Metalloporphyrin Dendrimers with Folding Arms**

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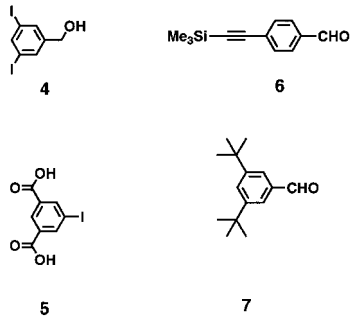
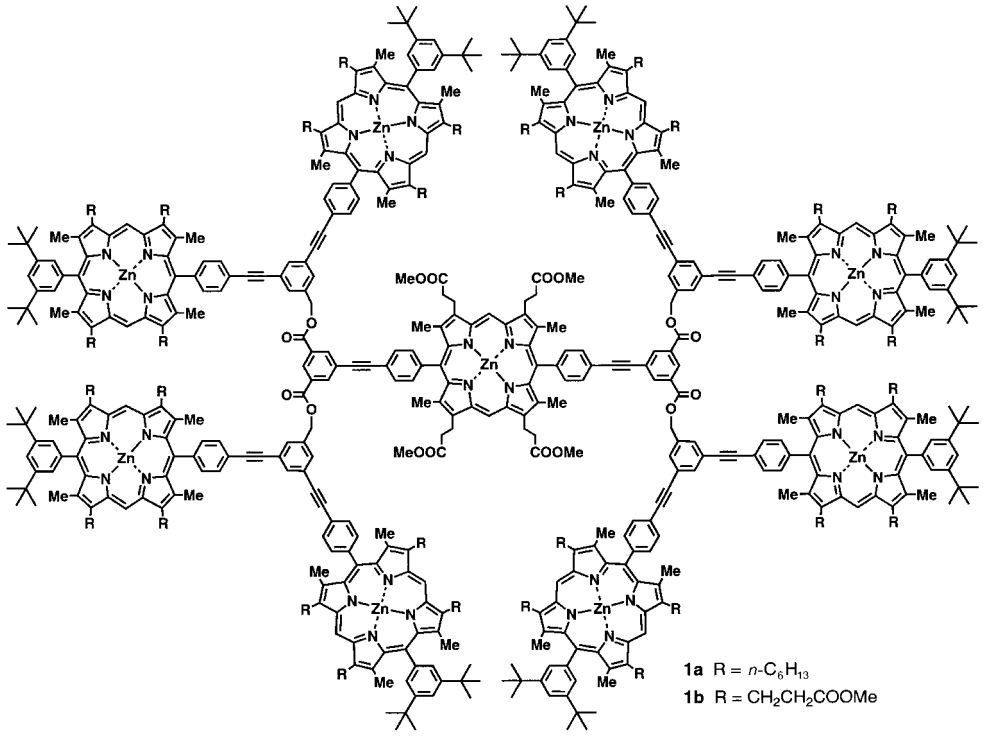
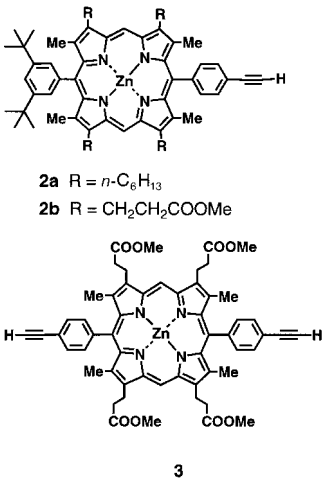
In memory of Ralph Raphael

We report here a new dendrimer system, **1**, possessing unusual features: It contains metalloporphyrins as the main building block both for the central core and the periphery,[1–3] and it has been constructed with a combination of rigid and flexible linkers in such a way that its four "arms" can fold in a cooperative and predetermined manner in response to the bifunctional ligand 1,4-diazabicyclo[2.2.2]octane (DABCO).



As high solubility of the dendrimer in a variety of solvents is essential for synthesis, characterization, and spectroscopic analysis, the main porphyrin building block is the unsymmetrical porphyrin **2** carrying two *tert*-butyl groups and either *n*-hexyl (**2a**) or methoxycarbonylethyl groups (**2b**) in the β positions; **2a** and **2b** were prepared on a gram scale by mixed condensation[7] of aldehydes **6**[8] and **7**[9] with dipyrromethane **8a** or **8b**[10] followed by metalation, desilylation, and separation from symmetrical analogues.[11] The yields given below, and the spectroscopic data in the Experimental Section, are generally for the **a** series; they are similar for the **b** series except where noted. The central porphyrin unit **3** was prepared as described previously.[8]





The efficient strategy applied for the synthesis of **1** has the potential to be generalized, for example, to light-harvesting model photosynthetic systems: It employs readily available unsymmetrical and symmetrical porphyrins **2** and **3** as the chromophore building blocks, and 3,5-diiodobenzyl alcohol (**4**) and 5-iodoisophthalic acid (**5**) as the branching units. The Pd-mediated[4] and Mitsunobu[5] coupling reactions avoid any activation or deprotection steps.[6]

The dendrimer was assembled as shown in Schemes 1 and 2 by Pd-mediated and Mitsunobu coupling reactions under mild and neutral to basic conditions in order to avoid acidic or forcing conditions that might cause demetalation and transmetalation, respectively. The rigid dendritic wedge **9a** was prepared in 90% yield, as shown in Scheme 1, under conditions which generate the Pd^0 reagent in situ and avoid the use of any copper cocatalysts that might lead to oxidative

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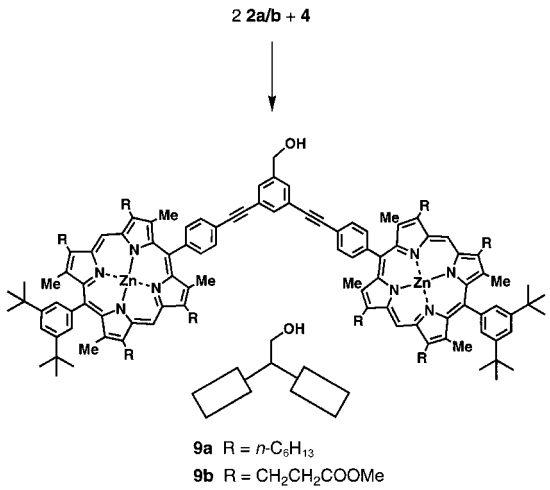
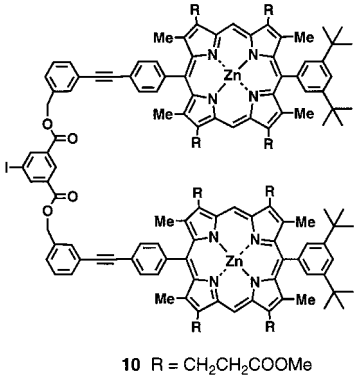
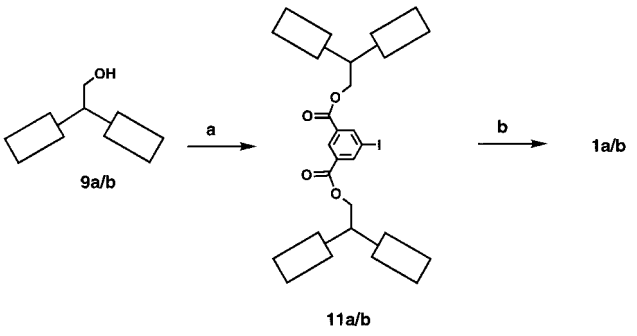


Scheme 1. Synthesis of rigid dendritic wedge **9**: cat. $[Pd_2(dba)_3]$, Ph_3As, Et_3N/CH_2Cl_2, room temperature (RT), 90% (for **9a**). dba = dibenzylideneacetone.

dimerization of the alkyne components.[4] As expected, the UV/Vis spectrum of **9a** was almost identical to that of **2a** as there can be little interaction between the porphyrins, but the fast atom bombardment (FAB) mass spectrum confirmed the successful formation of **9a** ($m/z = 2213$ $[M+H]^+$). For comparison of binding properties, the flexible dimer **10** was also prepared.



Mitsunobu condensation of **9a** with **5** afforded the four-porphyrin wedge **11a** in 85% yield (Scheme 2); its key structural features were confirmed by ^1H NMR spectroscopy and MALDI-TOF mass spectrometry (MALDI = matrix-assisted laser desorption ionization, TOF = time of flight).



Scheme 2. Synthesis of dendritic wedge **11** and dendrimer **1**: a) **5** (0.5 equiv), Ph_3P, DIAD, THF, RT, 85% (for **11a**); b) **3** (0.5 equiv), cat. $[Pd_2(dba)_3]$, Ph_3As, Et_3N/THF, RT, 60% (for **1a**). DIAD = diisopropyl azodicarboxylate.

Finally the nine-porphyrin dendrimer **1a** was prepared by Pd^0-catalyzed coupling of two molecules of **11a** with the central porphyrin core **3** (Scheme 2); the 60% yield of isolated product corresponds to about 78% per coupling step. It is important to note that the all-ester dendrimer **1b** was impossible to separate chromatographically from wedge **11b** and from the intermediate containing one four-porphyrin wedge coupled to **3**. Use of two different peripheral substitution patterns for the successive porphyrin layers in **1a** has no bearing on binding properties, but helps spectroscopic characterization and microanalytical differentiation, and gives great control over chromatographic mobility: Since the ester porphyrins are more polar, **1a** is distinctively more polar than **11a**, which facilitates the separation. Dendrimer **1a** is too large for successful FAB mass spectrometry, but its electrospray mass spectrum displayed weak peaks at $m/z =$ 2523, 2018, and 1685, consistent with multiply charged species $[M+4H]^{4+}$, $[M+5H]^{5+}$, and $[M+6H]^{6+}$, respectively. The MALDI-TOF mass spectrum showed a maximum at $m/z =$ 10087, consistent with the expected structure; the average molecular weight calculated for **1a** ($C_{660}H_{804}N_{36}O_{16}Zn_9$) is 10085.

A key feature of the design of **1** (and its component wedge **11**) is that each of the "arms" of the rigid porphyrin dimer is independent, but can be brought together with the other by cooperative binding of the two ends of DABCO as illustrated in Figure 1. Both ^1H NMR and UV/Vis spectra confirm that this occurs as expected: A DABCO molecule tightly bound to two Zn–porphyrin units gives a characteristic ^1H NMR signal at $\delta = -5$, while monomers or dimers that are incapable of intramolecular binding do not.[3b, 12] As expected, when 0.5 equivalents of DABCO per porphyrin unit are added, **10**, **11**, and **1a** give a sharp signal at $\delta = -5$, while the rigid **9** does not. On addition of excess DABCO the ligand resonance at $\delta = -5$ broadens and then disappears through exchange.[3b, 12]

At the porphyrin concentrations used for UV/Vis titrations (10^{-7} M), binding of DABCO to monomers (or to **9**) results in a shift of the Soret absorption from 412 to 426 nm. This is typical of a 1:1 porphyrin–DABCO complex;[12] analysis of the titration curves gives a binding constant (binding to monomer) of about $10^5\,M^{-1}$. By contrast, binding of DABCO to **10**, **11**, or **1a** leads through an isosbestic point to a Soret maximum at 420 nm (Figure 2); this blue shift of 6 nm is characteristic of a 2:1 porphyrin–DABCO complex[12] and is due to exciton coupling between the parallel porphyrin units.[13] It is difficult to extract precise binding constants from such complex systems: Each arm in **11** and **1a** will bind two DABCO molecules, and each DABCO molecule will have a first and second binding interaction. However, the fact that an exciton-coupled spectrum is obtained with a porphyrin concentration of 10^{-7} M implies that the second binding constant for the first DABCO molecule is at least $10^7\,M^{-1}$. Binding of the first DABCO molecule preorganizes the second binding site and leads to an exciton-coupled spectrum for that second site (as implied in Figure 1b).

The second DABCO molecule is likely to be bound even more strongly: The exciton-coupled spectrum persists even in the presence of 21000-fold excess DABCO for **11** and **1a**, and a fully sharp band at 426 nm is not achieved until almost

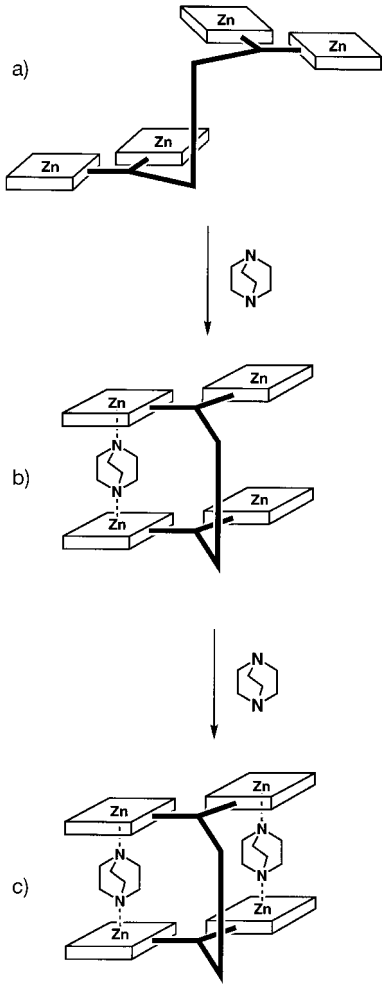


Figure 1. Cartoon representation of the DABCO-induced folding of **11** and **1**.

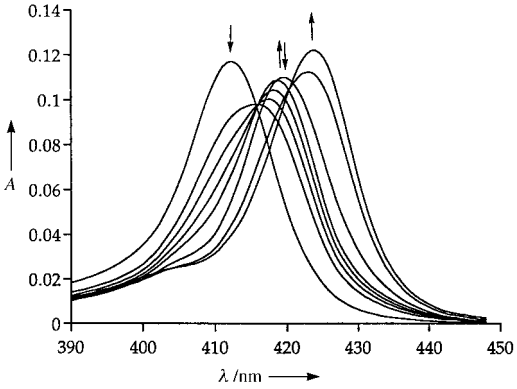


Figure 2. UV/Vis titration of **11a** with DABCO. Number of equivalents added per tetramer: 0, 0.6, 1.2, 3, 12, 7700, 250000, 900000.

10^6-fold excess is added. By contrast, **10** begins to lose exciton coupling after addition of only 7000-fold excess DABCO. The core porphyrin of **1a** is unable to bind DABCO in this 2:1 cooperative fashion, but (in the absence of a vast excess of DABCO) its single aborption around 426 nm is not readily detected in the presence of eight absorptions with $\lambda_{max} =$ 420 nm.

The convergent approach described here, which makes use of alternating coupling reactions,[6] gives easy access to dendrimers in general. Since any electron acceptor, electron donor, or metalloporphyrin could be chosen as the core for the present system, the electrochemical and photophysical properties of the resulting dendrimer can be fine-tuned. Finally, the conformational sensitivity of **1** to ligands may have profound effects on its viscosity, photophysics, and other properties; these are currently under investigation.

Experimental Section

9a: A solution of **2a** (250 mg, 0.24 mmol), **4** (40 mg, 0.11 mmol), $[Pd_2(dba)_3]$ (22 mg, 0.022 mmol), and $AsPh_3$ (40 mg, 0.13 mmol) in CH_2Cl_2/Et_3N (1/1, 10 mL) in a Schlenk tube was degassed twice (freeze-pump-thaw). The mixture was stirred at room temperature under argon for 15 h. After removal of the solvent, the reaction mixture was subjected to chromatography (silica, hexane/chloroform/ethyl acetate 10/1/1) to give **9a** (220 mg, 90%) as a purple solid. ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 0.93$ (t, $J = 7$ Hz, 12H), 0.94 (t, $J = 7$ Hz, 12H), 1.20–1.60 (m, 70H), 1.78 (quint, $J = 7$ Hz, 16H), 2.22 (quint, $J = 7$ Hz, 16H), 2.46 (s, 12H), 2.58 (s, 12H), 3.90–4.10 (m, 16H), 4.64 (s, 2H), 7.62–7.65 (m, 2H), 7.83 (t, $J = 2$ Hz, 2H), 7.95 (d, $J = 2$ Hz, 4H), 8.00 (d, $J = 8$ Hz, 4H), 8.17 (d, $J = 8$ Hz, 4H), 10.22 (s, 4H); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 149.7$ (s), 148.0 (s), 147.4 (s), 146.5 (s), 146.4 (s), 144.6 (s), 143.7 (s), 143.4 (s), 142.5 (s), 140.7 (s), 138.6 (s), 137.7 (s), 133.8 (d), 133.6 (d), 130.8 (d), 129.5 (d), 128.0 (d), 123.8 (s), 122.7 (s), 121.0 (d), 120.9 (s), 118.2 (s), 97.7 (d), 90.6 (s), 89.2 (s), 63.5 (t), 35.2 (t), 33.4 (t), 32.0 (t), 31.7 (q), 30.1 (t), 29.7 (t), 26.9 (s), 22.8 (t), 15.7 (q), 14.9 (q), 14.2 (q); UV/Vis (CH_2Cl_2): λ_{max} (lgε) = 412 (5.71), 538 (4.37), 574 (4.04); elemental analysis calcd for $C_{147}H_{188}N_8OZn_2$: C 79.75, H 8.60, N 5.06; found: C 79.67, H 8.59, N 4.74.

11a: A solution of DIAD (42 mg, 0.21 mmol) in THF (2 mL) was added to a solution of **9a** (190 mg, 0.086 mmol), **5** (12 mg, 0.041 mmol), and PPh_3 (55 mg, 0.21 mmol) in THF (5 mL) at room temperature. After stirring of the mixture at room temperature for 4 h, solvent was removed and the residue was subjected to chromatography (silica, hexane/chloroform/ethyl acetate 20/1/1 →10/1/1) to give **11a** (163 mg, 85%) as a purple solid. ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 0.95$ (t, $J = 7$ Hz, 24H), 0.96 (t, $J = 7$ Hz, 24H), 1.25–1.70 (m, 136H), 1.78 (quint, $J = 7$ Hz, 32H), 2.10–2.35 (m, 32H), 2.51 (s, 24H), 2.52 (s, 24H), 3.84 (t, $J = 7$ Hz, 16H), 4.01 (t, $J = 7$ Hz, 16H), 5.61 (s, 4H), 7.89 (t, $J = 2$ Hz, 4H), 7.94 (d, $J = 2$ Hz, 4H), 8.03 (d, $J = 2$ Hz, 8H), 8.05–8.20 (m, 18H), 8.80 (d, $J = 1$ Hz, 2H), 8.98 (t, $J = 1$ Hz, 1H), 10.10 (s, 8H); ^{13}C NMR (62.9 MHz, $CDCl_3$): $\delta = 164.3$ (s), 149.7 (s), 148.0 (s), 147.3 (s), 146.5 (s), 146.2 (s), 144.6 (s), 143.5 (s), 143.4 (s), 143.0 (d), 142.5 (s), 138.6 (s), 137.5 (s), 136.4 (s), 134.9 (d), 133.5 (d), 132.2 (s), 131.7 (d), 130.8 (d), 130.6 (d), 128.0 (d), 124.6 (s), 122.5 (s), 121.0 (d), 120.9 (s), 118.0 (s), 97.6 (d), 91.3 (s), 89.0 (s), 66.8 (t), 35.2 (t), 33.3 (t), 32.0 (t), 31.7 (q), 30.0 (t), 29.7 (t), 26.8 (s), 26.6 (s), 22.8 (t), 15.6 (q), 14.9 (q), 14.2 (q); UV/Vis (CH_2Cl_2): λ_{max} (lgε) = 412 (6.29), 538 (4.96), 574 (4.57); MALDI-TOF-MS: m/z: 4684.4 $[M+H]^+$ (calcd 4684.6); elemental analysis calcd for $C_{302}H_{377}IN_{16}O_4Zn_4$: C 77.44, H 8.11, N 4.79; found: C 77.27, H 8.22, N 4.71.

1a: Following the same procedure as for **9a**, except with THF/Et_3N (1/1) as solvent mixture, **1a** was obtained from **3** and **11a** in 60% yield as a purple solid. ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 0.90$ (t, $J = 7$ Hz, 48H), 0.91 (t, $J = 7$ Hz, 48H), 1.25–1.85 (m, 336H), 2.00–2.30 (m, 64H), 2.35–2.60 (m, 108H), 2.77 (t, $J = 7$ Hz, 8H), 3.37 (s, 12H), 3.60–4.04 (m, 72H), 5.75 (s, 8H), 7.86 (t, $J = 2$ Hz, 8H), 7.95–8.20 (m, 68H), 8.85 (d, $J = 2$ Hz, 4H), 9.11 (d, $J = 2$ Hz, 2H), 9.56 (s, 2H), 10.00 (s, 16H); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 173.2$ (s), 165.2 (s), 149.8 (s), 148.0 (s), 147.4 (s), 147.2 (s), 146.4 (s), 146.2 (s), 145.7 (s), 144.7 (s), 144.4 (s), 143.5 (s), 143.4 (s), 142.5 (s), 141.5 (s), 138.7 (s), 138.6 (s), 137.5 (s), 137.3 (d), 136.7 (s), 135.0 (d), 133.6 (d), 131.5 (d), 131.3 (s), 131.2 (d), 130.9 (d), 128.0 (d), 124.9 (s), 124.7 (s), 122.6 (s), 121.0 (d), 120.9 (s), 118.7 (s), 117.9 (s), 97.5 (d), 97.2 (d), 92.2 (s), 91.3 (s), 89.1 (s), 88.5 (s), 66.8 (t), 51.4 (q), 36.7 (t), 35.2 (t), 33.3 (t), 32.0 (t), 31.7 (q), 30.0 (t), 29.8 (t), 26.8 (s), 26.6 (s), 22.8 (t), 15.6 (q), 15.0 (q), 14.2 (q); UV/Vis (CH_2Cl_2): λ_{max} (lgε) = 412 (6.52), 540 (5.25), 574 (4.95); elemental analysis calcd for $C_{660}H_{804}N_{36}O_{16}Zn_9$: C 78.60, H 8.03, N 5.00; found: C 78.47, H 8.07, N 4.74.

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[11] Crystallographic data (excluding structure factors) for the structure (**2b**) reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-101442. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Windmill-Like Porphyrin Arrays as Potent Light-Harvesting Antenna Complexes**

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Photosynthetic organisms use light-harvesting complexes to capture weak sunlight. Upon photoexcitation, energy migration occurs between these pigments until a reaction center is encountered, where charge separation occurs. The energy migration is rapid and can involve hundreds of pigments.[1] A number of synthetic models have been developed in order to understand light-harvesting phenomena at the molecular level.[2] Ordered supramolecular arrays of porphyrins are also of interest for the design of molecular electronic devices.[3, 4] Here we report a novel one-pot synthesis of orthogonally arranged windmill-like porphyrin arrays involving a *meso*–*meso*-linked diporphyrin unit as an energy sink. This is an extension of our recent synthesis of *meso*–*meso*-linked porphyrin oligomers from a Zn^{II} 5,15-diarylporphyrin and Ag^{I} ions in $CHCl_3$.[5]

The synthetic route to porphyrin tetramers **3-Zn** and **3-Ni** is outlined in Scheme 1. Condensation of formyl-substituted **1-Zn** and 3,5-di-*tert*-butylbenzaldehyde with 2,2′-dipyrrylmethane under Lindsey conditions[4] afforded hybrid diporphyrin **2-Zn** in 31% yield. Treatment of **2-Zn** with one equivalent of $AgPF_6$ at room temperature in $CHCl_3$ for 10 h followed by preparative size-exclusion chromatography (SEC) gave porphyrin tetramer **3-Zn** in 5% yield (40% of **2-Zn** was recovered). The fast atom bombardment (FAB) mass spectrum of **3-Zn** contains a parent ion peak at $m/z = 3254$ (calcd for $C_{206}H_{230}N_{16}O_4Zn_4$: $m/z = 3255$), and the ^1H NMR spectrum (500 MHz) showed signals for three *meso* protons at $\delta = 10.58$ (β-unsubstituted Zn^{II} porphyrin), 10.28, and 10.11 (Zn^{II} octaalkylporphyrin) as well as for eight β protons of the β-unsubstituted Zn^{II} porphyrin at $\delta = 9.78$, 9.69, 9.61, 9.28, 9.26, 8.86, 8.48, and 8.31 characteristic of the *meso*–*meso*-linked diporphyrins.[5]

The UV/Vis spectrum of **3-Zn** shows a broad Soret band at 413.5 nm with a shoulder at 447 nm (see Figure 2b). The latter can be assigned as a low-energy portion of split Soret bands characteristic of the *meso*–*meso*-linked diporphyrins.[5] Formation of the *meso*–*meso*-linked diporphyrin can be accounted for in terms of the initial one-electron oxidation of the zinc porphyrin with Ag^{I} followed by nucleophilic attack of

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