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Strategic Synthesis of 2,6-Pyridylene-Bridged β-to-β Porphyrin Nanorings through Cross-Coupling

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Since the crystal structure of LH2 was elucidated to be circularly arranged chromophoric assemblies,[1–3] much effort has been devoted towards the synthesis of cyclic porphyrin arrays to study the excitation energy transfer (EET) and electronic coupling along the wheel.[4] These cyclic porphyrin arrays are also interesting in host–guest chemistry,[5] single-molecule photochemistry,[6] nonlinear optical (NLO) materials[7] and so on.[8–12] Cyclic porphyrin arrays are constructed by means of covalent bonds, noncovalent bonds, or metal coordination bonds.[8–12] Although the last two are beneficial to construct cyclic porphyrin arrays, those are often unstable toward solvent change or addition of other competing species. The covalently bonded arrays are structurally robust, but often difficult to synthesize. In addition, the final macrocyclization steps are the most tedious and generally need assistance from a suitable template.[5] Although there are some reports on covalently bonded cyclic porphyrin arrays, most of them were constructed through *meso*-to-*meso* bridging methods. As rare examples, we recently reported two β,β′-bridged cyclic porphyrin arrays with a 1,3-butadiyne or a 2,5-thienyl spacer.[13] Herein, we wish to report the efficient synthesis of 2,6-pyridylene-bridged β-to-β porphyrin nanorings by Suzuki–Miyaura coupling, which is particularly effective for medium to large porphyrin rings.

We have achieved the synthesis of 2,5-thienylene-bridged cyclic porphyrin dimers and trimers, but it was difficult to expand the size of the macrocycle beyond trimers. We then examined the Suzuki–Miyaura coupling of β,β′-diborylated $\mathrm{Ni^{II}}$ porphyrin **1** with 2,6-dibromopyridine, which provided linear oligomers as the main products. However, we noticed that bromopyridyl-terminated oligomers were selectively obtained with the use of an excess amount of 2,6-dibromopyridine. For instance, β,β′-diborylporphyrin **1**–$\mathrm{Ni^{II}}$[14] was cross-coupled with 2,6-dibromopyridine (5 equiv) under standard conditions to give **1**–Br in 80 % yield, along with **2**–Br (10 %) and **3**–Br (2 %) (Scheme 1). It is worth noting that deborylated products were hardly detected in this reaction. Compound **2**–Br was also obtained in 42 % yield through the three-component coupling of **1** (1 equiv), **1**–Br (2.5 equiv), and 2,6-dibromopyridine (2.5 equiv). Further cross-coupling of **1** (1 equiv) with **1**–Br (5 equiv) or **2**–Br (5 equiv) afforded **3**–Br or **5**–Br in 50 or 45 % yields, respectively. Compound **7**–Br was prepared in 50 % yield from **1** and **3**–Br.

With the linear precursors **2**–Br, **3**–Br, **5**–Br, and **7**–Br in hand, we examined the cyclization with **1** through a 1:1 Suzuki–Miyaura coupling reaction, which worked very effectively to give porphyrin rings **3**–Ni, **4**–Ni, **6**–Ni, and **8**–Ni in 60, 58, 55, and 55 % yields, respectively, even without any template. Treatment of **3**–Ni, **4**–Ni, **6**–Ni, and **8**–Ni with sulfuric acid in chloroform at room temperature induced $\mathrm{Ni^{II}}$ demetalation to provide **3**–H, **4**–H, **6**–H, and **8**–H quantitatively, which were all converted into **3**–Zn, **4**–Zn, **6**–Zn, and **8**–Zn upon treatment with $\mathrm{Zn(OAc)_2}$ in quantitative yields.

These newly synthesized porphyrin rings were fully characterized by high-resolution mass spectrometry and

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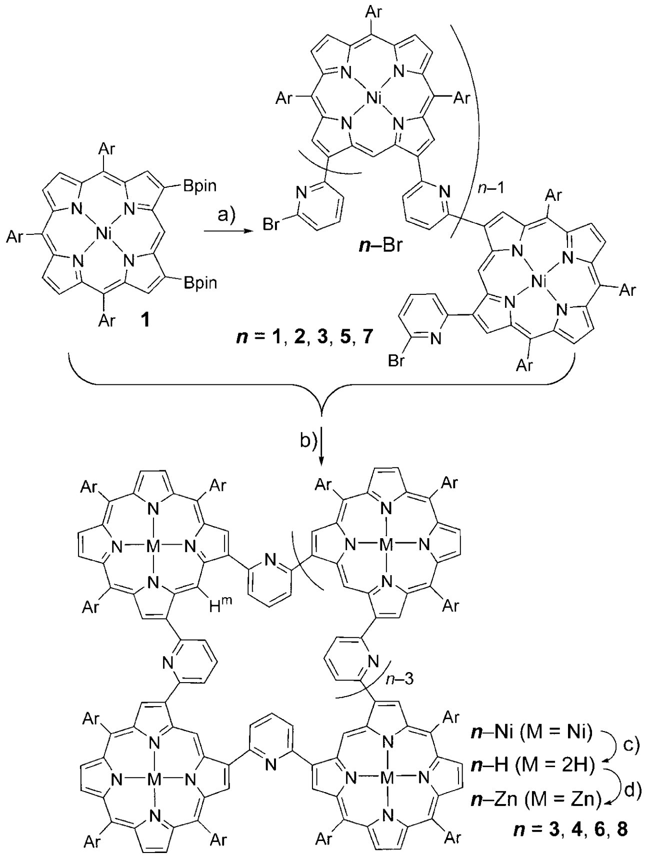

Scheme 1. Synthesis of porphyrin nanorings. Reagents and conditions: a) 2,6-dibromopyridine (5.0 equiv) or bis(bromopyridyl)oligoporphyrins (5.0 equiv), $[Pd_2(dba)_3]$, PPh_3, Cs_2CO_3, CsF, toluene/DMF, reflux; b) **1** (1.0 equiv), ***n***–Br (1.0 equiv), $[Pd_2(dba)_3]$, PPh_3, Cs_2CO_3, CsF, toluene/DMF, reflux; c) H_2SO_4, $CHCl_3$, room temperature; d) $Zn(OAc)_2 \cdot 2H_2O$, $MeOH/CHCl_3$, room temperature, Ar = 3,5-di-*tert*-butylphenyl, dba = *trans,trans*-dibenzylideneacetone; Bpin = 3,3,4,4-tetramethyl-2,5-dioxaborolanyl.

^1H NMR, UV/Vis absorption, and fluorescence spectroscopies (see the Supporting Information). Characteristically, the ^1H NMR spectra of the cyclic structures in $CDCl_3$ at room temperature exhibited singlet peaks for the *meso*-protons (H^m), except for the trimers **3**–Ni, **3**–H, and **3**–Zn. In the case of **3**–Ni, the ^1H NMR spectrum at −50 °C in $[D_8]$toluene exhibited two peaks for the *meso* protons in a 2:1 ratio, suggesting the presence of two distinguishable porphyrins at this temperature.[15] The same feature was also observed for the pyridyl protons. Interestingly, the ^1H NMR spectrum of **3**–Ni at −50 °C exhibited a high-field-shifted pyridyl proton at $\delta = 4.26$ ppm, which merged with other pyridyl protons in the normal region at higher temperatures. In contrast, four, six, and eight pyridyl protons appear in the upfield region in the case of **4**–Ni, **6**–Ni, and **8**–Ni, respectively. These results would indicate that these porphyrin wheels exhibit flexible conformations, but the conformational changes for the trimers are somewhat slower.

Definitive structural assignments have been accomplished by X-ray diffraction analysis for **3**–Ni and **4**–Ni, both of which reveal seriously ruffled porphyrin structures (Figure 1).[16] In **3**–Ni, the mean plane deviations are 0.37, 0.32, and 0.28 Å for porphyrins A, B, and C, which are connected with center-to-center distances of 10.7 (A–B), 12.39 (B–C), and 10.72 (C–A) Å and with dihedral angles of 75.9, 45.7, and 76.3°, respectively. Of the three pyridylene bridges, only py-B takes a different conformation with its nitrogen atom pointing outward. The *para*-proton of py-B is located just above porphyrin A. This location can explain the observed upfield shift of the particular pyridyl proton at $\delta = 4.26$ ppm. The tetramer **4**–Ni takes a pseudo S_4 symmetric zigzag structure, in which four porphyrins are sorted into two identical sets: porphyrins A and B and porphyrins C and D. Porphyrins A and B (hence C and D) are nearly perpendicular with a large dihedral angle of 88°, whereas porphyrins A and C (hence B and D) are nearly parallel with a small dihedral angle of 21.8°. The center-to-center distances are 8.32 and 11.36 Å for porphyrins A and C and for B and D. All of the pyridylene bridges are pointing inward.

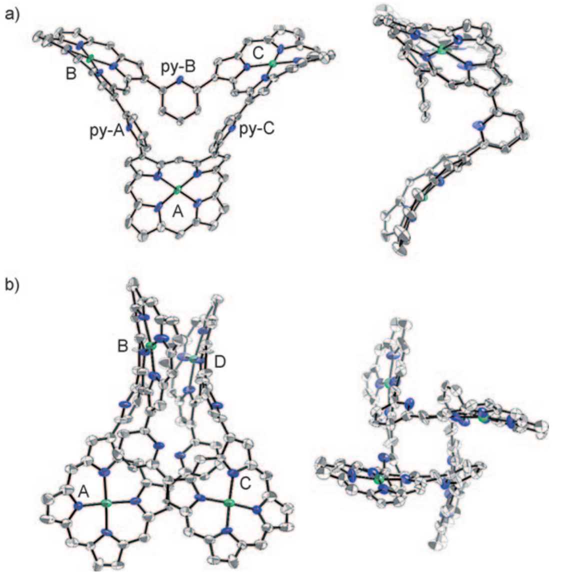

Figure 1. X-ray structures of the porphyrin wheels. a) Top and side views of **3**–Ni and b) top and side views of **4**–Ni. The thermal ellipsoids are shown at the 50 % probability level. *meso*-Aryl groups and hydrogen atoms are omitted for clarity.

The UV/Vis absorption and fluorescence spectra of the Zn^{II}–porphyrins were measured in toluene (Figure 2). All of the nanorings display substantially perturbed absorption spectra, in which the Soret bands of **3**–Zn, **4**–Zn, and **6**–Zn are all split into 2 peaks around 430 and 445 nm, whereas **8**–Zn exhibits only one characteristic broad Soret band at 442 nm. A slight redshift of the Soret band along with broadening was observed as the ring was enlarged. This trend can also be seen in the case of its free base and nickel series (see Figure S18 in the Supporting Information). Interestingly, the shapes of the Soret bands are significantly changed with the metal ion, and there is no split in the nickel series. The fluorescence spectra of cyclic arrays all ex-

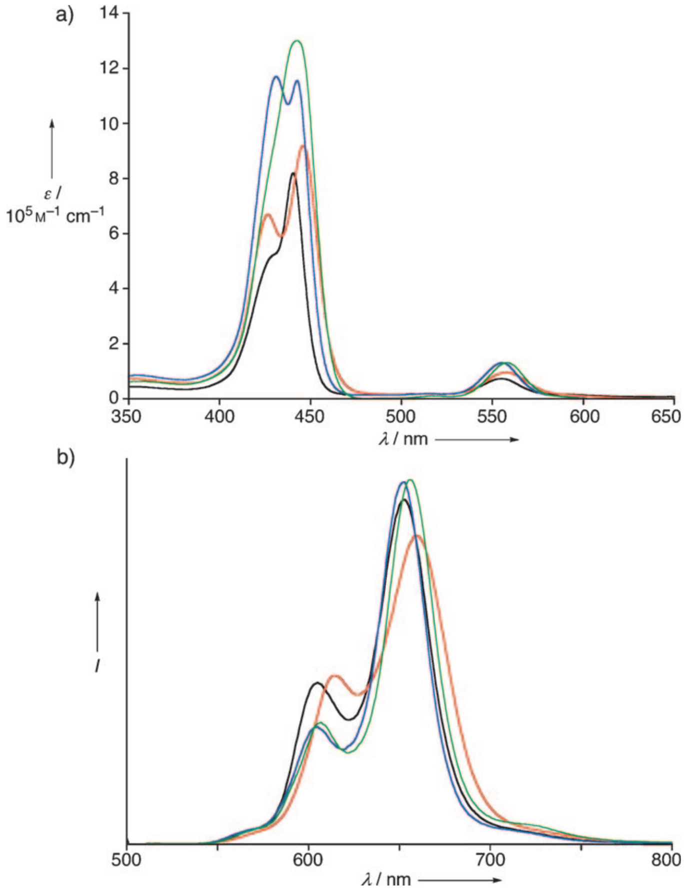

Figure 2. a) UV/Vis absorption and b) emission spectra of **3**–Zn (black line), **4**–Zn (red line), **6**–Zn (blue line), and **8**–Zn (green line) in toluene. Samples were excited at the absorption maxima.

hibit typical vibronic structures with fluorescence quantum yields of around 0.035. The maximum emission peaks are redshifted in the order **3**–Zn ≈ **6**–Zn < **8**–Zn < **4**–Zn, in line with the absorption peak maximum wavelengths. The band positions and shapes in the absorption and fluorescence spectra indicate that there exist unique excitonic and electronic communications in the cyclic porphyrin units. In particular, tetramer cases exhibited the largest excitonic interaction among the series, probably reflecting its semi-rigid and extended structure.

To obtain information on the relative orientation between the absorption and emission transition dipole moments, we measured the fluorescence excitation anisotropy (see Figure S22 in the Supporting Information).[17] The absolute anisotropy values of all the nanorings were smaller than 0.1 in the whole excitation region, reflecting that the reorientation of the transition dipole moment occurs in the nanorings.[18] This indicates that the singlet–singlet excited-state energy transfer is quite efficient along the ring.[19] The time-resolved fluorescence decay profiles of nanorings were measured in toluene (see Figure S23 in the Supporting Information). The lifetimes of Zn^{II}–porphyrin arrays[20,13b] generally become shorter as the number of porphyrin moieties increases due to the acceleration of a nonradiative process caused by the reduced energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). However, the lifetimes of singlet excited states become longer as the number of porphyrin units increases from **3**–Zn and **4**–Zn to **6**–Zn and **8**–Zn (Table 1). Their lifetimes are also longer than that of zinc–tetraphenylporphyrin (Zn–TPP).

Table 1. Optical properties of nanorings.

Compound	λ_{em} [nm][a]	τ_f [ns][b]	Φ_F[c]
Zn–TPP	644	2.13	0.033
3–Zn	653	2.67	0.032
4–Zn	659	2.58	0.035
6–Zn	653	3.07	0.035
8–Zn	657	3.09	0.033

[a] Fluorescence maximum wavelength. [b] Singlet excited-state lifetime. [c] Fluorescence quantum yield.

In summary, we have achieved the synthesis of β-2,6-pyridylene-bridged porphyrin nanorings in good yields with Suzuki–Miyaura cyclization of 6-bromopyridine-terminated linear oligoporphyrins with diborylated porphyrin **1**. These porphyrin arrays exhibit weak electronic coupling among porphyrins and longer singlet-excited state lifetimes, which have an apparent advantage in the process of excitation energy transfer. Further exploration into their photophysical properties and interactions with other molecules are currently underway in our laboratory.

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Keywords: cross-coupling · fluorescence · host–guest chemistry · nanorings · porphyrinoids

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[15] We used [D$_8$]toluene instead of $CDCl_3$ as a solvent for ^{1}H NMR spectroscopy measurements of the trimers to prevent overlapping of solvent signal with the aryl peaks.

[16] Crystal data of **3**–Ni: $C_{209}H_{230}Cl_1N_{15}Ni_3O_1$; $M=3179.66$; triclinic; space group $P\bar{1}$ (No. 2); $a=20.769(2)$, $b=21.468(2)$, $c=26.889(3)$ Å; $\alpha=73.037(2)$, $\beta=84.358(2)$, $\gamma=66.661(2)^\circ$; $V=10527.1(18)$ Å^3; $Z=2$; $\rho_{calcd}=1.003\,g\,cm^{-3}$; $T=90(2)$ K; 54021 measured reflections; 36424 unique reflections; $R=0.0953$ ($I>2.0\sigma(I)$); $R_w=0.2807$ (all data); GOF = 0.961. Crystal data of **4**–Ni: $C_{268}H_{292}N_{20}Ni_4$; $M=4028.06$; tetragonal; space group $I4_1/a$ (No. 88); $a=24.472(3)$, $c=52.747(6)$ Å; $V=31589(6)$ Å^3; $Z=4$; $\rho_{calcd}=0.847\,g\,cm^{-3}$; $T=90(2)$ K; 71293 measured reflections; 11644 unique reflections; $R=0.0991$ ($I>2.0\sigma(I)$); $R_w=0.2912$ (all data); GOF = 1.018. The contribution to the scattering arising from the presence of disordered solvents in the crystals was removed by use of the utility SQUEEZE in the PLATON software package.[21] CCDC-754843 and 754844 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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