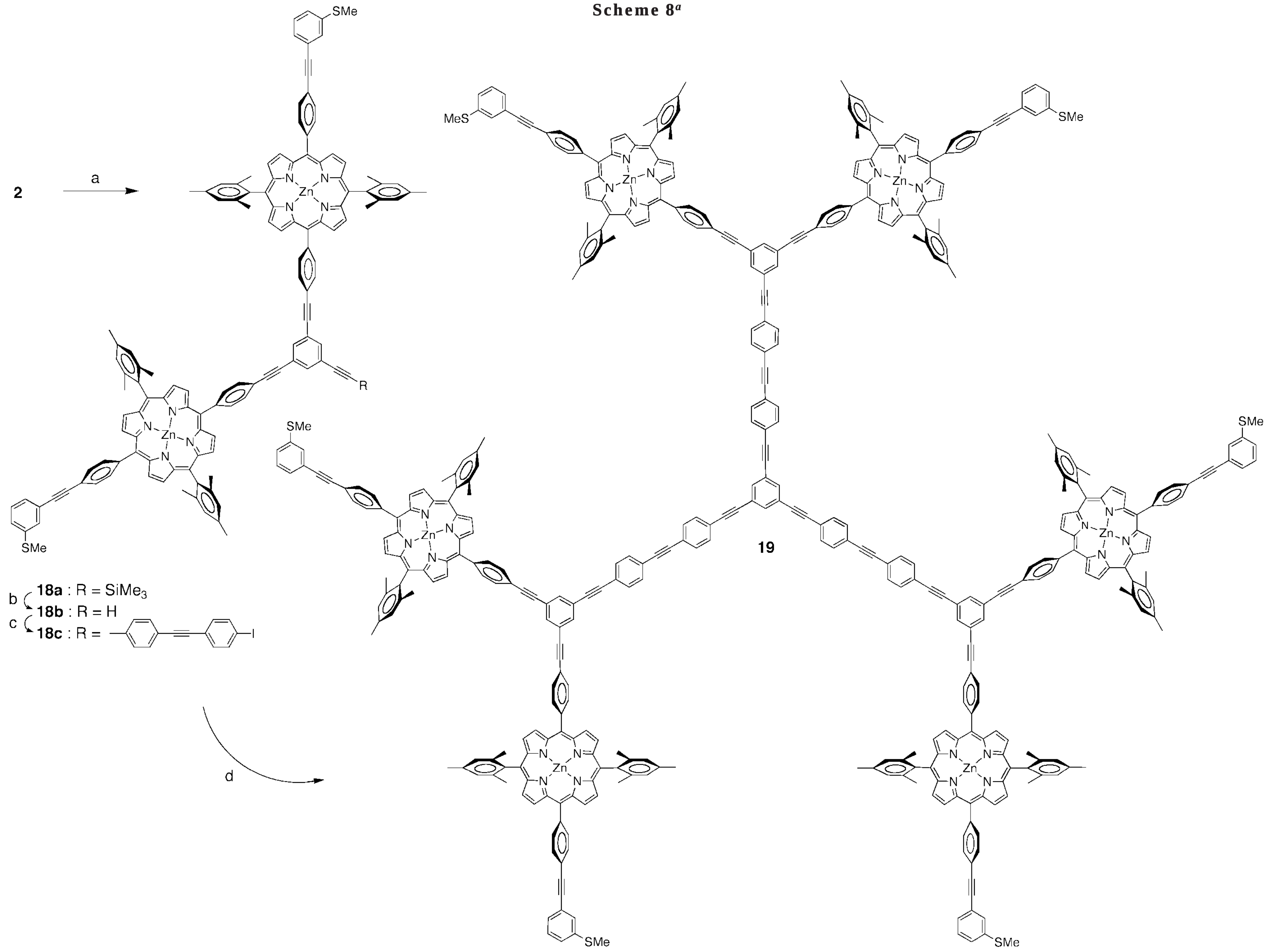
Scheme 8[a]



[a] Key: (a) **8c**, Pd_2dba_3, $AsPh_3$, DMF/Et_3N, 30 °C, 6 h (61%); (b) TBAF, THF (80%); (c) 4,4′-diiodotolane, $Pd(PPh_3)_4$, DMF/Et_3N, 45 °C, 18 h (82%); (d) **1c**, same conditions as in a, 5 h (28%).

solvent was removed under reduced pressure, and the crude product was purified by CC (CH_2Cl_2/hexane: gradient from 1:9 to 7:3) to yield 29 mg (65%) of **3** as a colorless oil: ^1H NMR (200.00 MHz) δ 0.23 (s, 9H), 1.59 (s, 6H), 2.02 (br s, 1H), 7.47 (t, $J = 1.5$, 1H), 7.69 (t, $J = 1.5$, 1H), 7.73 (t, $J = 1.5$, 1H); ^{13}C NMR (50.30 MHz) δ −0.2, 31.3, 65.5, 79.8, 92.9, 95.6, 96.6, 102.2, 124.6, 125.0, 134.1, 139.9, 140.0; CI-MS 383 ($M + H^+$, 7); FAB-MS 365 ($M + H^+ - H_2O$, 100). Anal. Calcd for $C_{16}H_{19}IOSi$ (382.32): C, 50.27; H, 5.01. Found: C, 49.95; H, 4.87.

3,3-Diethyl-1-(4-ethynylphenyl)-1-triazene (4)[43] was obtained in 82% yield (109 mg) as a colorless oil, after purification by CC (CH_2Cl_2/hexane 3:7), reacting 3,3-diethyl-1-[4-[(trimethylsilyl)ethynyl]phenyl]-1-triazene[33] (181 mg, 0.66 mmol) with TBAF (0.68 mmol) in THF (22 mL), as described for **1e**: ^1H NMR (200.00 MHz) δ 1.27 (s, $J = 7.1$, 6H), 3.07 (s, 1H), 3.77 (q, $J = 7.1$, 4H), 7.36 and 7.45 (AA′XX′, $J_{AX} = 8.8$, 4H); ^{13}C NMR (50.30 MHz) δ 12.8, 45.0, 76.5, 84.4, 118.5, 120.4, 132.8, 151. Anal. Calcd for $C_{12}H_{15}N_3$ (201.27): C, 71.61; H, 7.51; N, 20.88. Found: C, 71.82; H, 7.49; N, 20.70.

3,3-Diethyl-1-[4-[[4-[(trimethylsilyl)ethynyl]phenyl]ethynyl]phenyl]-1-triazene (5a) was obtained in 81% yield (82.9 mg), after purification by CC (CH_2Cl_2/hexane 1:4), reacting **4** (55 mg, 0.273 mmol) with (4-iodophenyl)ethynyltrimethylsilane[44] (82 mg, 0.273 mmol) in the presence of $Pd(PPh_3)_4$ (17.7 mg, 15 μmol) and CuI (5.7 mg, 30 μmol), in 4.3 mL of toluene/Et_3N at 35 °C, as described for **1d**: mp 122−123 °C; ^1H NMR (200.00 MHz) δ 0.26 (s, 9H), 1.28 (t, $J = 7.1$, 6H), 3.78 (q, $J = 7.1$, 4H), 7.41−7.49 (m, 8H); ^{13}C NMR (50.30 MHz) δ −0.07, 12.9, 44.0, 88.8, 92.1, 96.0, 104.8, 119.1, 122.6, 123.8, 120.4, 131.3, 131.9, 132.3, 151.3; EI-MS 373 (M^+, 18), 273 ($[M - Et_2N_3]^+$, 100), 258 ($[M - Et_2N_3 - Me]^+$, 73). Anal. Calcd for $C_{23}H_{27}N_3Si$ (373.57): C, 73.95; H, 7.28; N, 11.25. Found: C, 73.77; H, 7.30; N, 10.97.

[[4-[(4-Iodophenyl)ethynyl]phenyl]ethynyl]trimethylsilane (5b). To a thick-walled screw cap tube was added a solution of **5a** (71.7 mg, 0.192 mmol) in iodomethane (7 mL). The tube was flushed with argon and sealed and heated to 130 °C for 12 h. The reaction mixture was cooled to room temperature, and the solvent was removed under reduced pressure. The crude product was purified by CC (hexane) to yield 68.8 mg (90%) of **5b**: mp 248 °C (lit.[32] mp 248−250 °C).

[[4-[[4-[(Triisopropylsilyl)ethynyl]phenyl]ethynyl]phenyl]ethynyl]trimethylsilane (5c). Air was removed from a solution of **5b** (80 mg, 0.2 mmol) and ethynyltriisopropylsilane (66.6 μL, 0.3 mmol) in 5 mL of Et_3N by blowing argon for 30 min. Then, $Pd(PPh_3)_2Cl_2$ (7 mg, 0.01 mmol) and CuI (3.8 mg, 0.02 mmol) were added before the mixture was stirred at 45 °C for 12 h. Thereafter, the solvent was removed under reduced pressure, and the crude product was purified by CC (hexane) to yield 90 mg (99%) of **5c**.[44]

[[4-[(4-Ethynylphenyl)ethynyl]phenyl]ethynyl]triisopropylsilane (5d) was obtained as described for **1c**, reacting **5c** (104.1 mg, 0.229 mmol) in 7.5 mL of THF with 0.229 mL of aqueous NaOH (1 N) for 30 min. After purification by CC (hexane), 75.6 mg (86%) of **5d** was obtained: mp 45−46 °C. Other analytical data agree with those given in ref 44.

1-Iodo-3-(methylthio)benzene (6a). A solution of 0.203 g (1.0 mmol) of 1-bromo-3-(methylthio)benzene in 6 mL of Et_2O was cooled to −75 °C before 1.5 mL of a solution of *tert*-butyllithium (1.5 M in pentane, 2.25 mmol) was added dropwise. After the addition was complete, the reaction mixture was stirred for 30 min at −75 °C, and then a solution of 0.8 g (3.15 mmol) of iodine in 10 mL of Et_2O was added dropwise. The mixture was then stirred at −75 °C for 10 min and at −20 °C for further 10 min. Ethanol was then added before the mixture was poured into an aqueous sodium thiosulfate solution and extracted with CH_2Cl_2. The organic layer was dried (Na_2SO_4), the solvent was removed under reduced pressure, and the crude product was purified by CC (CH_2Cl_2/hexane 1:19) to yield 0.229 g (91%) of **6a** as a colorless oil: ^1H NMR (200.00 MHz) δ 2.46 (s, 3H), 6.99 (t, $J = 7.8$, 1H), 7.20 (ddd, $J = 7.8, 1.7, 1.7$, 1H), 7.46 (ddd, $J = 7.8, 1.7, 1.7$, 1H), 7.56 (t, $J = 1.7$, 1H); ^{13}C NMR (50.30 MHz) δ 15.7, 94.7, 125.7, 130.2, 134.0, 134.7, 141.0; EI-MS 250 (M^+, 100), 123 ($[M - I]^+$, 50), 108 ($[M - CH_3 - I]^+$, 51). Anal. Calcd for C_7H_7IS (250.10): C, 33.62; H, 2.82. Found: C, 33.75; H, 2.78.

Triisopropyl[[3-(methylthio)phenyl]ethynyl]silane (6b). Air was removed from a solution of **6a** (125 mg, 0.5 mmol) in 8 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 ethynyltriisopropylsilane (0.33 mL, 1.5 mmol) were added. Thereafter, the mixture was stirred at 20 °C for 2 h. The solvent was removed under reduced pressure, and the residue was purified by CC (CH_2Cl_2/hexane 1:19) to yield 149 mg (98%) of **6b** as a colorless oil: ^1H NMR (200.00 MHz) δ 1.13 (m, 21H), 2.47 (s, 3H), 7.16−7.27 (m, 3H), 7.32−7.36 (m, 1H); ^{13}C NMR (50.30 MHz) δ 11.3, 15.8, 18.7, 91.0, 106.6, 124.2, 126.6, 128.5, 128.8, 129.8, 138.7; EI-MS 304 (M^+, 34), 261 ($[M - i\text{-}Pr]^+$, 100). Anal. Calcd for $C_{18}H_{28}SSi$ (304.57): C, 70.98; H, 9.27. Found: C, 71.22; H, 9.39.

1-Ethynyl-3-(methylthio)benzene (6c) was obtained in 99% yield (71.4 mg) as a colorless oil, as described for **4**, from **6b** (148 mg, 0.49 mmol), after purification by CC (CH_2Cl_2/hexane 1:19): ^1H NMR (200.00 MHz) δ 2.47 (s, 3H), 3.08 (s, 1H), 7.20−7.27 (m, 3H), 7.34−7.37 (m, 1H); ^{13}C NMR (50.30 MHz) δ 15.6, 77.5, 83.2, 122.7, 126.9, 128.6, 128.7, 129.5, 138.9; EI-MS 148 (M^+, 100). Anal. Calcd for C_9H_8S (148.22): C, 72.93; H, 5.44. Found: C, 73.17; H, 5.31.

[5,15-Bis(4-iodophenyl)-10,20-bis(mesityl)porphinato(2-)]zinc (7). To a solution of 5,15-bis(4-iodophenyl)-10,20-bis(mesityl)porphine[45] (117 mg, 0.123 mmol) in 16 mL of $CHCl_3$/MeOH (9:1) was added zinc acetate monohydrate (490 mg, 2.23 mmol), and the mixture was refluxed for 1 h. Thereafter, the mixture was washed with water and dried (Na_2SO_4), and the solvent was evaporated. The residue was purified by CC ($CHCl_3$/hexane 2:3) to yield 124 mg (99%) of **7**: UV/vis (CH_2Cl_2) 306 (4.18), 422 (5.68), 550 (4.31), 590 (3.65); ^1H NMR (360.14 MHz) δ 1.81 (s, 12H), 2.63 (s, 6H), 7.28 (s, 4H), 7.96 and 8.07 (AA′XX′, $J_{AX} = 8.3$, 8H), 8.77 (d, $J = 4.6$, 4H), 8.85 (d, $J = 4.6$, 4H); FAB-MS 1014.9 (calcd average mass for $C_{50}H_{38}I_2N_4Zn$ 1014.07).

[15-(4-Iodophenyl)-10,20-bis(mesityl)-5-[4-[[3-(methylthio)phenyl]ethynyl]phenyl]porphinato(2−)]zinc (8a). Air was removed from a solution of **7** (95 mg, 94 μmol) and **6c** (13.9 mg, 94 μmol) in 8 mL of DMF/Et_3N (5:1) by blowing argon for 20 min. Then, Pd_2dba_3 (6.5 mg, 7.1 μmol) and $AsPh_3$ (17.3 mg, 56.5 μmol) were added, and deaeration was continued for 10 min. Thereafter, the mixture was heated at 45 °C for 3 h. The solvent was removed under reduced pressure, and the crude product was purified by CC. Three fractions were obtained: unreacted **7** (26.6 mg; 28%), **8a** (39.7 mg; 41%), and [10,20-bis(mesityl)-5,15-bis[4-[[3-(methylthio)phenyl]ethynyl]phenyl]porphinato(2−)]zinc (20.7 mg; 21%), which were successively eluted with $CHCl_3$/hexane (7:13), $CHCl_3$/hexane (9:11), and $CHCl_3$/hexane (11:9). **8a**: UV/vis (CH_2Cl_2) 422 (5.65), 550 (4.32), 592 (3.77); ^1H NMR (200.00 MHz) δ 1.82 (s, 12H), 2.43 (s, 3H), 2.63 (s, 6H), 7.18−7.23 (m, 1H), 7.28 (s, 4H), 7.30 (t, $J = 7.9$, 1H), 7.38−7.46 (m, 2H), 7.91 and 8.24 (AA′XX′, $J_{AX} = 8.1$, 4H), 7.97 and 8.08 (AA′XX′, $J_{AX} = 8.4$, 4H), 8.79 and 8.86 (2 × d, $J = 4.7$, 4H), 8.79 and 8.90 (2 × d, $J = 4.7$, 4H); FAB-MS 1035.1 (calcd average mass for $C_{59}H_{45}IN_4SZn$ 1034.38).

[10,20-Bis(mesityl)-5-[4-[[3-(methylthio)phenyl]ethynyl]phenyl]-15-[4-[(trimethylsilyl)ethynyl]phenyl]porphinato(2−)]zinc (8b). Air was removed from a solution of **8a** (21 mg, 20.3 μmol) in 6 mL of DMF/Et_3N (5:1) by blowing argon for 20 min. Then, Pd_2dba_3 (1.4 mg, 1.5 μmol), $AsPh_3$ (3.7 mg, 12.1 μmol), and TMSA (28 μL, 0.2 mmol) were added. Thereafter, the mixture was heated at 45 °C for 3 h. The solvent was removed under reduced pressure, and the crude product was purified by CC (CH_2Cl_2/hexane 9:11 and then 11:9) to yield 16.1 mg (79%) of **8b**: UV/vis (CH_2Cl_2) 422 (5.73), 550 (4.37), 590 (3.71); ^1H NMR (200.00 MHz) δ 0.38 (s, 9H), 1.82 (s, 12H), 2.34 (s, 3H), 2.63 (s, 6H), 7.13 (m, 1H), 7.28 (s, 4H), 7.28 (m, 1H), 7.32 (m, 1H), 7.41 (m, 1H), 7.86 and 8.19 (AA′XX′, J_{AX} =

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8.4, 4H), 7.91 and 8.24 (AA′XX′, $J_{AX} = 8.2$, 4H), 8.78 and 8.85 (2 × d, $J = 4.7$, 4H), 8.80 and 8.90 (2 × d, $J = 4.7$, 4H); FAB-MS 1004.9 (calcd average mass for $C_{64}H_{54}N_4SSiZn$ 1004.69).

[15-(4-Ethynylphenyl)-10,20-bis(mesityl)-5-[4-[[3-(methylthio)phenyl]ethynyl]phenyl]porphinato(2−)]zinc (8c) was obtained as described for **1c**, reacting **8b** (13.5 mg, 13.4 μmol) in 4 mL of THF with 2.5 mL of NaOH (1 N) for 5 h. After purification by CC ($CHCl_3$/hexane 1:1 then 3:2), 10.9 mg (87%) of **8c** was obtained: UV/vis (CH_2Cl_2) 422 (5.67), 510 (3.77), 549 (4.35), 590 (3.78); ^{1}H NMR (360.14 MHz) δ 1.83 (s, 12H), 2.39 (s, 3H), 2.63 (s, 6H), 3.30 (s, 1H), 7.16 (ddd, $J = 7.8, 1.9, 1.1$, 1H), 7.28 (s, 4H), 7.29 (t, $J = 7.8$, 1H), 7.38 (t, $J = 1.9$), 7.41 (dt, $J = 7.8, 1.1$, 1H), 7.87 and 8.20 (AA′XX′, $J_{AX} = 8.4$, 4H), 7.91 and 8.24 (AA′XX′, $J_{AX} = 8.3$, 4H), 8.77 and 8.84 (2 × d, $J = 4.6$, 4H), 8.82 and 8.88 (2 × d, $J = 4.6$, 4H); FAB-MS 932.7 (calcd average mass for $C_{61}H_{46}N_4SZn$ 932.51).

[15-[4-[[4-[(4-Iodophenyl)ethynyl]phenyl]ethynyl]phenyl]-10,20-bis(mesityl)-5-[4-[[3-(methylthio)phenyl]ethynyl]phenyl]porphinato(2−)]zinc (8d). Air was removed from a solution of **8c** (12.1 mg, 13.0 μmol) and 4,4′-diiodotolane[27,46] (28.5 mg, 66.3 μmol) in 7 mL of DMF/Et_3N (5:1) by blowing argon for 20 min. Then, $Pd(PPh_3)_4$ (2.4 mg, 2.1 μmol) was added, and deaeration was continued for 10 min before 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 ($CHCl_3$/hexane: gradient from 3:7 to 11:9) to yield 14.2 mg (89%) of **8d**: UV/vis (CH_2Cl_2) 320 (4.78), 423 (5.70), 550 (4.40), 590 (3.87); ^{1}H NMR (360.14 MHz) δ 1.83 (s, 12H), 2.46 (s, 3H), 2.63 (s, 6H), 7.21 (ddd, $J = 8.0, 1.7, 1.1$, 1H), 7.28 and 7.72 (AA′XX′, $J_{AX} = 8.6$, 4H), 7.29 (s, 4H), 7.31 (t, $J = 8.0$, 1H), 7.43 (ddd, $J = 8.0, 1.7, 1.1$, 1H), 7.44 (t, $J = 1.7$, 1H), 7.57 and 7.65 (AA′XX′, $J_{AX} = 8.6$, 4H), 7.92 and 8.24 (2 × AA′XX′, $J_{AX} = 8.2$, 2 × 4H), 8.80 (2 × d, $J = 4.6$, 4H), 8.90 (2 × d, $J = 4.6$, 4H); FAB-MS 1235.2 (calcd average mass for $C_{75}H_{53}IN_4SZn$ 1234.62).

[10,20-Bis(mesityl)-5-[4-[[3-(methylthio)phenyl]ethynyl]phenyl]-15-[4-[[4-[[4-[(triisopropylsilyl)ethynyl]phenyl]ethynyl]phenyl]ethynyl]phenyl]porphinato(2−)]zinc (8e). Air was removed from a solution of **8a** (23.1 mg, 22.3 μmol) and **5d** (17.0 mg, 44.4 μmol) in 6 mL of DMF/Et_3N (5:1) by blowing argon for 20 min. Then, Pd_2dba_3 (1.5 mg, 1.6 μmol) and $AsPh_3$ (4.1 mg, 13.4 μmol) were added, and deaeration was continued for 10 min before the mixture was heated at 45 °C for 4 h. The solvent was removed under reduced pressure, and the crude product was purified by CC ($CHCl_3$/hexane: gradient from 2:8 to 2:3) to yield 21.6 mg (75%) of **8e**: UV/vis (CH_2Cl_2) 266 (4.99), 326 (4.88), 424 (5.72), 550 (4.44), 588 (3.85); ^{1}H NMR (360.14 MHz) δ 1.15 (m, 21H), 1.83 (s, 12H), 2.35 (s, 3H), 2.63 (s, 6H), 7.13 (m, 1H), 7.28 (s, 4H), 7.33 (m, 1H), 7.40 (m, 1H), 7.43 (m, 1H), 7.49 (s, 4H), 7.57 and 7.65 (AA′XX′, $J_{AX} = 8.6$, 4H), 7.92 and 8.24 (2 × AA′XX′, $J_{AX} = 8.3$, 2 × 4H), 8.80 (d, $J = 4.6$, 4H), 8.90 and 8.91 (2 × d, $J = 4.6$, 4H); FAB-MS 1289.7 (calcd average mass for $C_{86}H_{74}N_4SSiZn$ 1289.08).

[15-[4-[[4-[(4-Ethynylphenyl)ethynyl]phenyl]ethynyl]phenyl]-10,20-bis(mesityl)-5-[4-[[3-(methylthio)phenyl]ethynyl]phenyl]porphinato(2−)]zinc (8f). To a solution of **8e** (20 mg, 15.5 μmol) in 2 mL of THF was added TBAF (1 M in THF, 16 μL, 16 μmol), and the mixture was stirred at 20 °C for 1 h. A few grains of $CaCl_2$ were added to remove any excess of fluoride (cf. ref 42) before the solvent was evaporated, and the crude product was purified by CC ($CHCl_3$/hexane: gradient from 2:8 to 2:3) to yield 9.4 mg (53%) of **8f**: UV/vis (CH_2Cl_2) 324 (4.81), 424 (5.72), 550 (4.41), 590 (3.80); ^{1}H NMR (360.14 MHz) δ 1.83 (s, 12H), 2.46 (s, 3H), 2.63 (s, 6H), 3.20 (s, 1H), 7.21 (m, 1H), 7.28 (s, 4H), 7.32 (m, 1H), 7.43 (m, 2H), 7.51 (m, 4H), 7.58 and 7.66 (AA′XX′, $J_{AX} = 8.3$, 4H), 7.92 and 8.24 (2 × AA′XX′, $J_{AX} = 8.3$, 2 × 4H), 8.80 (d, $J = 4.6$, 4H), 8.90 (2 × d, $J = 4.6$, 4H); FAB-MS 1133.3 (calcd avg mass for $C_{77}H_{54}N_4SZn$ 1132.74).

Triporphyrin 10a. Air was removed from a solution of **1c** (2.04 mg, 13.6 μmol) and **9a**[47] (39.1 mg, 52.8 μmol) in 9 mL of DMF/Et_3N (5:1) by blowing argon for 20 min. Then, $Pd(PPh_3)_4$ (7.7 mg, 6.7 μmol) was added, and deaeration was continued for 10 min before the mixture was heated at 45 °C for 20 h. The solvent was removed under reduced pressure, and the crude product was purified by CC ($CHCl_3$/hexane: gradient from 3:2 to 3:1) to yield 12.0 mg (44%) of **10a**: UV/vis (CH_2Cl_2) 288 (4.98), 374 (4.82), 420 (6.09), 516 (4.70), 550 (4.39), 590 (4.13); ^{1}H NMR (360.14 MHz) δ −2.76 (s, 6H), 7.73−7.82 (m, 27H), 8.03 and 8.29 (AA′XX′, $J_{AX} = 8.4$, 12H), 8.04 (s, 3H, H-benzenetriyl), 8.21−8.25 (m, 18H), 8.86 (s, 12H), 8.90 (s, 12H); ES$^+$-MS (in THF/MeOH) m/z 1989.3 ([MH]$^+$), 994.9 ([MH$_2$]$^{2+}$) (calcd average mass for $C_{144}H_{90}N_{12}$: 1988.38).

Triporphyrin 10b was obtained in 56% yield (11.1 mg), after purification by CC ($CHCl_3$/hexane: gradient from 3:7 to 3:2), reacting **1c** (1.37 mg, 9.1 μmol) with **9b**[27] (29.1 mg, 36.5 μmol) in the presence of $Pd(PPh_3)_4$ (4.7 mg, 4.1 μmol), in 6 mL of DMF/Et_3N, as described for **10a**: UV/vis (CH_2Cl_2) 293 (5.04), 416 (5.85), 528 (4.74); ^{1}H NMR (500.13 MHz) δ 7.65−7.73 (m, 27H), 7.92 and 8.06 (AA′XX′, $J_{AX} = 8.2$, 12H), 7.96 (s, 3H, H-benzenetriyl), 8.00−8.04 (m, 18H), 8.75 (s, 12H), 8.79 (2 × d, $J = 4.7$, 12H); FAB-MS 2158.7 (calcd average mass for $C_{144}H_{84}N_{12}Ni_3$: 2158.49).

Triporphyrin 10c was obtained in 65% yield (20.3 mg), after purification by two successive CC ($CHCl_3$/hexane 7:3), reacting **1c** (2.15 mg, 14.3 μmol) with **9c**[27] (46 mg, 57.2 μmol) in the presence of $Pd(PPh_3)_4$ (7.4 mg, 6.4 μmol), in 9 mL DMF/Et_3N, as described for **10a**: UV/vis (CH_2Cl_2) 298 (4.98), 422 (6.14), 548 (4.81), 589 (4.20); UV/vis (benzene) 292 (4.97), 425 (6.12), 550 (4.81), 590 (4.22); EMS (benzene) λ_{em} 602, 650; ^{1}H NMR (500.13 MHz) δ 7.73−7.80 (m, 27H), 8.02 and 8.29 (AA′XX′, $J_{AX} = 8.2$, 12H), 8.04 (s, 3H, H-benzenetriyl), 8.22−8.25 (m, 18H), 8.96 (s, 12H), 9.00 and 9.01 (2 × d, $J = 4.7$, 12H); ES-MS 2179.0 (calcd average mass for $C_{144}H_{84}N_{12}Zn_3$ 2178.47); FAB-MS 2178.3 (M$^+$), 1089 (M^{2+}).

Triporphyrin 10d. Method A. 10d was obtained in 66% yield (8.4 mg), after purification by two successive CC ($CHCl_3$/hexane gradient from 3:2 to 7:3), reacting **1c** (0.69 mg, 4.6 μmol) with **9d**[27] (18.5 mg, 18.4 μmol) in the presence of $Pd(PPh_3)_4$ (2.4 mg, 2.1 μmol), in 6 mL of DMF/Et_3N, as described for **10a**. **Method B.** Air was removed from a solution of **1e** (3.11 mg, 4.14 μmol) and **9c** (13.2 mg, 16.5 μmol) in 2.8 mL of DMF/Et_3N (5:1) by blowing argon for 20 min. Then, Pd_2dba_3 (0.46 mg, 0.5 μmol) and $AsPh_3$ (1.24 mg, 4.05 μmol) were added, and deaeration was continued for 10 min, before the mixture was heated at 30 °C during 4 h. Then, the same amounts of Pd_2dba_3 and $AsPh_3$ were added again, and stirring was continued for 2 h. The solvent was removed under reduced pressure, and the crude product was purified by CC ($CHCl_3$/hexane: gradient from 3:7 to 4:1) to yield 7.0 mg (61%) of **10d**: UV/vis (CH_2Cl_2) 349 (5.27), 422 (6.13), 549 (4.75), 589 (4.18); UV/vis (benzene) 342 (5.27), 425 (6.11), 550 (4.79), 590 (4.23); EMS (benzene) λ_{em} 602, 650; ^{1}H NMR (500.13 MHz) δ 7.55 and 7.57 (AA′XX′, $J_{AX} = 8.6$, 12H), 7.61 and 7.68 (AA′XX′, $J_{AX} = 8.4$, 12H), 7.71 (s, 3H, H-benzenetriyl), 7.73−7.81 (m, 27H), 7.95 and 8.25 (AA′XX′, $J_{AX} = 8.3$, 12H), 8.21−8.24 (m, 18H), 8.96 (s, 12H), 8.97 and 8.98 (2 × d, $J = 4.7$, 12H); FAB-MS 2778.8 (calcd avg mass for $C_{192}H_{108}N_{12}Zn_3$ 2779.19).

Triporphyrin 10e was obtained in 44% yield (6.0 mg), after purification by CC ($CHCl_3$/hexane: gradient from 1:1 to $CHCl_3$), reacting **1e** (3.03 mg, 4.04 μmol) with **9d** (17.6 mg, 17.6 μmol) in the presence of Pd_2dba_3 (0.48 mg, 0.52 μmol) and $AsPh_3$ (1.27 mg, 4.15 μmol), in 3.2 mL of DMF/Et_3N, as described for **10d** (method B): UV/vis ($CHCl_3$) 364 (5.44), 424 (6.02), 552 (4.66), 592 (4.24), 598 (4.22); ^{1}H NMR (500.13 MHz) δ 7.52−7.58 (m, 36 H), 7.61 and 7.68 (AA′XX′, $J_{AX} = 8.3$, 12H), 7.69 (s, 3H, H-benzenetriyl), 7.73−7.80 (m, 27H), 7.94 (apparent d, $J = 8.1$, 6H), 8.21−8.25 (m, 24H), 8.95 (s, 12H), 8.96 and 8.98 (2 × d, $J = 4.7$, 12H); ES$^+$-MS (in $CHCl_3$/MeOH/HCOOH) m/z 1595.8 ([M − 3Zn + 8H]$^{2+}$), 1064.2 ([M − 3Zn +

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9H]$^{3+}$) (calcd average mass for $C_{240}H_{132}N_{12}Zn_3$ 3379.90). Atomic absorption calcd: Zn, 5.80. Found: Zn, 5.76.

Triporphyrin 11a was obtained in 57% yield (7.6 mg), after purification by CC ($CHCl_3$/hexane: gradient from 2:3 to 7:3), reacting **1c** (0.70 mg, 4.7 μmol) with **8a** (19.5 mg, 18.9 μmol) in the presence of $Pd(PPh_3)_4$ (2.5 mg, 2.2 μmol), in 12 mL of DMF/Et_3N, as described for **10a**: UV/vis (CH_2Cl_2) 294 (5.19), 425 (6.16), 550 (4.91), 590 (4.37); ^1H NMR (500.13 MHz) δ 1.85 (s, 36H), 2.51 (s, 9H), 2.64 (s, 18H), 7.25 (ddd, J = 8.0, 1.9, 1.1, 3H), 7.30 (2 × s, 12H), 7.33 (t, J = 8.0, 3H), 7.44 (ddd, J = 7.7, 1.5, 1.1, 3H), 7.49 (t, J = 1.5, 3H), 7.93 and 8.25 (AA′XX′, J_{AX} = 8.4, 12H), 8.02 and 8.31 (AA′XX′, J_{AX} = 8.5, 12H), 8.03 (s, 3H, H-benzenetriyl), 8.81 and 8.91 (2 × d, J = 4.6, 12H), 8.83 and 8.95 (2 × d, J = 4.6, 12H); ES$^+$-MS (in $CHCl_3$/MeOH) m/z 2870.4 ([MH]$^+$), 1435.1 ([MH$_2$]$^{2+}$), 956.5 ([MH$_3$]$^{3+}$) (calcd average mass for $C_{189}H_{138}N_{12}S_3Zn_3$ 2869.59).

Triporphyrin 11b. Method A. 11b was obtained in 66% yield (5.8 mg), after purification by CC ($CHCl_3$/hexane gradient from 1:1 to 7:3), reacting **1c** (0.38 mg, 2.5 μmol) with **8d** (12.6 mg, 10.2 μmol) in the presence of $Pd(PPh_3)_4$ (1.3 mg, 1.1 μmol), in 6.5 mL of DMF/Et_3N, as described for **10a**. **Method B. 11b** was obtained in 22% yield (1.5 mg), after purification by CC ($CHCl_3$/hexane: gradient from 1:1 to 7:3), reacting **8f** (9.2 mg, 8.1 μmol) with **1a** (0.90 mg, 1.97 μmol) in the presence of $Pd(PPh_3)_4$ (1 mg, 0.9 μmol), in 4 mL of DMF/Et_3N, as described for **10a**. **Method C. 11b** was prepared as described for **10d** (method B), reacting **1e** (2.12 mg, 2.82 μmol) with **8a** (11.7 mg, 11.3 μmol) in the presence of Pd_2dba_3 (0.38 mg, 0.41 μmol) and $AsPh_3$ (1.02 mg, 3.33 μmol), in 2.3 mL of DMF/Et_3N at 30 °C for 5 h. After purification by CC ($CHCl_3$/hexane: gradient from 2:3 to 7:3), 4.7 mg (48%) was obtained: UV/vis (CH_2Cl_2) 342 (5.35), 4.24 (6.14), 510 (4.27), 550 (4.86), 592 (4.35); ^1H NMR (500.13 MHz) δ 1.84 (s, 36H), 2.53 (s, 9H), 2.64 (s, 18H), 7.26 (ddd, J = 7.9, 1.9, 1.1, 3H), 7.29 (2 × s, 12H), 7.34 (dd, J = 7.9, 7.7, 3H), 7.44 (dt, J = 7.7, 1.1, 3H), 7.50 (t, J = 1.9, 3H), 7.57 and 7.59 (AA′XX′, J_{AX} = 8.7, 12H), 7.61 and 7.68 (AA′XX′, J_{AX} = 8.4, 12H), 7.72 (s, 3H, H-benzenetriyl), 7.93 and 8.25 (AA′XX′, J_{AX} = 8.1, 12H), 7.94 and 8.26 (AA′XX′, J_{AX} = 8.1, 12H), 8.81 and 8.90 (2 × d, J = 4.6, 12H), 8.81 and 8.91 (2 × d, J = 4.6, 12H); ES$^+$-MS (in $CHCl_3$/MeOH) m/z 1735.1 ([MH$_2$]$^{2+}$) (calcd average mass for $C_{237}H_{162}N_{12}S_3Zn_3$ 3470.32).

Triporphyrin 11c was obtained in 54% yield (6.0 mg), after purification by CC ($CHCl_3$/hexane: gradient from 9:11 to 4:1), reacting **1e** (2.04 mg, 2.72 μmol) with **8d** (13.7 mg, 11.1 μmol) in the presence of Pd_2dba_3 (0.57 mg, 0.62 μmol) and $AsPh_3$ (1.49 mg, 4.87 μmol), in 3.8 mL of DMF/Et_3N, as described for **10d** (method B): UV/vis (CH_2Cl_2) 366 (5.43), 424 (6.01), 552 (4.72), 584 (4.26), 592 (4.29); ^1H NMR (500.13 MHz) δ 1.84 (s, 36H), 2.53 (s, 9H), 2.64 (s, 18H), 7.26 (m, 3H), 7.30 (s, 12H), 7.33 (t, J = 7.7, 3H), 7.44 (dt, J = 7.7, 1.4, 3H), 7.51 (t, J = 1.9, 3H), 7.52−7.57 (m, 36H), 7.60 and 7.68 (AA′XX′, J_{AX} = 8.3, 12H), 7.69 (s, 3H), 7.92 and 8.23 (AA′XX′, J_{AX} = 8.1, 12H), 7.93 and 8.24 (AA′XX′, J_{AX} = 8.1, 12H), 8.80 and 8.90 (2 × d, J = 4.7, 12H), 8.80 and 8.90 (2 × d, J = 4.7, 12H); ES$^+$-MS (in $CHCl_3$/MeOH/HCOOH) m/z 1294.5 ([M − 3Zn + 9H]$^{3+}$) (calcd average mass for $C_{285}H_{186}N_{12}S_3Zn_3$ 4071.00). Atomic absorption calcd: Zn, 4.82. Found: Zn, 4.77.

[[4-[[4-[[5-Iodo-3-[(trimethylsilyl)ethynyl]phenyl]ethynyl]phenyl]ethynyl]phenyl]ethynyl]triisopropylsilane (12). Air was removed from a solution of **2** (39.6 mg, 92.9 μmol) and **5d** (32.0 mg, 83.6 μmol) in 6 mL of pyridine/Et_3N (1:1) by blowing argon for 20 min. Then, $Pd(PPh_3)_4$ (5.4 mg, 4.7 μmol) and CuI (1.8 mg, 9.4 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 hexane to CH_2Cl_2/hexane 1:24) to yield 34.8 mg (61%) of **12**: ^1H NMR (200.00 MHz) δ 0.25 (s, 9H), 1.14 (m, 21H), 7.46 (s, 4H), 7.49 (m, 4H), 7.58 (t, J = 1.5, 1H), 7.77 (t, J = 1.5, 1H), 7.81 (t, J = 1.5, 1H); ^{13}C NMR (50.30 MHz) δ −0.2, 11.3, 18.7, 88.8, 90.7, 90.8, 91.3, 93.0, 96.8, 102.2, 106.6, 122.5, 122.8, 123.4, 123.6, 124.9, 125.2, 131.4, 131.6, 132.0, 134.0, 139.9, 140.2; FAB-MS 681 (M$^+$, 78), 637 ([M − *i*-Pr]$^+$, 85), 595 ([M − 2*i*-Pr]$^+$, 50), 567 (100). Anal. Calcd for $C_{38}H_{41}ISi_2$ (680.83): C, 67.04; H, 6.07. Found: C, 67.12; H, 6.11.

[10,20-Bis(mesityl)-5-[4-[[3-(methylthio)phenyl]ethynyl]phenyl]-15-[4-[[5-[[4[[4-[(triisopropylsilyl)ethynyl]phenyl]ethynyl]phenyl]ethynyl]-3-[(trimethylsilyl)ethynyl]phenyl]ethynyl]phenyl]porphinato(2−)]zinc (13a) was obtained in 81% yield (10.8 mg), after purification by CC ($CHCl_3$/hexane: gradient from 2:3 to 1:1), reacting **12** (6.1 mg, 8.9 μmol) with **8c** (10.0 mg, 10.7 μmol) in the presence of $Pd(PPh_3)_4$ (1.5 mg, 1.3 μmol), in 2 mL of DMF/Et_3N, as described for **10a**: UV/vis (CH_2Cl_2) 334 (4.98), 422 (5.74), 550 (4.42), 592 (3.84); ^1H NMR (360.14 MHz) δ 0.30 (s, 9H), 1.14 (m, 21H), 1.83 (s, 12H), 2.47 (s, 3H), 2.64 (s, 6H), 7.23 (ddd, J = 7.4, 1.4, 1.1, 1H), 7.29 (s, 4H), 7.32 (t, J = 7.4, 1H), 7.43 (dt, J = 7.4, 1.1, 1H), 7.44 (t, J = 1.4, 1H), 7.47 (s, 4H), 7.53 (s, 4H), 7.66, 7.75 and 7.78 (3 × t, J = 1.4, 3 × 1H, H-4, H-2 and H-6 benzenetriyl, respectively), 7.91 and 8.25 (AA′XX′, J_{AX} = 8.3, 4H), 7.92 and 8.24 (AA′XX′, J_{AX} = 8.3, 4H), 8.80 (2 × d, J = 4.6, 4H), 8.90 (2 × d, J = 4.6, 4H); FAB-MS 1484.8 (calcd average mass for $C_{99}H_{86}N_4SSi_2Zn$ 1485.41).

[15-[4-[[5-[[4-[(4-Ethynylphenyl)ethynyl]phenyl]ethynyl]-3-(ethynyl)phenyl]ethynyl]phenyl]-10,20-bis(mesityl)-5-[4-[[3-(methylthio)phenyl]ethynyl]phenyl]porphinato-(2−)]zinc (13b) was obtained in 95% yield (8.2 mg), as described for **8f**, from **13a** (10.2 mg, 6.9 μmol), after 10 min reaction time and purification by CC ($CHCl_3$/hexane 11:9): UV/vis (CH_2Cl_2) 330 (4.90), 422 (5.68), 550 (4.38), 592 (3.82); ^1H NMR (360.14 MHz) δ 1.83 (s, 12H), 2.51 (s, 3H), 2.64 (s, 6H), 3.17 (s, 1H), 3.19 (s, 1H), 7.24 (m, 1H), 7.29 (s, 4H), 7.33 (t, J = 7.7, 1H), 7.44 (dt, J = 7.7, 1.4, 1H), 7.49 (s, 4H), 7.52 (t, J = 1.4, 1H), 7.54 (s, 4H), 7.67, 7.76 and 7.82 (3 × t, J = 1.5, 3 × 1H, H-4, H-2 and H-6 benzenetriyl, respectively), 7.92 and 8.24 (2 × AA′XX′, J_{AX} = 8.3, 2 × 4H), 8.80 and 8.90 (2 × d, J = 4.6, 4H), 8.81 and 8.90 (2 × d, J = 4.6, 4H); FAB-MS 1255.7 (calcd average mass for $C_{87}H_{58}N_4SZn$ 1256.89).

Triporphyrin 14 was obtained in 67% yield (6.7 mg), after purification by two successive CC ($CHCl_3$/hexane: gradient from 1:1 to 7:3), reacting **13b** (3.6 mg, 2.9 μmol) with **8d** (8.9 mg, 7.2 μmol) in the presence of $Pd(PPh_3)_4$ (1 mg, 0.9 μmol), in 5.5 mL of DMF/Et_3N, as described for **10a**: UV/vis (CH_2Cl_2) 358 (5.23), 424 (6.07), 550 (4.77), 592 (4.23); ^1H NMR (500.13 MHz) δ 1.84 (s, 24H), 1.85 (s, 12H), 2.54 (s, 9H), 2.64 (s, 12H), 2.65 (s, 6H), 7.27 (ddd, J = 8.0, 1.9, 1.1, 3H), 7.29 (s, 8H), 7.30 (s, 4H), 7.34 (t, J = 7.6, 3H), 7.45 (ddd, J = 7.6, 1.9, 1.1, 3H), 7.52 (t, J = 1.9, 3H), 7.55 and 7.56 (2 × s, 8H), 7.58 (m, 4H), 7.60 (s, 4H), 7.60 and 7.67 (AA′XX′, J_{AX} = 8.4, 4H), 7.62 and 7.68 (AA′XX′, J_{AX} = 8.4, 4H), 7.76, 7.83 and 7.85 (3 × t, J = 1.5, 3 × 1H, H-benzenetriyl), 7.92 and 8.24 (AA′XX′, J_{AX} = 8.1, 8H), 7.93 and 8.25 (AA′XX′, J_{AX} = 8.3, 4H), 7.94 and 8.25 (2 × AA′XX′, J_{AX} = 8.2, 8H), 7.95 and 8.27 (AA′XX′, J_{AX} = 8.2, 4H), 8.803 and 8.900 (2 × d, J = 4.7, 8H), 8.806 and 8.900 (2 × d, J = 4.7, 4H), 8.807 and 8.904 (2 × d, J = 4.7, 4H), 8.810 and 8.906 (2 × d, J = 4.6, 4H), 8.820 and 8.920 (2 × d, J = 4.7, 4H); ES$^+$-MS (in $CHCl_3$/MeOH) m/z 1640.9 ([M − 3Zn + 8H]$^{2+}$), 1094.4 ([M − 3Zn + 9H]$^{3+}$), 821.0 ([M − 3Zn + 10H]$^{4+}$) (calcd average mass for $C_{237}H_{162}N_{12}S_3Zn_3$ 3470.32). Atomic absorption calcd: Zn, 5.65. Found: Zn, 5.55.

[2-Methyl-4-[5-[(trimethylsilyl)ethynyl]-3-[[4-(10,15,20-triphenyl-21*H*,23*H*-porphin-5-yl)phenyl]ethynyl]phenyl]-3-butyn-2-olato(2−)-*N*^{21},*N*^{22},*N*^{23},*N*^{24}]zinc (15a) was obtained in 92% yield (32.3 mg), after purification by CC ($CHCl_3$/hexane 7:3), reacting **3** (14 mg, 36.6 μmol) with [5-(4-ethynylphenyl)-10,15,20-triphenylporphinato(2−)]zinc[27] (28.3 mg, 40.3 μmol) in the presence of $Pd(PPh_3)_4$ (6.3 mg, 5.5 μmol), in 9 mL of DMF/Et_3N, as described for **10a**: UV/vis (CH_2Cl_2) 290 (4.56), 421 (5.71), 510 (3.68), 549 (4.35), 589 (3.79); ^1H NMR (500.13 MHz) δ 0.28 (s, 9H), 1.62 (s, 6H), 1.97 (s, 1H), 7.55, 7.66 and 7.72 (3 × t, J = 1.6, 3 × 1H, H-6, H-4 and H-2 benzenetriyl, respectively), 7.73−7.80 (m, 9H), 7.90 and 8.22 (AA′XX′, J_{AX} = 8.3, 4H), 8.20−8.24 (m, 6H), 8.95 (s, 4H), 8.95 and 8.97 (2 × d, J = 4.7, 4H); FAB-MS 956.4 (calcd average mass for $C_{62}H_{46}N_4OSiZn$ 956.54).

[4-[5-Ethynyl-3-[[4-(10,15,20-triphenyl-21*H*,23*H*-porphin-5-yl)phenyl]ethynyl]phenyl]-2-methyl-3-butyn-2-olato-(2−)-*N*^{21},*N*^{22},*N*^{23},*N*^{24}]zinc (15b) was obtained in 94% yield (25.7 mg), as described for **8f**, from **15a** (29.5 mg, 30.8 μmol) after 3 h reaction time and purification by CC ($CHCl_3$/hexane 4:1): UV/vis (CH_2Cl_2) 290 (4.57), 421 (5.72), 512 (3.67), 548 (4.36), 589 (3.74); ^1H NMR (500.13 MHz) δ 1.62 (s, 6H), 1.97 (s, 1H), 3.14 (s, 1H), 7.55, 7.70 and 7.72 (3 × t, $J = 1.6$, 3 × 1H, H-6, H-4 and H-2 benzenetriyl, respectively), 7.73−7.80 (m, 9H), 7.91 and 8.23 (AA′XX′, $J_{AX} = 8.3$, 4H), 8.20−8.24 (m, 6H), 8.95 (s, 4H), 8.95 and 8.97 (2 × d, $J = 4.7$, 4H). FAB-MS: 884.2 (calcd average mass for $C_{59}H_{38}N_4OZn$: 884.36).

Diporphyrin 16a was obtained in 86% yield (36.3 mg), after purification by CC (CH_2Cl_2/hexane: gradient from 7:3 to 4:1), reacting **15b** (24 mg, 27.1 μmol) with **9b** (28.1 mg, 35.2 μmol) in the presence of $Pd(PPh_3)_4$ (4.7 mg, 4.1 μmol), in 12 mL of DMF/Et_3N, as described for **10a**: UV/vis (CH_2Cl_2) 291 (4.87), 420 (5.89), 534 (4.49), 547 (4.54), 590 (4.03); ^1H NMR (500.13 MHz) δ 1.70 (s, 6H), 2.05 (s, 1H), 7.74 (t, $J = 1.6$, 1H, H-benzenetriyl between NiTPP and alcohol), 7.76 (t, $J = 1.6$, 1H, H-benzenetriyl between ZnTPP and alcohol), 7.91 (t, $J = 1.6$, 1H, H-benzenetriyl between NiTPP and ZnTPP), 7.66−7.73 (m, 9H), 7.74−7.81 (m, 9H), 7.89 and 8.05 (AA′XX′, $J_{AX} = 8.4$, 4H), 7.96 and 8.26 (AA′XX′, $J_{AX} = 8.3$, 4H), 8.00−8.03 (m, 6H), 8.21−8.24 (m, 6H), 8.75 (s, 4H), 8.77 and 8.78 (2 × d, $J = 4.9$, 4H), 8.96 (s, 4H), 8.98 and 8.99 (2 × d, $J = 4.7$, 4H); FAB-MS 1554.0 (calcd average mass for $C_{103}H_{64}N_8NiOZn$ 1553.79).

Diporphyrin 16b. To a solution of **16a** (36.5 mg, 23.5 μmol) in 10 mL of toluene/*i*-PrOH (1:1) was added solid KOH (11 mg), and the mixture was heated under reflux for 2 h. After cooling, the remaining KOH was filtered off and the solvent was evaporated. The crude product was purified by CC ($CHCl_3$/hexane 3:2) to yield 31.4 mg (89%) of **16b**: UV/vis (CH_2Cl_2) 290 (4.79), 420 (5.86), 532 (4.36), 548 (4.45), 588 (3.78); ^1H NMR (500.13 MHz) δ 3.20 (s, 1H), 7.65−7.72 (m, 9H), 7.73−7.80 (m, 9H), 7.79 (t, $J = 1.6$, 1H, H-benzenetriyl between NiTPP and acetylene), 7.81 (t, $J = 1.6$, 1H, H-benzenetriyl between ZnTPP and acetylene), 7.88 and 8.04 (AA′XX′, $J_{AX} = 8.4$, 4H), 7.94 (t, $J = 1.6$, 1H, H-benzenetriyl between NiTPP and ZnTPP), 7.96 and 8.25 (AA′XX′, $J_{AX} = 8.3$, 4H), 8.00−8.03 (m, 6H), 8.21−8.24 (m, 6H), 8.75 (s, 4H), 8.76 and 8.78 (2 × d, $J = 4.9$, 4H), 8.96 (s, 4H), 8.97 and 8.99 (2 × d, $J = 4.7$, 4H); FAB-MS 1495.4 (calcd average mass for $C_{100}H_{58}N_8NiZn$ 1495.69).

Triporphyrin 17a was obtained in 82% yield (23.8 mg), after purification by two successive CC ($CHCl_3$/hexane 1:1 then 3:2), reacting **16b** (20.6 mg, 13.8 μmol) with **9a** (13.4 mg, 18.1 μmol) in the presence of $Pd(PPh_3)_4$ (3.2 mg, 2.8 μmol), in 8 mL of DMF/Et_3N, as described for **10a**: UV/vis (CH_2Cl_2) 292 (5.04), 420 (6.09), 520 (4.58), 548 (4.62), 590 (4.13), 650 (3.84); UV/vis (benzene) 292 (4.97), 424 (6.06), 520 (4.55), 550 (4.61), 590 (4.08), 648 (3.52); EMS (benzene) λ_{em} 603, 655, 719; ^1H NMR (500.13 MHz) δ −2.75 (s, 2H), 7.65−7.73 (m, 9H), 7.73−7.81 (m, 18H), 7.94 and 8.07 (AA′XX′, $J_{AX} = 8.2$, 4H), 8.00 and 8.28 (AA′XX′, $J_{AX} = 8.3$, 4H), 8.00 and 8.28 (AA′XX′, $J_{AX} = 8.3$, 4H), 7.99−8.04 (m, 3H, H-benzenetriyl), 8.01−8.04 (m, 6H), 8.21−8.25 (m, 12H), 8.76 (s, 4H), 8.79 (s, 4H), 8.86 (s, 4H), 8.90 (s, 4H), 8.96 (s, 4H), 9.00 and 9.01 (2 × d, $J = 4.7$, 4H); FAB-MS 2108.0 (calcd average mass for $C_{144}H_{86}N_{12}NiZn$ 2108.45).

Triporphyrin 17b. Method A. To a solution of **17a** (16.0 mg, 7.6 μmol) in $CHCl_3$/MeOH (9:1) was added copper acetate monohydrate (9.1 mg, 45.6 μmol), and the mixture was stirred at 20 °C for 15 min. Thereafter, the mixture was washed with water and dried (Na_2SO_4), and the solvent was evaporated. The residue was purified by CC ($CHCl_3$/hexane 3:2) to yield 15.5 mg (94%) of **17b**. **Method B. 17b** was obtained in 62% yield (6.7 mg), after purification by CC ($CHCl_3$/hexane: gradient from 2:3 to 3:2), reacting **16b** (7.5 mg, 5.0 μmol) with [5-(4-iodophenyl)-10,15,20-triphenylporphinato(2−)]copper[27] (5.2 mg, 6.5 μmol) in the presence of $Pd(PPh_3)_4$ (1.5 mg, 1.3 μmol), in 3 mL of DMF/Et_3N, as described for **10a**: UV/vis (CH_2Cl_2) 296 (4.71), 418 (5.98), 540 (4.69); UV/vis (benzene) 294 (5.05), 420 (5.99), 542 (4.72); EMS (benzene) λ_{em} 602, 649; ^1H NMR (500.13 MHz) δ 7.67−7.70 (m, 9H), 7.72−7.80 (m, 9H), 7.92 and 8.07 (AA′XX′, $J_{AX} = 7.8$, 4H), 7.96−8.04 (m, 3H, H-benzenetriyl), 8.00 and 8.27 (AA′XX′, $J_{AX} = 7.0$, 4H), 8.01−8.03 (m, 6H), 8.22−8.24 (m, 6H), 8.75 (s, 4H), 8.79 (s, 4H), 8.96 (s, 4H), 8.99 (s, 4H); signals for H-phenyl, H-phenylene, and β-H on CuTPP are either very broad or unperceptible; FAB-MS 2172.0 (calcd average mass for $C_{144}H_{84}CuN_{12}NiZn$ 2169.98).

Triporphyrin 17c. To a solution of **17b** (7.5 mg, 3.5 μmol) in $CHCl_3$ (5 mL) was added TFA (0.5 mL), and the mixture was stirred at 20 °C for 2 h. Then the mixture was poured into saturated aqueous 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 3:2 then 3:1) to yield 7.1 mg (97%) of **17c**: UV/vis (CH_2Cl_2) 294 (5.13), 418 (6.04), 532 (4.70); UV/vis (benzene) 290 (4.92), 420 (6.02), 536 (4.60); EMS (benzene) λ_{em} 656, 720; ^1H NMR (500.13 MHz) δ −2.76 (s, 2H), 7.67−7.72 (m, 9H), 7.75−7.80 (m, 9H), 7.93 and 8.07 (AA′XX′, $J_{AX} = 7.8$, 4H), 7.96−8.04 (m, 3H, H-benzenetriyl), 8.00 and 8.27 (AA′XX′, $J_{AX} = 7.8$, 4H), 8.01−8.03 (m, 6H), 8.22−8.24 (m, 6H), 8.76 (s, 4H), 8.79 (s, 4H), 8.86 (s, 4H), 8.89 (s, 4H); signals for H-phenyl, H-phenylene and β-H on CuTPP are either very broad or unperceptible; FAB-MS 2107.0 (calcd average mass for $C_{144}H_{86}CuN_{12}Ni$ 2106.62).

Diporphyrin 18a was obtained in 61% yield (13.8 mg), as described for **8e**, reacting **2** (4.7 mg, 11.1 μmol) with **8c** (31.1 mg, 33.4 μmol) in the presence of Pd_2dba_3 (1.17 mg, 1.28 μmol) and $AsPh_3$ (3.13 mg, 10.22 μmol), in 6.4 mL of DMF/Et_3N at 30 °C after 6 h reaction time and purification by CC ($CHCl_3$/hexane: gradient from 1:1 to 3:2): UV/vis (CH_2Cl_2) 266 (4.98), 294 (4.97), 422 (5.93), 550 (4.64), 590 (3.99), 594 (3.99); ^1H NMR (360.14 MHz) δ 0.33 (s, 9H), 1.84 (s, 24H), 2.51 (s, 6H), 2.64 (s, 12H), 7.25 (ddd, $J = 7.6$, 1.5, 1.2, 2H), 7.29 (s, 8H), 7.32 (t, $J = 7.6$, 2H), 7.44 (dt, $J = 7.6$, 1.5, 2H), 7.49 (t, $J = 1.5$, 2H), 7.81 (d, $J = 1.8$, 2H, H-benzenetriyl), 7.92 and 8.24 (AA′XX′, $J_{AX} = 8.2$, 8H), 7.93 (t, $J = 1.8$, 1H, H-benzenetriyl), 7.95 and 8.27 (AA′XX′, $J_{AX} = 8.2$, 8H), 8.80 and 8.90 (2 × d, $J = 4.6$, 8H), 8.81 and 8.91 (2 × d, $J = 4.6$, 8H); ES^+-MS (in $CHCl_3$/MeOH/HCOOH): 1973.0 ($[M - Zn + 3H]^+$), 1909.5 ($[M - 2Zn + 5H]^+$), 955.1 ($[M - 2Zn + 6H]^{2+}$) (calcd average mass for $C_{133}H_{102}N_8S_2SiZn_2$ 2035.29).

Diporphyrin 18b was obtained in 80% yield (10.6 mg), as described for **8f**, from **18a** (13.8 mg, 6.8 μmol) after 1 min reaction time and purification by CC ($CHCl_3$/hexane: gradient from 3:2 to 7:3): UV/vis (CH_2Cl_2) 262 (4.89), 291 (4.97), 422 (5.87), 550 (4.62), 584 (4.03), 592 (4.08); ^1H NMR (360.14 MHz) δ 1.84 (s, 24H), 2.53 (s, 6H), 2.64 (s, 12H), 3.22 (s, 1H), 7.26 (ddd, $J = 7.6$, 1.5, 1.2, 2H), 7.29 (s, 8H), 7.33 (t, $J = 7.6$, 2H), 7.44 (dt, $J = 7.6$, 1.5, 2H), 7.50 (t, $J = 1.5$, 2H), 7.82 (d, $J = 1.5$, 2H, H-benzenetriyl), 7.92 and 8.24 (AA′XX′, $J_{AX} = 8.2$, 8H), 7.96 and 8.27 (AA′XX′, $J_{AX} = 8.2$, 8H), 7.97 (t, $J = 1.5$, 1H, H-benzenetriyl), 8.80 and 8.90 (2 × d, $J = 4.4$, 8H), 8.82 and 8.92 (2 × d, $J = 4.6$, 8H); ES^+-MS (in $CHCl_3$/MeOH/HCOOH) 1837.2 ($[M - 2Zn + 5H]^+$), 919.1 ($[M - 2Zn + 6H]^{2+}$) (calcd average mass for $C_{130}H_{94}N_8S_2Zn_2$ 1963.11).

Diporphyrin 18c was obtained in 82% yield (9.9 mg), after purification by CC ($CHCl_3$/hexane: gradient from 1:1 to 7:3), reacting **18b** (10.5 mg, 5.3 μmol) with 4,4′-diiodotolane (42.3 mg, 98.4 μmol) in the presence of $Pd(PPh_3)_4$ (3.2 mg, 2.8 μmol), in 6 mL of DMF/Et_3N, as described for **8d**: UV/vis (CH_2Cl_2) 298 (5.00), 422 (5.88), 550 (4.59), 590 (3.94); ^1H NMR (360.14 MHz) δ 1.84 (s, 24H), 2.55 (s, 6H), 2.64 (s, 12H), 7.26 (m, 2H), 7.28 and 7.72 (AA′XX′, $J_{AX} = 8.6$, 4H), 7.29 (s, 8H), 7.34 (dd, $J = 7.9$, 7.5, 2H), 7.45 (ddd, $J = 7.5$, 1.5, 1.2, 2H), 7.53 (t, $J = 1.5$, 2H), 7.56 and 7.60 (AA′XX′, $J_{AX} = 9.0$, 4H), 7.88 (d, $J = 1.5$, 2H, H-benzenetriyl), 7.93 and 8.24 (AA′XX′, $J_{AX} = 8.2$, 8H), 7.97 (t, $J = 1.5$, 1H, H-benzenetriyl), 7.97 and 8.28 (AA′XX′, $J_{AX} = 8.2$, 8H), 8.80 and 8.90 (2 × d, $J = 4.6$, 8H), 8.82 and 8.92 (2 × d, $J = 4.9$, 8H); ES^+-MS (in $CHCl_3$/MeOH/HCOOH) 1101.6 ($[M - Zn + 3H]^{2+}$), 1070.3 ($[M - 2Zn + 6H]^{2+}$) (calcd average mass for $C_{144}H_{101}IN_8S_2Zn_2$ 2265.22).

Dendrimeric hexaporphyrin 19 was obtained in 28% yield (4.0 mg), as described for **8e**, reacting **18c** (20.2 mg, 9.0 μmol) with **1c** (0.32 mg, 2.13 μmol) in the presence of Pd_2dba_3 (0.76 mg, 0.83 μmol) and $AsPh_3$ (2.04 mg, 6.66 μmol), in 2.4 mL of DMF/Et_3N at 30 °C after 5 h reaction time and purification by two successive CC ($CHCl_3$/hexane: gradient from 3:2 to 9:1): UV/vis ($CHCl_3$) 264 (5.37), 298 (5.44), 336 (5.41), 426 (6.30), 552 (5.01), 584 (4.61), 592 (4.61); ^1H NMR

(500.13 MHz) δ 1.84 (s, 72H, *o*-CH_3 mesityl), 2.55 (s, 18H, SMe), 2.64 (s, 36H, *p*-CH_3 mesityl), 7.26 (m, 6H, H-4 methylthiophenyl), 7.30 (s, 24H, H-mesityl), 7.34 (dd, $J = 8.2, 7.6$, 6H, H-5 methylthiophenyl), 7.45 (dt, $J = 7.6$, 6H, H-6 methylthiophenyl), 7.53 (m, 6H, H-2 methylthiophenyl), 7.55 and 7.57 (AA′BB′, 12H, H-phenylene on central benzenetriyl), 7.59 and 7.62 (AA′BB′, $J_{AB} = 7.8$, 12H, H-phenylene), 7.70 (s, 3H, H-central benzenetriyl), 7.89 (d, $J = 1.6$, 6H, H-benzenetriyl), 7.93 and 8.25 (AA′XX′, $J_{AX} = 8.2$, 24H, H-outside phenylene on porphine), 7.97 (t, $J = 1.6$, 3H, H-benzenetriyl), 7.98 and 8.29 (AA′XX′, $J_{AX} = 8.0$, 24H, H-inside phenylene on porphine), 8.81 and 8.90 (2 × d, $J = 4.7$, 24H, outside β-H on porphine), 8.82 and 8.93 (2 × d, $J = 4.7$, 24H, inside β-H on porphine); ES^+-MS (in $CHCl_3$/MeOH/HCOOH) *m*/*z* 1546.4 ($[M - 6Zn + 16H]^{4+}$), 1237.4 ($[M - 6Zn + 17H]^{5+}$), 1031.4 ($[M - 6Zn + 18H]^{6+}$) (calcd average mass for $C_{444}H_{306}N_{24}S_6Zn_6$ 6562.10). Atomic absorption calcd: Zn, 5.98. Found: Zn, 5.88.

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Supporting Information Available: Copies of NMR spectra (58 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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