Synthesis and Light-Harvesting Properties of Niphaphyrins

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The synthesis of *niphaphyrins*, a new class of rigid, snowflake-shaped porphyrin hexamers designed to mimic the light-harvesting antenna complexes of photosynthetic purple bacteria, is described. In these D_6- or D_3-symmetric assemblies, six porphyrin macrocycles, as free bases or as zinc chelates, are covalently attached to the six positions of a benzene core through rigid ethynyl linkers. A very efficient singlet excited-state energy transfer has been observed from the Zn chelates to the free-base porphyrin (Fb) chromophores in a niphaphyrin in which three zinc porphyrin chelates alternate with three porphyrin free bases. The overall yield of energy transfer (Φ_{ET}) has been estimated as 98%.

Introduction

Natural light-harvesting antenna complexes consist of large assemblies of chlorophyll or bacteriochlorophyll (Bchl) molecules along with some accessory pigments, which are held in specific spatial arrangements by a proteinic scaffold. Elucidation of the X-ray structures of the antenna complexes of *Rhodopseudomonas acidophila*[1] and *Rhodospirillium molischianum*[2] has shown that, in these procaryotes, they consist of two concentric circular arrays of bacteriochlorophyll molecules, containing a total of 27 and 24 chromophores, respectively, and that these moieties are non-covalently bound to apoproteins. In the inner ring, which contains two-thirds of the chromophores, the planes of the overlapping bacteriochlorophyll *a* molecules are perpendicularly oriented with respect to the plane of the thyllakoid membrane, whereas in the outer ring, which contains one-third of the chromophores, the planes of these moieties are almost parallel to the membrane plane. These spatial arrangements allow for a most efficient energy transfer through Förster induced dipole–dipole resonance from the short- to the long-wavelength-absorbing pigments within the photosynthetic unit.

In the present article, the synthesis of a new class of porphyrin array is reported, which has been designed to model the natural arrangement of chromophores in the inner rings of the aforementioned antenna complexes. In the synthetic models **4a–c**, six porphyrin macrocycles are covalently bound through rigid ethynyl linkers to the six positions of a benzene core, which replaces the protein scaffold of the natural complex. Such snowflake-shaped porphyrin hexamers, for which we suggest the trivial name *niphaphyrins*,[3] belong semantically to the group of *stellular* (star-like) porphyrins, different types of which have been synthesized in our laboratory[4,5] and elsewhere.[6–13] Compounds **4a**,**c** are, however, the first examples of D_{6h}-symmetric porphyrin hexamers in which rotation of the individual porphyrin chromophores is strongly restricted by intramolecular interactions. A star-shaped porphyrin hexamer has recently been described,[14] but, in contrast to the niphaphyrins, the chromophores of this system are bound to the central benzene through flexible oxymethyl linkages, which permit a variety of conformations and interchromophoric distances. In the cyclic arrays **4a–c**, the diameters of which amount to 4.67 nm, the centre-to-centre interchromophoric distance is 1.32 nm, and is thus still larger than that in the corresponding natural systems, where the average distance between the complexed Mg^{II} ions is only 0.9 nm.

Results and Discussion

Attempts to synthesize the D_6-symmetric niphaphyrins **4a** and **4c** in a single step, either by reacting hexaethynylbenzene[15] with [5-(4-iodophenyl)-10,15,20-tetraphenylporphinato]zinc(II)[16] or by coupling of [5-(4-ethynylphenyl)-10,15,20-tetraphenylporphinato]zinc(II)[16] with either hexabromo- or hexaiodobenzene,[17] in the presence of Pd^{II} and Cu^{I} as catalysts, were unsuccessful in our hands. In NEt_3 at 100 °C (cf. ref.[15,18]) as well as in NEt_3/DMSO at 50 °C (cf. ref.[19]), the reaction led to complex mixtures in which the desired product could not be detected. Under milder conditions (Pd^0, copper-free, and a temperature below 50 °C), an inseparable mixture of lower coupling products was obtained rather than the expected six-fold coupled hexaethynylbenzene. Two other reports[11,13] of unsuccessful attempts to perform six-fold couplings of hexaiodobenzene with ethynyl-substituted porphyrins have recently appeared.

Thus, a three-step sequential synthesis was attempted, using a hexaethynylbenzene derivative (**2**) bearing protected and unprotected ethynyl groups at the 1,3,5- and 2,4,6-positions, respectively. This core, the synthesis of which has recently been reported by Rubin et al.,[20] enables the synthesis of both D_6-symmetric arrays, such as **4a** and **4b**, as well as D_3-symmetric arrays, such as **4b**, in which two different metallation states of the porphyrin chromophores are present in the same molecule.

Reactions of 5-(4-iodophenyl)-10,15,20-triphenylporphine (**1a**) and the corresponding zinc chelate **1b** with **2** in the presence of Pd_2dba_3 and triphenylarsane (cf. ref.[21]) led

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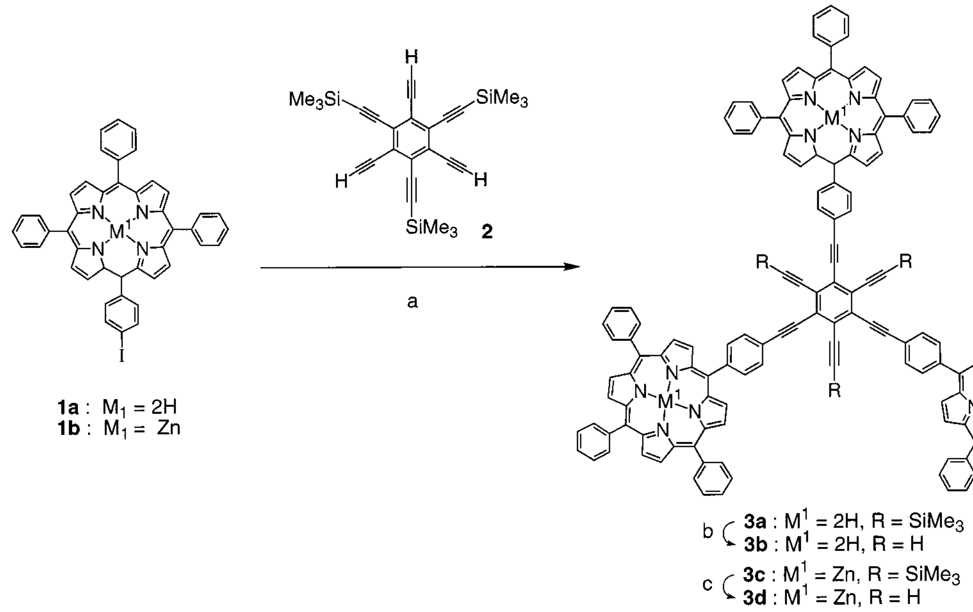
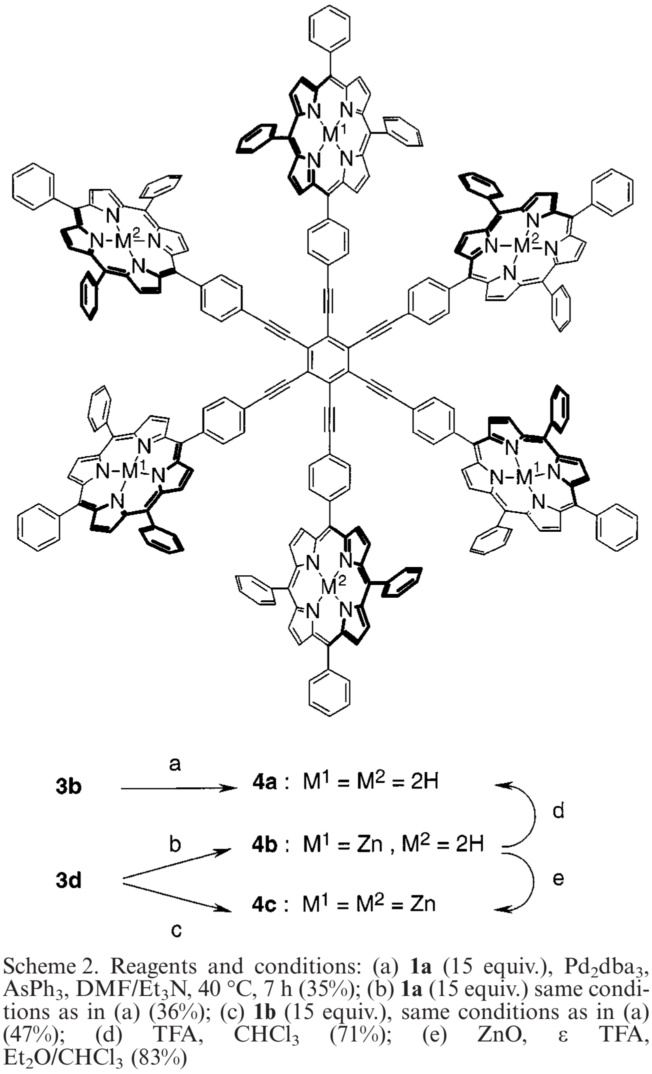


Scheme 1. Reagents and conditions: (a) **2** (1 equiv.), **1a** or **1b** (5 equiv.), Pd_2dba_3, $AsPh_3$, DMF/Et_3N, 40 °C, 6 h (50% of **3a**; 37% of **3c**); (b) 1 M NaOH, THF (70%); (c) 1 M NaOH, THF (81%)

to the porphyrin trimers **3a** and **3c**, respectively, from which the trimethylsilyl protecting groups were removed to afford **3b** and **3d**, respectively (Scheme 1). Coupling of the porphyrin trimer **3b** with a large excess of **1a**, using the same catalyst as above, afforded the free-base porphyrin hexamer **4a**. Analogously, when **3d** was treated with **1b**, the Zn^{II} chelate hexamer **4c** was obtained. On the other hand, reaction of **3d** with **1a** furnished niphaphyrin **4b**, in which three zinc porphyrin chelates alternate with three porphyrin free bases. The overall yields of these three-step sequences amounted to 12% for **4a**, 11% for **4b**, and 14% for **4c**. Alternatively, the D_6-symmetric niphaphyrins **4a** and **4c** could be obtained from **4b** by treatment with acid or by metallation with zinc oxide, respectively (Scheme 2).

Disregarding a red shift of 2–3 nm and a slight broadening of the Soret band, the absorption spectra of the niphaphyrins **4a–c** in benzene correspond to the composite spectrum of the porphyrin monomers, thus indicating weak interactions between the chromophores in the ground state (Figure 1). In the three arrays, the emission spectra are red-shifted by 1 to 2 nm (Figure 2). The fluorescence quantum yields of the free-base hexamer **4a** (Φ_f = 12.1%) and the Zn^{II} chelate hexamer **4c** (Φ_f = 3.8%) are slightly higher than those of TPP (Φ_f = 11%[22]) and ZnTPP (Φ_f = 3.3%[23]), respectively. However, a very efficient intramolecular singlet excited-state energy transfer from the Zn^{II} chelates to the free base porphyrin (Fb) chromophores is observed in the Zn_3Fb_3 hexamer **4b** (Figure 2). By comparison with a solution containing a mixture of the corresponding porphyrin monomers in a 1:1 ratio, the overall yield of energy transfer (Φ_{ET}) was estimated as 98%.

Since the transfer of singlet excited-state energy in **4b** takes place, to some extent, by intramolecular through-bond interactions (Dexter mechanism), which is not operative in the natural light-harvesting arrays, comparison of the



Scheme 2. Reagents and conditions: (a) **1a** (15 equiv.), Pd_2dba_3, $AsPh_3$, DMF/Et_3N, 40 °C, 7 h (35%); (b) **1a** (15 equiv.) same conditions as in (a) (36%); (c) **1b** (15 equiv.), same conditions as in (a) (47%); (d) TFA, $CHCl_3$ (71%); (e) ZnO, ε TFA, $Et_2O/CHCl_3$ (83%)

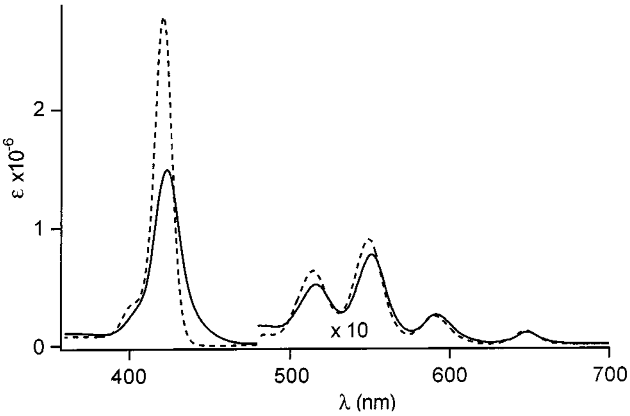


Figure 1. Absorption spectra of **4b** (——) and of a solution of the porphyrin monomers ZnTPP and TPP in a 3:3 ratio (----) in benzene at room temperature

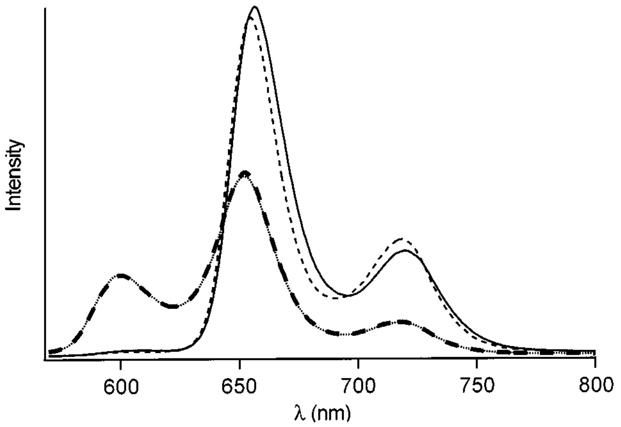


Figure 2. Measured emission spectra of **4b** (——) and of a solution of the porphyrin monomers ZnTPP and TPP in a 3:3 ratio (– – –) in benzene at room temperature (λ_{ex} = 550 nm, A_{550} = 0.036); calculated curves for Φ_{ET} = 0% (······) and for Φ_{ET} = 98% (----)

electronic energy-transfer dynamics in the niphaphyrins described here with that in circular porphyrin hexamers, the synthesis of which has recently been achieved in our laboratory,[24] provides a sound basis for further studies of energy transfer within chromophores, the spatial arrangement of which mimics the light-harvesting arrangement in purple bacteria and other photosynthetic organisms.

Experimental Section

General Remarks: All air- and/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 Merck silica gel 60 F_{254} (0.2 mm) precoated aluminium foil. – Column chromatography (CC): Merck silica gel 60 (0.040–0.063 mm, 230–400 mesh). – UV/Vis spectra were recorded on a Hewlett–Packard 8452A diode-array or a Perkin–Elmer Lambda 40 spectrometer; λ_{max} (log ε) in nm. – Emission spectra (EMS): Perkin–Elmer LS 50B fluorescence spectrometer; λ_{em} in nm. – NMR: Bruker AM 360 (^{1}H, 360.14 MHz) or Bruker Avance DRX 500 (500.13 MHz), in $CDCl_3$ solution unless otherwise stated; chemical shifts (δ) are given in ppm relative to Me_4Si as an internal standard, *J* values in Hz. – Mass spectra: Bruker 4.7T BioAPEX II FT/ICR mass spectrometer, ES$^+$ (electrospray ionization, positive mode). – Tris(dibenzylideneacetone)dipalladium (Pd_2dba_3) and triphenylarsane were purchased from Aldrich Chemie (CH-9471 Buchs); dimethylformamide (DMF), tetrahydrofuran (THF), trifluoroacetic acid (TFA), and other reagents from Fluka Chemie AG (CH-9471 Buchs).

5,5′,5′′-[{2,4,6-Tris[(trimethylsilyl)ethynyl]-1,3,5-benzenetriyl}-tris(2,1-ethynediyl-4,1-phenylene)]tris(10,15,20-triphenyl-21*H*,23*H*-porphine) (3a): Air was removed from a solution of 5-(4-iodophenyl)-10,15,20-triphenylporphine[25] (**1a**) (44 mg, 59.4 μmol) and [(2,4,6-triethynyl-1,3,5-benzenetriyl)tri-2,1-ethynediyl]tris(trimethylsilane) (**2**)[20] (5.2 mg, 11.9 μmol) in 9 mL of DMF/Et_3N (5:1) by passing argon through it for 30 min. Pd_2dba_3 (3.3 mg, 3.6 μmol) and $AsPh_3$ (8.8 mg, 28.8 μmol) were added, deaeration was continued for 10 min, and then the mixture was heated at 40 °C for 6 h. The solvent was subsequently removed under reduced pressure and the crude product was purified by CC ($CHCl_3$/hexane, gradient from 1:1 to 7:3) to yield 13.5 mg (50%) of **3a**. – ^{1}H NMR (360.14 MHz, $CDCl_3$): δ = –2.75 (s, 6 H, NH), 0.52 (s, 27 H, $SiMe_3$), 7.73–7.81 (m, 27 H, phenyl *m*- and *p*-H), 8.20–8.25 (m, 18 H, phenyl *o*-H), 8.08 and 8.30 (AA′XX′, J_{AX} = 8.2 Hz, 12 H, phenylene H), 8.86 (s, 12 H, β-H on exterior of porphine), 8.91 (m, 12 H, β-H on interior of porphine). – UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 351 (5.01), 420 (6.02), 516 (4.82), 552 (4.64), 592 (4.50), 648 (4.43). – ES$^+$-MS (in THF): *m/z* = 1139.5 [M + 2H]$^{2+}$, 760.0 [M + 3H]$^{3+}$ (calcd. avg. mass for $C_{159}H_{114}N_{12}Si_3$: 2276.99).

5,5′,5′′-[(2,4,6-Triethynyl-1,3,5-benzenetriyl)tris(2,1-ethynediyl-4,1-phenylene)]tris(10,15,20-triphenyl-21*H*,23*H*-porphine) (3b): To a solution of **3a** (7.2 mg, 3.16 μmol) in THF (8.2 mL) was added aqueous NaOH (1 M, 4.1 mL) and the mixture was stirred vigorously at 20 °C for 4 h. After evaporation of the THF, CH_2Cl_2 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, 7:3) to yield 4.6 mg (70%) of **3b**. – ^{1}H NMR (360.14 MHz, $CDCl_3$): δ = –2.75 (s, 6 H, NH), 4.08 (s, 3 H, C≡CH), 7.73–7.82 (m, 27 H, phenyl *m*- and *p*-H), 8.21–8.26 (m, 18 H, phenyl *o*-H), 8.11 and 8.31 (AA′XX′, J_{AX} = 8.3 Hz, 12 H, phenylene H), 8.86 (s, 12 H, β-H on exterior of porphine), 8.91 (m, 12 H, β-H on interior of porphine). – UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 348 (4.63), 420 (5.91), 515 (4.55), 552 (4.28), 592 (3.99), 645 (3.96). – ES$^+$-MS (in THF/HCOOH): *m/z* = 1031.2 [M + 2 H]$^{2+}$, 687.8 [M + 3 H]$^{3+}$, 516.4 [M + 4 H]$^{4+}$ (calcd. avg. mass for $C_{150}H_{90}N_{12}$: 2060.44).

{μ$_3$-[{5,5′,5′′-[{2,4,6-Tris[(trimethylsilyl)ethynyl]-1,3,5-benzenetriyl}tris(2,1-ethynediyl-4,1-phenylene)]tris(10,15,20-triphenyl-21*H*,23*H*-porphinato-*N*^{21},*N*^{22},*N*^{23},*N*^{24})}(6–)]}trizinc (3c): Reaction of **1b**[16] (53 mg, 65.9 μmol) with **2**[20] (5.8 mg, 13.2 μmol) in the presence of Pd_2dba_3 (3.8 mg, 4.1 μmol) and $AsPh_3$ (10.2 mg, 33.2 μmol) in 10 mL of DMF/Et_3N as described for **3a**, with subsequent purification by CC ($CHCl_3$/hexane, gradient from 1:1 to 4:1), afforded 12.1 mg (37%) of **3c**. – ^{1}H NMR (360.14 MHz, $CDCl_3$): δ = 0.52 (s, 27 H, $SiMe_3$), 7.73–7.80 (m, 27 H, phenyl *m*- and *p*-H), 8.21–8.25 (m, 18 H, phenyl *o*-H), 8.08 and 8.31 (AA′XX′, J_{AX} = 8.2 Hz, 12 H, phenylene H), 8.96 (s, 12 H, β-H on exterior of porphine), 9.00 and 9.02 (2 d, *J* = 4.7 Hz, 12 H, β-H on interior of porphine). – UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 332 (4.79), 348 (4.78), 421 (6.02), 549 (4.77), 587 (4.34). – ES$^+$-MS (in $CHCl_3$/MeOH): *m/z* = 1234.4 [M + 2 H]$^{2+}$, 823.1 [M + 3 H]$^{3+}$ (calcd. avg. mass for $C_{159}H_{108}N_{12}Si_3Zn_3$: 2467.08).

{μ$_3$-[{5,5′,5′′-[(2,4,6-Triethynyl-1,3,5-benzenetriyl)tris(2,1-ethynediyl-4,1-phenylene)]tris(10,15,20-triphenyl-21*H*,23*H*-

porphinato-N^{21},N^{22},N^{23},N^{24})}(6-)]}trizinc (3d): Reaction of **3c** (8.0 mg, 3.24 μmol) in THF (8 mL) with NaOH (1 M, 4 mL) for 3 h as described for **3b**, with subsequent purification by CC ($CHCl_3$/hexane, 7:3), afforded 5.9 mg (81%) of **3d**. – ^1H NMR (360.14 MHz, $CDCl_3$): δ = 4.08 (s, 3 H, C≡CH), 7.72–7.80 (m, 27 H, phenyl *m*- and *p*-H), 8.21–8.25 (m, 18 H, phenyl *o*-H), 8.11 and 8.31 (AA′XX′, J_{AX} = 8.4 Hz, 12 H, phenylene H), 8.95 (s, 12 H, β-H on exterior of porphine), 8.99 and 9.01 (2 d, *J* = 4.8 Hz, 12 H, β-H on interior of porphine). – UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 348 (5.10), 421 (6.05), 549 (4.83), 585 (4.51). – ES^+-MS (in $CHCl_3$/MeOH/HCOOH): *m/z* = 1031.2 $[M - 3 Zn + 8 H]^{2+}$, 687.8 $[M - 3 Zn + 9 H]^{3+}$ (calcd. avg. mass for $C_{150}H_{84}N_{12}Zn_3$: 2250.53).

Niphaphyrin 4a. – Method A: Air was removed from a solution of **3b** (4.5 mg, 2.18 μmol) and **1a** (24.5 mg, 33.1 μmol) in 2.7 mL of DMF/Et_3N (5:1) by passing argon through it for 30 min. Pd_2dba_3 (1.2 mg, 1.31 μmol) and $AsPh_3$ (3.2 mg, 10.5 μmol) were added, deaeration was continued for 10 min, and then the mixture was heated at 40 °C for 7 h. The solvent was subsequently removed under reduced pressure and the crude product was purified by twofold CC ($CHCl_3$/hexane, gradient from 3.2 to 17:3) to yield 3.0 mg (35%) of **4a**. – **Method B:** A solution of **4b** (1.21 mg, 0.30 μmol) in 2.2 mL of $CHCl_3$/TFA (3:1) was stirred at 20 °C for 3.5 h. It was then poured into saturated aqueous Na_2CO_3 solution and the organic layer was separated, washed with water, and dried (Na_2SO_4). The solvent was evaporated and the residue was purified by CC ($CHCl_3$/hexane, 7:3) to yield 0.82 mg (71%) of **4a**. – ^1H NMR (500.13 MHz, $CDCl_3$) (assignments made with the aid of NOE experiments): δ = –2.88 (s, 12 H, NH), 7.39 (m, 24 H, 10,20-phenyl *m*-H), 7.46 (m, 12 H, 10,20-phenyl *p*-H), 7.66–7.74 (m, 18 H, 15-phenyl *m*- and *p*-H), 7.92 (m, 24 H, 10,20-phenyl *o*-H), 8.13 (m, 12 H, 15-phenyl *o*-H), 8.41 and 8.45 (AA′XX′, J_{AX} = 8.4 Hz, 24 H, 5-phenylene H), 8.66 (d, *J* = 4.7 Hz, 12 H, 2-H and 8-H), 8.69 (d, *J* = 4.9 Hz, 12 H, 12-H and 18-H), 8.75 (d, *J* = 4.9 Hz, 12 H, 13-H and 17-H), 8.91 (d, *J* = 4.7 Hz, 12 H, 3-H and 7-H). – UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 348 (4.63), 420 (6.25), 517 (4.97), 552 (4.69), 591 (4.43), 646 (4.39). – UV/Vis (benzene): λ_{max} = 422, 516, 552, 592, 649. – ES^+-MS (in THF/HCOOH): *m/z* = 1300.5 $[M + 3 H]^{3+}$, 975.6 $[M + 4 H]^{4+}$, 780.7 $[M + 5 H]^{5+}$, 650.8 $[M + 6 H]^{6+}$ (calcd. avg. mass for $C_{282}H_{174}N_{24}$: 3898.64).

Niphaphyrin 4b: Reaction of **3d** (6.0 mg, 2.67 μmol) with **1a** (30 mg, 40.5 μmol) in the presence of Pd_2dba_3 (1.47 mg, 1.6 μmol) and $AsPh_3$ (3.9 mg, 12.7 μmol) in 2.0 mL of DMF/Et_3N as described for **4a** (Method A), with subsequent purification by twofold CC ($CHCl_3$/hexane, gradient from 2:3 to 4:1), afforded 3.9 mg (36%) of **4b**. – ^1H NMR (500.13 MHz, $CDCl_3$) (assignments made with the aid of data from 2D experiments): δ = –2.90 (s, 6 H, NH), 7.38 (m, 12 H, 10,20-phenyl *m*-H of TPP), 7.42 (m, 12 H, 10,20-phenyl *m*-H of ZnTPP), 7.49 (m, 12 H, 10,20-phenyl *p*-H), 7.66–7.74 (m, 18 H, 15-phenyl *m*- and *p*-H), 7.92 (m, 12 H, 10,20-phenyl *o*-H of TPP), 7.95 (m, 12 H, 10,20-phenyl *o*-H of ZnTPP), 8.12 (m, 6 H, 15-phenyl *o*-H of TPP), 8.15 (m, 6 H, 15-phenyl *o*-H of ZnTPP), 8.39 and 8.46 (AA′XX′, J_{AX} = 8.3 Hz, 12 H, 5-phenylene H of ZnTPP), 8.41 and 8.45 (AA′XX′, J_{AX} = 8.5 Hz, 12 H, 5-phenylene H of TPP), 8.63 (d, *J* = 4.6 Hz, 6 H, 2-H and 8-H of TPP), 8.68 (d, *J* = 4.4 Hz, 6 H, 12-H and 18-H of TPP), 8.74 (d, *J* = 4.4 Hz, 6 H, 13-H and 17-H of TPP), 8.79 (d, *J* = 4.7 Hz, 6 H, 2-H and 8-H of ZnTPP), 8.81 (d, *J* = 4.6 Hz, 6 H, 12-H and 18-H of ZnTPP), 8.86 (d, *J* = 4.6 Hz, 6 H, 13-H and 17-H of ZnTPP), 8.90 (d, *J* = 4.6 Hz, 6 H, 3-H and 7-H of TPP), 9.02 (d, *J* = 4.7 Hz, 6 H, 3-H and 7-H of ZnTPP). – UV/Vis (CH_2Cl_2): λ_{max} = 355, 420, 516, 549, 589, 647. – UV/Vis (benzene): λ_{max} (log ε) = 359 (5.04), 423 (6.17), 516 (4.71), 551 (4.89), 591 (4.41), 649 (4.03). – ES^+-MS (in THF): *m/z* = 2045.2 $[M + 2 H]^{2+}$, 1363.8 $[M + 3 H]^{3+}$ (calcd. avg. mass for $C_{282}H_{168}N_{24}Zn_3$: 4088.73).

Niphaphyrin 4c. – Method A: Reaction of **3d** (5.0 mg, 2.22 μmol) with **1b** (27 mg, 33.6 μmol) in the presence of Pd_2dba_3 (1.20 mg, 1.32 μmol) and $AsPh_3$ (3.2 mg, 10.5 μmol) in 1.7 mL of DMF/Et_3N as described for **4a** (Method A), with subsequent purification by twofold CC ($CHCl_3$/hexane, gradient from 1:1 to 4:1, then $CHCl_3$/hexane/Et_3N, 80:20:1), afforded 4.5 mg (47%) of **4c**. – **Method B:** To a solution of **4b** (1.25 mg, 0.306 μmol) in 6 mL of Et_2O/$CHCl_3$ (2:1), zinc oxide (6.9 mg, 0.085 mmol) and TFA (2 μL) were added. The mixture was stirred at 20 °C for 30 min, then filtered through a short column of silica gel to yield 1.1 mg (83%) of **4c**. – ^1H NMR (500.13 MHz, $CDCl_3$): δ = 7.40 (m, 24 H, 10,20-phenyl *m*-H), 7.44 (m, 12 H, 10,20-phenyl *p*-H), 7.66–7.74 (m, 18 H, 15-phenyl *m*- and *p*-H), 7.94 (m, 24 H, 10,20-phenyl *o*-H), 8.13 (m, 12 H, 15-phenyl *o*-H), 8.40 and 8.46 (AA′XX′, J_{AX} = 8.1 Hz, 24 H, 5-phenylene H), 8.75 (d, *J* = 4.4 Hz, 12 H, 2-H and 8-H), 8.80 (d, *J* = 4.5 Hz, 12 H, 12-H and 18-H), 8.85 (d, *J* = 4.5 Hz, 12 H, 13-H and 17-H), 9.01 (d, *J* = 4.4 Hz, 12 H, 3-H and 7-H). – UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 352 (4.86), 421 (6.32), 516 (4.09), 548 (5.10), 588 (4.46). – UV/Vis (benzene): λ_{max} = 353, 424, 551, 591. – MALDI-MS (dithranol): *m/z* = 4279.8 [M + 1] (calcd. avg. mass for $C_{282}H_{162}N_{24}Zn_6$: 4278.82).

Acknowledgments

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