**Keywords:** cooperative effects · coordination modes · dendrimers · porphyrinoids

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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 $\delta = 10.58$ ($\beta$-unsubstituted $Zn^{II}$ porphyrin), 10.28, and 10.11 ($Zn^{II}$ octaalkylporphyrin) as well as for eight $\beta$ protons of the $\beta$-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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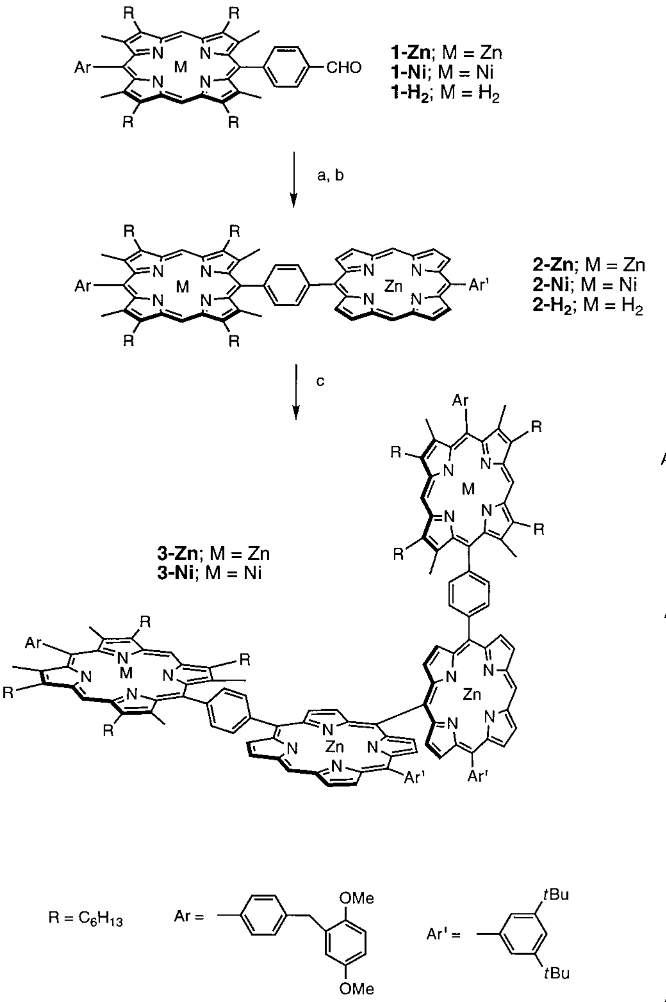
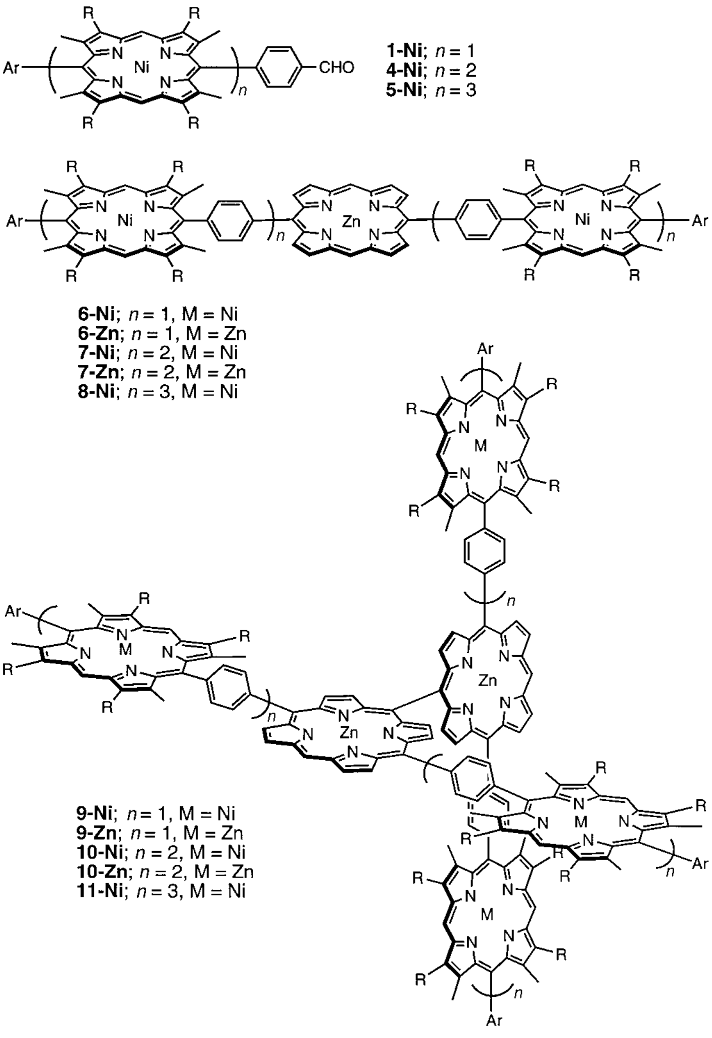


Scheme 1. Synthesis of the porphyrin tetramers **3**. a) 2,2′-Dipyrrylmethane, 3,5-di-*tert*-butylbenzaldehyde, trifluoroacetic acid (TFA), $CH_2Cl_2$; *p*-chloranil; b) $Zn(OAc)_2$, $MeOH/CH_2Cl_2$; c) $AgPF_6/MeCN$, $CHCl_3$.

a molecule of neutral zinc porphyrin. This mechanism is supported by the synthesis of the same diporphyrin by anodic electrochemical oxidation.[6] Since the potential for the one-electron oxidation of the $Zn^{II}$ octaalkylporphyrin is 0.14 V lower than that of the reacting *β*-unsubstituted $Zn^{II}$ porphyrin,[7] oxidation of the former should be easier, leading to preferential generation of the corresponding radical cation. However, this radical cation is probably unreactive due to severe steric hindrance, and instead the radical cation of the *β*-unsubstituted $Zn^{II}$ porphyrin, which is slowly formed either by a bimolecular reaction with $Ag^I$ ions or by intramolecular endothermic hole transfer from the radical cation of the $Zn^{II}$ octaalkylporphyrin, reacts with a neutral *β*-unsubstituted $Zn^{II}$ porphyrin.

The low yield of **3-Zn** suggested undesirable side reactions of the radical cation of the $Zn^{II}$ octaalkylporphyrin. We therefore lowered the oxidation potential of the $Zn^{II}$ octaalkylporphyrin by transmetalation ($Zn^{II} \rightarrow Ni^{II}$) or demetalation to the corresponding free porphyrin base.[7] The hybrid porphyrin dimer **2-Ni** was prepared in 21 % yield from **1-Ni** under the same conditions, and **2-H$_2$** was obtained in 80 % yield by reaction of **2-Zn** with 1N HCl. Upon treatment with 1.7 equivalents of $AgPF_6$ in $CHCl_3$, **2-Ni** gave porphyrin tetramer **3-Ni** in 30 % yield (26 % of **2-Ni** was recovered), but **2-H$_2$** gave only trace amounts of tetramer **3-H$_2$**. Based on these results, we decided to employ a $Ni^{II}$ porphyrin as the "protecting group" for the *β*-octaalkylporphyrin.

We next prepared the symmetric, linear 1,4-phenylene-bridged porphyrin trimer **6-Ni** (51 % yield), pentamer **7-Ni** (68 %), and heptamer **8-Ni** (80 %), again under Lindsey conditions,[4] from the formyl-substituted nickel porphyrin monomer **1-Ni**, dimer **4-Ni**, and trimer **5-Ni**, respectively (Scheme 2). The reaction of **6-Ni** with two equivalents of AgPF$_6$ produced porphyrin hexamer **9-Ni** along with porphyrin nonamer **12-Ni**, as monitored by analytical SEC (Figure 1); the retention times for **9-Ni** and **12-Ni** were 19.9 and 19.3 min, respectively. After 22 h **9-Ni** and **12-Ni** were separated by preparative SEC and isolated in 50 and 3 % yields, respectively (47 % of **6-Ni** was recovered). The molecular weights of these porphyrin arrays were determined by MALDI-TOF mass spectrometry (MALDI = matrix-assisted laser desorption ionization, TOF = time of flight): **6-Ni**: *m*/*z* = 2494 (calcd for $C_{158}H_{180}N_{12}Ni_2O_4Zn$: 2493), **9-Ni**: *m*/*z* = 4985 (calcd for $C_{316}H_{358}N_{24}Ni_4O_8Zn_2$: 4985), **12-Ni**: *m*/*z* = 7476



Scheme 2. Synthesis of the higher porphyrin oligomers.

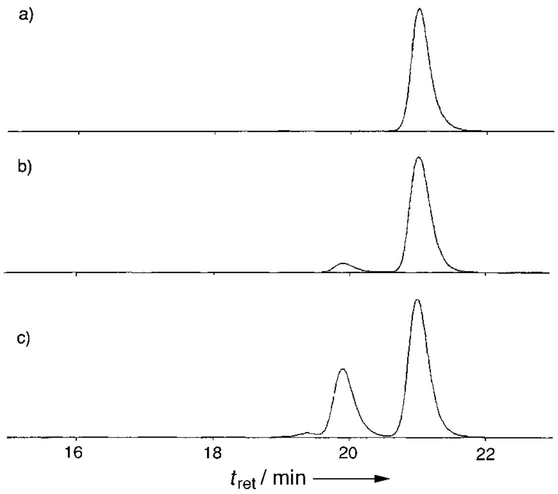


Figure 1. Analytical size-exclusion chromatograms obtained after the reaction of **6-Ni** with $AgPF_6$. a) Before reaction, b) after 4 h, c) after 12 h.

(calcd for $C_{474}H_{536}N_{36}Ni_6O_{12}Zn_3$: 7478).[8] The reaction of the linear porphyrin pentamer **7-Ni** with three equivalents of $AgPF_6$ for 25 h afforded porphyrin decamer **10-Ni** (MALDI-TOF-MS: $m/z = 8321$; calcd for $C_{532}H_{638}N_{40}Ni_8O_8Zn_2$: 8320) in 35% yield (15% of **7-Ni** was recovered). In this reaction we also obtained a fraction (15% yield) that probably contains the 15-mer, as judged by analytical SEC.[9] Finally, the reaction of the porphyrin heptamer **8-Ni** provided the 14-mer **11-Ni** (MALDI-TOF-MS: $m/z = 11\,640$; calcd for $C_{748}H_{918}N_{56}Ni_{12}O_8Zn_2$: 11656) in 14% yield. The regioselectiviy of this coupling reaction is quite high, and we could not detect any oligomers coupled at other positions.

To examine the photophysical properties of the windmill-like porphyrin arrays, the hexamer **9-Ni** and the decamer **10-Ni** were transformed into the corresponding $Zn^{II}$ porphyrins **9-Zn** and **10-Zn** by demetalation with trifluoroacetic acid and 10% $H_2SO_4$ in refluxing toluene followed by insertion of $Zn^{II}$ with $Zn(OAc)_2$. The UV/Vis spectra of **2-Zn**, **6-Zn**, and **7-Zn** in $CH_2Cl_2$ show split Soret bands that are characteristic of 1,4-phenylene-linked $Zn^{II}$ porphyrin oligomers and relatively unperturbed Q bands; their fluorescence spectra are also similar (Figure 2a). On the other hand, the spectra of oligomers **3-Zn**, **9-Zn**, and **10-Zn** display broader Soret and Q bands (Figure 2b). As with the tetramer **3-Zn**, the spectrum of the hexamer **9-Zn** exhibits a shoulder at about 450 nm due to the low-energy portion of split Soret bands (see above),[5] but such a band is almost hidden in the spectrum of **10-Zn**. The steady-state fluorescence spectra of **3-Zn**, **9-Zn**, and **10-Zn** are all composed of dual emissions from the peripheral porphyrin rings ($\lambda_{max} = 580$ and 629 nm) and from the diporphyrin core ($\lambda_{max} = 651$ nm). The reduced fluorescence intensity of the peripheral porphyrin rings suggests a singlet–singlet energy transfer to the diporphyrin core. This is consistent with the slightly lower energy of the $S_1$ state of the diporphyrin (ca. 2.08 eV; for the peripheral porphyrin: 2.15 eV)[5]. The time-resolved picosecond fluorescence spectra of **3-Zn** (Figure 3) revealed that the emission from the peripheral porphyrin rings that predominated at an

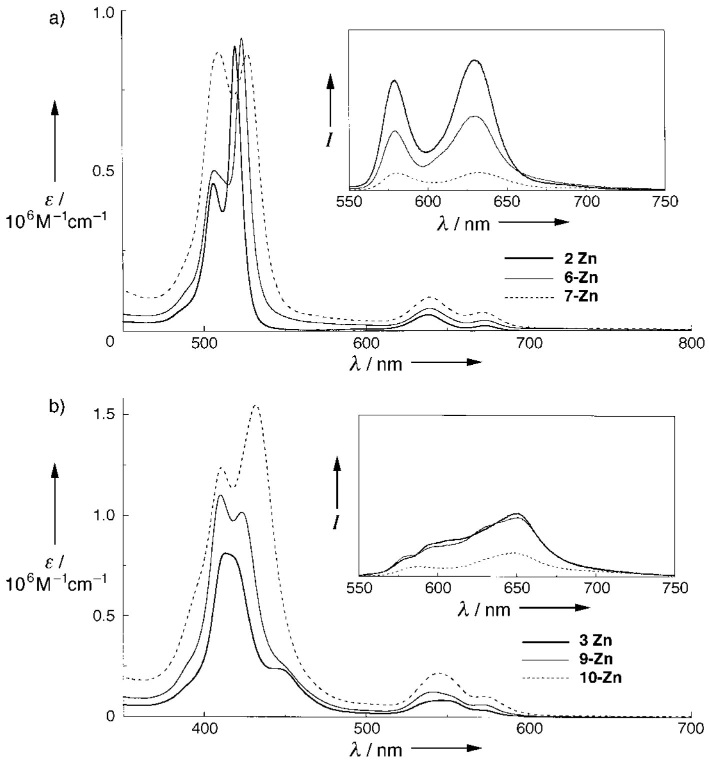
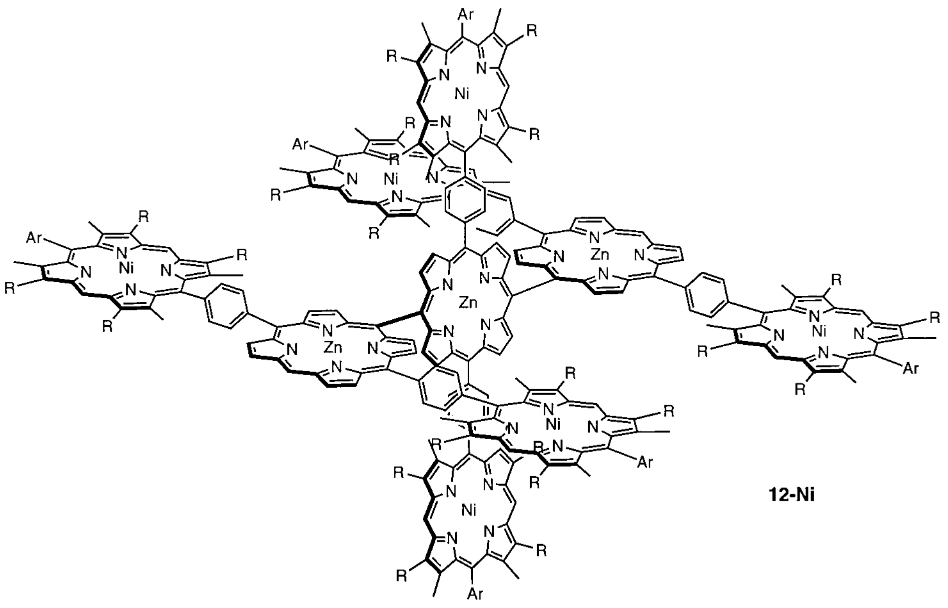


Figure 2. a) UV/Vis spectra of **2-Zn**, **6-Zn**, and **7-Zn** in $CH_2Cl_2$; the inset showes the steady-state fluorescence emission spectra taken for excitation at 540 nm of a solution with the absorbance at 540 nm adjusted at 0.10. b) Corresponding spectra of **3-Zn**, **9-Zn**, and **10-Zn** in $CH_2Cl_2$.



**12-Ni**

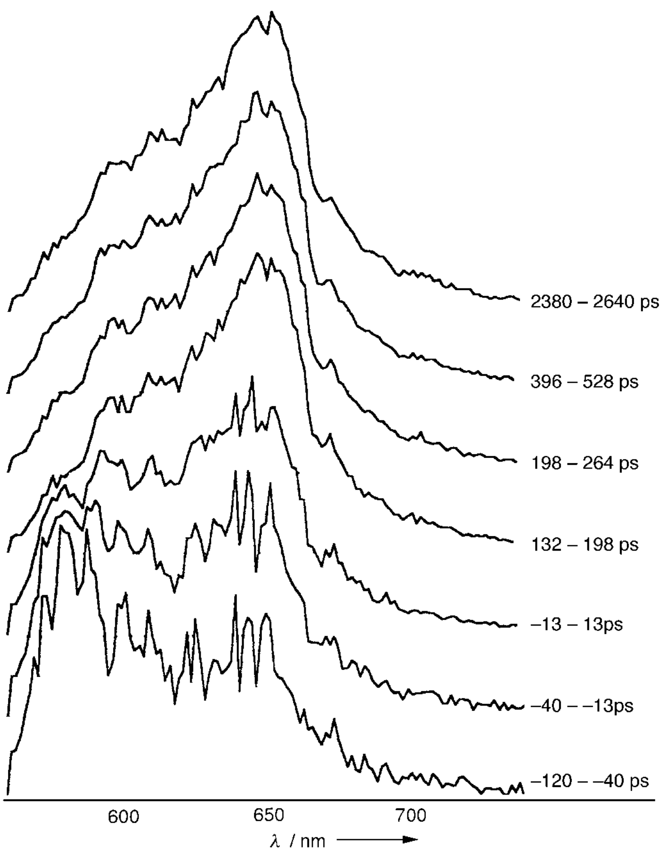


Figure 3. Time-resolved fluorescence emission spectra of **3-Zn** in $CH_2Cl_2$ taken after excitation at 532 nm. The times given correspond to the time difference from time at which the highest intensity was measured for the profile.

early stage decayed more rapidly than that from the diporphyrin core. The fluorescence decay at 580 nm can be analyzed as a double exponential function with time constants of 27 ps (72 %) and 1.6 ns (28 %). We have interpreted that the short-lived component mainly reflects the decay of the $S_1$ state of the peripheral porphyrin rings and that the longer lived component mainly reflects the decay of the $S_1$ state of the diporphyrin core.[10] Time-resolved fluorescence spectra of **9-Zn** and **10-Zn** are also similar to those of **3-Zn**, and indicate efficient flow of the excitation energy from the peripheral porphyrin rings to the diporphyrin core, even in larger arrays, while the singlet excited state lifetime of the *meso–meso* diporphyrin is not unaffected.

The coupling reaction described here enables a one-step construction of large, windmill-like porphyrin arrays with well-defined architectures that are soluble in common organic solvents. This fairly good solubility may arise from their orthogonal molecular arrangement, which may suppress porphyrin π–π stacking. Such orthogonal porphyrin arrays with a molecular length of more than 90 Å may be interesting in view of a concept for molecular electronic devices proposed by Aviram,[11] in which double-minimum potentials for a single electron has been suggested to serve as a fundamental unit of a molecular device. The coupling reaction is also of mechanistic interest. Considering that the oxidation potentials of the $Ni^{II}$ octaalkylporphyrin and β-unsubstitued $Zn^{II}$ porphyrin are almost the same and that the central β-unsubstitued $Zn^{II}$ porphyrin is buried between the bulky peripheral $Ni^{II}$ porphyrin rings, not only a direct oxidation of the $Zn^{II}$ porphyrin with $Ag^I$ ions but also an indirect oxidation pathway (oxidation of the $Ni^{II}$ porphyrin with $Ag^I$ ions and subsequent hole transfer) may generate the $Zn^{II}$ porphyrin radical cation. The formation of the *meso–meso*-linked diporphyrin should thus be facilitated.

## *Experimental Section*

A 50-mL round-bottom flask was charged with **6-Ni** (39 mg, 15.7 mmol) and $CHCl_3$ (10 mL) and then covered with foil. A solution of $AgPF_6$ (31 mmol) in acetonitrile was added all at once. The progess of the reaction was monitored by analytical size-exclusion HPLC (JAIGEL-2.5 H, 3H-AF, and 4H-AF columns in series). The mixture was stirred for 22 h, diluted with water, and extracted with $CHCl_3$. The organic layer was separated, washed with water, and dried over anhydrous $Na_2SO_4$. A saturated solution of $Zn(OAc)_2$ in methanol was added, and the resulting solution was heated at reflux for 1 h, diluted with water, and extracted with $CHCl_3$. The organic layer was separated and dried over $Na_2SO_4$. The products were separated by preparative size-exclusion HPLC (Japan Analytical Industry Co. Ltd., recycling system with JAIGEL-1H, 2H, and 2.5H columns in series). Elution with $CHCl_3$ yielded three major fractions in the following order: materials of higher molecular weight containing a trace amount of the nonamer **12-Ni**, the hexamer **9-Ni** (19.4 mg, 50 %), and the starting trimer **6-Ni** (18.5 mg, 47 %). Isolation of the nonamer **12-Ni** and higher oligomers was difficult. The first fractions of several runs were combined and applied repeatedly to the same column, and **12-Ni** was isolated in an average yield of about 3 %.

**12-Ni**: $^1H$ NMR (500 MHz, $CDCl_3$): $\delta = 10.71$ (s, 2H; *meso*-H), 9.82 (d, $J = 4.0$ Hz, 4H; β-H), 9.64 (d, $J = 4.0$ Hz, 4H; β-H), 9.56 (br, 4H; *meso*-H), 9.41 (br, 4H; *meso*-H), 9.34 (d, $J = 4.0$ Hz, 4H; β-H), 9.33 (s, 4H; *meso*-H), 9.26 (d, $J = 4.0$ Hz, 4H; β-H), 8.76 (d, $J = 4.0$ Hz, 4H; β-H), 8.69 (d, $J = 8.5$ Hz, 8H; Ar), 8.65 (m, 8H; β-H and Ar), 8.32 (d, $J = 8.5$ Hz, 8H; Ar), 8.16 (d, $J = 8.0$ Hz, 4H; Ar), 7.75 (d, $J = 8.5$ Hz, 8H; Ar), 7.65 (d, $J = 8.5$ Hz, 4H; Ar), 7.44 (d, $J = 8.5$ Hz, 8H; Ar), 7.36 (d, $J = 8.5$ Hz, 4H; Ar), 6.90–6.76 (m, 18H; dimethoxy-Ar), 4.23 (s, 8H; Ar$CH_2$Ar), 4.15 (s, 4H; Ar$CH_2$Ar), 3.87 (s, 12H; OMe), 3.87–3.46 (m, 48H; β-hexyl), 3.81 (s, 12H; OMe), 3.75 (s, 6H; OMe), 3.46 (s, 6H; OMe), 3.00, 2.68, 2.58, 2.56 (2 × br, 2 × s, 72H; β-Me), 2.36–0.62 (m, 264H; β-hexyl); MALDI-TOF-MS: calcd av mass for $C_{474}H_{536}N_{36}Ni_6O_{12}Zn_3$: $m/z$ 7478; found: 7476; UV/Vis (benzene): $\lambda_{max} =$ 418.5 (Soret), 474.5, 533.0, 564.5 nm.

**10-Ni**: $^1H$ NMR (500 MHz, $CDCl_3$): $\delta = 10.69$ (s, 2H; *meso*-H), 9.81 (d, $J = 4.5$ Hz, 4H; β-H), 9.62 (d, $J = 4.5$ Hz, 4H; β-H), 9.56 (br, 8H; *meso*-H), 9.42 (br, 8H; *meso*-H), 9.22 (d, $J = 4.5$ Hz, 4H; β-H), 8.65 (d, $J = 8.0$ Hz, 8H; Ar), 8.55 (d, $J = 4.5$ Hz, 4H; β-H), 8.29 (d, $J = 8.0$ Hz, 8H; Ar), 8.12 (s, 16H; Ar), 7.74 (d, $J = 8.0$ Hz, 8H; Ar), 7.45 (d, $J = 8.0$ Hz, 8H; Ar), 6.90 (d, $J = 9.0$ Hz, 4H; dimethoxy-Ar), 6.86 (d, $J = 3.0$ Hz, 4H; dimethoxy-Ar), 6.81 (dd, $J = 9.0$, 3.0 Hz, 4H; dimethoxy-Ar), 4.23 (s, 8H; Ar$CH_2$Ar), 3.88 (s, 12H; OMe), 3.81 (s, 12H; OMe), 3.88–3.50 (m, 64H; β-hexyl), 2.96 (br, 24H; β-Me), 2.74 (br, 24H; β-Me), 2.60 (br, 24H; β-Me), 2.25 (br, 24H; β-Me), 2.20–0.65 (m, 352H; β-hexyl); MALDI-TOF-MS: calcd av mass for $C_{532}H_{638}N_{40}Ni_8O_8Zn_2$: $m/z$ 8320; found: 8321; UV/Vis (benzene): $\lambda_{max} =$ 410.0 (Soret), 430.0 (Soret), 534.0, 567.0 nm.

**11-Ni**: $^1H$ NMR (500 MHz, $CDCl_3$): $\delta = 10.69$ (s, 2H; *meso*-H), 9.81 (d, $J = 5.0$ Hz, 4H; β-H), 9.62 (d, $J = 4.0$ Hz, 4H; β-H), 9.56, 9.46, 9.44 (br, 2 × s, 24H; *meso*-H), 9.22 (br, 4H; β-H), 8.67 (d, $J = 8.0$ Hz, 8H; Ar), 8.54 (br, 4H; β-H), 8.30 (d, $J = 8.0$ Hz, 8H; Ar), 8.15 (s, 16H; Ar), 8.14 (s, 16H; Ar), 7.76 (d, $J = 7.5$ Hz, 8H; Ar), 7.46 (d, $J = 7.5$ Hz, 8H; Ar), 6.91 (d, $J = 8.5$ Hz, 4H; dimethoxy-Ar), 6.87 (d, $J = 2.5$ Hz, 4H; dimethoxy-Ar), 6.82 (dd, $J = 8.5$, 2.5 Hz, 4H; dimethoxy-Ar), 4.23 (s, 8H; Ar$CH_2$Ar), 3.88 (s, 12H; OMe), 3.82 (s, 12H; OMe), 3.73, 3.66 (2 × br, 96H; β-hexyl), 2.99 (br, 12H; β-Me), 2.62 (br, 12H; β-Me), 2.76, 2.27 (2 × s, 120H; β-Me), 2.20–2.08 (br, 96H; β-hexyl), 2.00–1.26 (br, 288H; β-hexyl), 1.20–0.85 (br, 144H; β-hexyl-$CH_3$); MALDI-TOF-MS: calcd av mass for $C_{748}H_{918}N_{56}Ni_{12}O_8Zn_2$: $m/z$ 11 656; found: 11 640; UV/Vis (benzene): $\lambda_{max} = 412.0$ (Soret), 434.0 (Soret), 535.5, 568.5 nm.

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[7] Potentials for the one-electron oxidation of **1-Zn**, **1-Ni**, **1-H$_2$**, and zinc 5,15-bis(3,5-di-*tert*-butyl-phenyl)porphyrin were measured by cyclic voltammetry in CHCl$_3$ to be 0.17, 0.32, 0.40, and 0.31 V, respectively, versus ferrocene/ferrocenium ion.

[8] All new porphyrin compounds reported here were fully characterized by $^1$H NMR spectroscopy (500 MHz) as well as FAB and MALDI-TOF mass spectrometry.

[9] In the analytical SEC, **7-Ni** and **10-Ni** eluted after 20.1 and 18.9 min, respectively, while the porphyrin 15-mer eluted after 18.1 min. The reaction of **10-Ni** with excess AgPF$_6$ afforded the porphyrin 20-mer, as judged by SEC (retention time: 17.9 min) and MALDI-TOF-MS ($m/z = 16666$; calcd for $C_{1064}H_{1274}N_{80}Ni_{16}O_{16}Zn_4$: 16640), in 20–30% yield. However, the very broad signals in the $^1$H NMR spectra of the 15-mer and 20-mer precluded their full characterization. These results may imply that not only the linear porphyrin arrays but also the windmill-like orthogonal porphyrin arrays are useful building blocks.

[10] Since the energy difference between the singlet excited state of the *meso–meso* diporphyrin and the peripheral porphyrin rings is small (0.07 eV), the energy transfer may be reversible and the dynamics of the photoexcited state of the windmill-like porphyrin arrays are very complicated.

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# Supramolecular Assembly of Heterogeneous Multiporphyrin Arrays—Structures of $[\{Zn^{II}(tpp)\}_2(tpyp)]$ and the Coordination Polymer $[\{[Mn^{III}(tpp)]_2(tpyp)(ClO_4)_2\}_\infty]$**

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Multiporphyrin architectures have diverse potential for applications as biomimetic models or functional materials for the transport of energy, charge, molecules, and ions.[1, 2] The formulations of light-harvesting porphyrin arrays and new receptors for selective catalysis has relied mostly on covalent synthesis of oligomeric arrays.[3, 4] For many years the construction of stable multiporphyrin arrays by supramolecular aggregation has remained relatively unexplored, in spite of the diverse molecular recognition algorithm that can be incorporated into the porphyrin building blocks. Recent investigations have shown, however, that predictable architectures of oligomers and polymers from metallomacrocyclic building blocks can be rationally designed by selection of the coordination geometry of metals and the structure of multitopic ligands involved in the supramolecular synthesis.

Examples of successful attempts to assemble supramolecular porphyrin structures, in solution as well as in the solid state, include the generation of patterns stabilized by external metal centers[5] or multidentate bridging ligands,[6] and the construction of aggregates by self-coordination of suitably functionalized lateral substituents of a given porphyrin entity directly to the metal center of an adjacent unit.[7] In the latter context, we have described the assembly of one-, two-, and three-dimensional homogeneous coordination polymers consisting of the Zn$^{II}$ tetra(4-pyridyl)porphyrin [Zn(tpyp)] or Zn$^{II}$ tetra(4-cyanophenyl)porphyrin moieties.[8] Self-assembly of hydrogen-bonded arrays of porphyrin molecules that are peripherally substituted with molecular recognition groups has also been reported.[9]

The *meso*-tetrapyridylporphyrin free base is representative of square-shaped building blocks containing symmetrically disposed ligating sites. This is thus an excellent ligand for tetrametalloporphyrin assemblies[4b, 10] and a potentially excellent building block for the generation of heterogeneous supramolecular networks in combination with other metalloporphyrin units. We report here on the assembly and structural characterization of the supramolecular oligomer $[\{Zn^{II}(tpp)\}_2(tpyp)]$ (**1**) and the uniquely architectured coordination polymer $[\{[Mn^{III}(tpp)]_2(tpyp)(ClO_4)_2\}_\infty]$ (**2**; tpp = tetraphenylphorphyrin). To our knowledge, the latter represents the first example of a well-defined two-dimensional coordination polymer incorporating at least two different porphyrin entities.

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