Porphyrinoids

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# Porphyrin "Lego Block" Strategy To Construct Directly meso–β Doubly Linked Porphyrin Rings**

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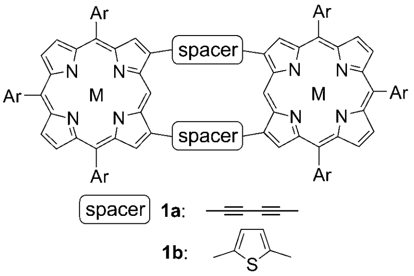
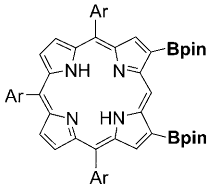
Electronically interacting multiporphyrinic systems have received much attention in light of their potential applications in optoelectronic devices, sensors, photovoltaic devices, nonlinear optical (NLO) materials, and photodynamic therapy (PDT) pigments.[1] To achieve desirable electronic and photophysical properties, the manipulation of interporphyrinic interactions is often essential.[2] Along this line, we reported $Ag^I$-promoted *meso–meso* coupling reactions of 5,15-diaryl substituted $Zn^{II}$ porphyrins and a subsequent DDQ/$Sc(OTf)_3$-induced oxidative fusion reaction (DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone; Tf = trifluoromethanesulfonyl) into porphyrin tapes,[3] which yielded extremely long molecules,[3b] extensively π-conjugated molecules,[3c] directly linked porphyrin rings,[3e] and an antiaromatic porphyrin sheet.[3f] These examples showed that the directly linked porphyrin arrays have a strong advantage of precise control in the large electronic interactions.

As another effective synthetic protocol, we explored Ir-catalyzed β-borylation reaction of *meso*-free *meso′*-aryl-type porphyrins.[4] These borylated porphyrins have been used for the construction of various functional oligomeric porphyrinoids, including doubly β-to-β bridged diporphyrins **1a** and **1b**, which have butadiyne[5a] and 2,5-thiophene spacers,[5b] respectively. Interestingly, these porphyrin dimers displayed large two-photon absorption (TPA) cross-section values.[2h] We envisioned that the replacement of a spacer by a porphyrin segment or an oligomeric porphyrin moiety would allow the construction of directly linked porphyrin rings of unique architectures. This idea was indeed shown to be correct. Herein, we report a porphyrin "Lego block" strategy, which provides directly multiply *meso*–β linked porphyrin rings efficiently.





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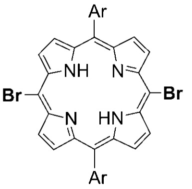

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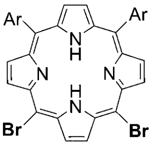

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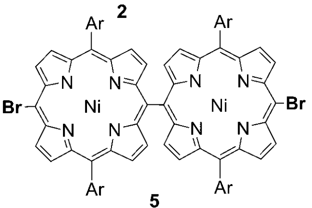

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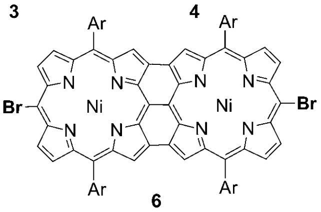

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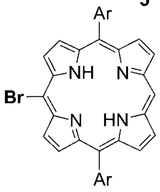

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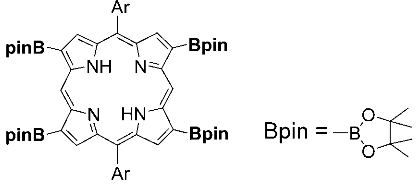

**8**

Ar = 3,5-di-*tert*-butylphenyl

Molecular building blocks **2**–**8** were prepared in this work. β,β′-Diborylporphyrin **2**[4a] was cross-coupled with 5,15-dibro-

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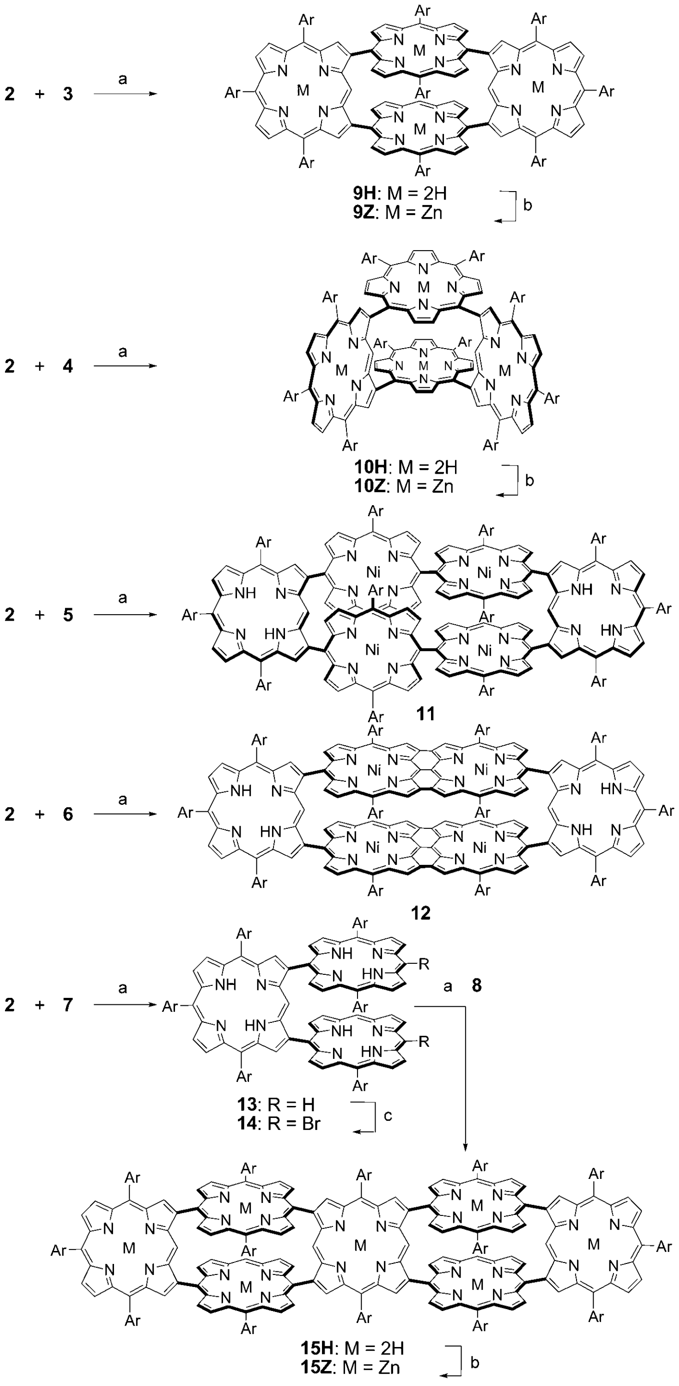
moporphyrin **3** by Suzuki–Miyaura reaction[6] ([Pd$_2$(dba)$_3$], PPh$_3$, Cs$_2$CO$_3$, and CsF) to provide *meso*-to-β directly linked tetrameric porphyrin ring **9H** in 21 % yield (Scheme 1). This yield is rather high, considering the four consecutive carbon–carbon bond-forming processes and the large molecular size involved. The $^1$H NMR spectrum of **9H** is quite simple, exhibiting a singlet signal at $\delta = 8.17$ ppm for the *meso*-protons, and a singlet signal and four doublet signals for the β-protons. The parent ion peak of **9H** was observed at *m*/*z* 3115.8 (calcd for $C_{220}H_{249}N_{16}$: 3115.8 ([$M$+H]$^+$)) in its MALDI-TOF mass spectrum. Zn$^{II}$ complex **9Z** was quantitatively prepared by the usual Zn$^{II}$ metalation. Similar cyclization of **2** and 5,10-dibromoporphyrin **4** gave bent tetramer **10H** in 16 % yield. Its MALDI-TOF mass spectrum is identical to that of **9H**, but the $^1$H NMR spectrum is quite different, exhibiting a singlet signal at $\delta = 10.42$ ppm for the *meso*-protons, and three singlet and four doublet signals for the β-protons, which is in line with the expected structure.

Definitive structural assignments of **9Z** and **10Z** were accomplished by single-crystal X-ray diffraction analysis, which revealed the respective "logical" structures (Figure 1).[7] The porphyrin macrocycles are relatively planar in both **9Z** and **10Z**, although the dihedral angles deviate slightly from the perpendicular situation, as is often seen for directly *meso*–β linked porphyrins.[8] In **9Z**, the central 5,15-linked porphyrin moiety is tilted by 62.4° to the adjacent 2,18-linked porphyrin moiety, and serious disorder of the porphyrin cores was observed for **10Z**, which showed dihedral angles ranging from 75 to 81°. The interplanar distance of the 5,15-linked porphyrin moieties in **9Z** is 6.1 Å and that of the 5,10-linked porphyrin moieties in **10Z** ranges from 4.3 to 8.8 Å.

The UV/Vis absorption spectrum of **9Z** shows a split Soret band at 417 and 455 nm and Q bands at 563 and 606 nm, and that of **10Z** shows a Soret band at 441 nm with a shoulder at 410 nm and Q bands at 558 and 596 nm (Figure 2). These differently split Soret bands of **9Z** and **10Z** can be understood in terms of exciton coupling theory[9] in the same manner as performed for the *meso*–



*Scheme 1.* Synthesis of a variety of multiporphyrin arrays with various links through Suzuki–Miyaura cross-coupling reactions. Reaction conditions: a) [Pd$_2$(dba)$_3$], PPh$_3$, Cs$_2$CO$_3$, CsF, DMF, toluene. b) Zn(OAc)$_2$, methanol, CH$_2$Cl$_2$. c) NBS, CHCl$_3$.

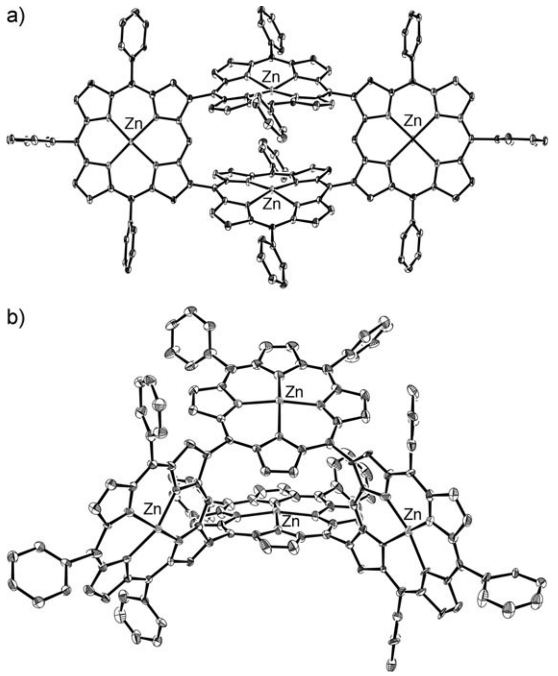


*Figure 1.* X-ray crystal structures of a) **9Z** (top) and b) **10Z** (bottom). *tert*-Butyl groups, hydrogen atoms, disordered parts, and solvent molecules are omitted for clarity. The ellipsoids are scaled to the 30 % probability level.

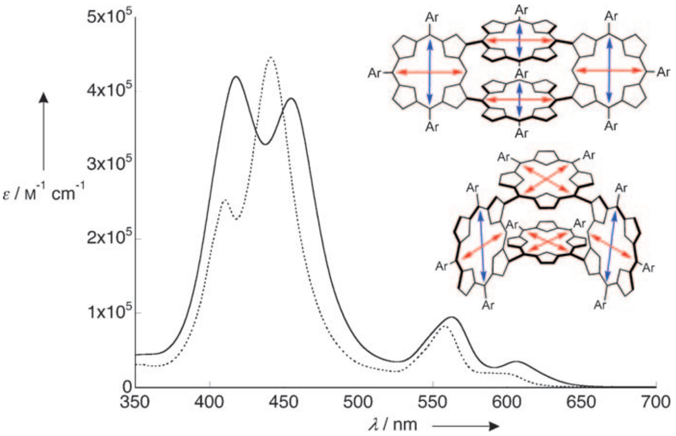


*Figure 2.* UV/Vis absorption spectra of **9Z** (solid line) and **10Z** (broken line) in $CH_2Cl_2$. Inset: Transition dipoles of the porphyrin rings.

*meso* linked $Zn^{II}$ porphyrin oligomers. It is appropriate to place two transition dipole moments for each porphyrin unit as shown in the inset of Figure 2. Given the roughly orthogonal conformations for the neighboring porphyrins in **9Z** and **10Z**, the exciton coupling of parallel transition dipoles ($\mu_{\parallel}$: red arrow) is effective but the other interactions between $\mu_{\parallel}$ and $\mu_{\perp}$ (blue arrow) should be cancelled to be zero. The interacting component leads to a red-shifted Soret band (455 nm for **9Z**, 441 nm for **10Z**), while the non-interacting component leaves a Soret band at the same position as for the porphyrin monomer (around 415 nm). It is likely that the observed intensity of the split Soret bands reflects the relative amplitude of the interacting (parallel) component to the non-interacting (perpendicular) one. The fluorescence spectrum of **9Z** exhibits a broad structure with a relatively high fluorescence quantum yield ($\Phi_F = 0.097$), whereas that of **10Z** exhibits a typical porphyrin-like vibronic structure and the quantum yield is lower ($\Phi_F = 0.072$) (see the Supporting Information).

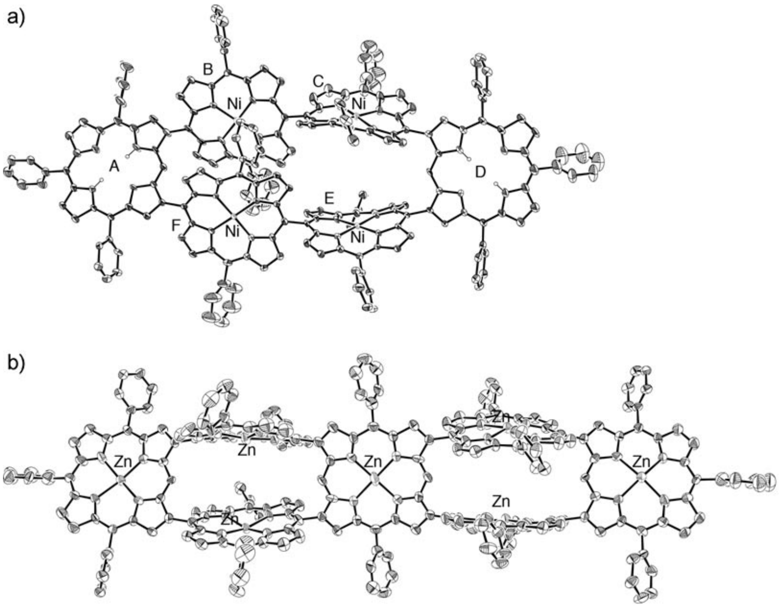


*Figure 3.* X-ray crystal structures of a) **11** and b) **15Z**. *tert*-Butyl groups, hydrogen atoms except for NH, and solvent molecules are omitted for clarity. The ellipsoids are scaled to the 30% probability level.

We then employed a *meso*–*meso* linked $Ni^{II}$ diporphyrin and a *meso*–*meso*, β–β, β–β triply linked $Ni^{II}$ diporphyrin as a spacer to construct hexamers **11** and **12** (Scheme 1). Suzuki–Miyaura coupling of **2** with **5**[10] and **6** successfully provided directly linked porphyrin hexamers **11** and **12** in 13 and 11% yields, respectively. The parent ion peaks were observed at *m*/*z* 4712.5 for **11** (calcd for $C_{316}H_{345}N_{24}Ni_4$: 4712.4 ($[M+H]^+$)) and at *m*/*z* 4704.4 for **12** (calcd for $C_{316}H_{337}N_{24}Ni_4$: 4705.0 ($[M+H]^+$)), respectively, in the MALDI-TOF mass spectra. The $^1$H NMR spectra of **11** and **12** were fully consistent with the expected structures (see the Supporting Information). More clearly, the X-ray crystal structure of **11** was revealed for crystals obtained by slow diffusion of acetonitrile into a solution in toluene (Figure 3a).[7] All four nickel(II) porphyrin rings take ruffled structures, whereas the two free-base porphyrin rings take planar structures. Dihedral angles between *meso*–*meso* linkages are almost perpendicular (87.6° for planes B–C, 85.2° for planes E–F), whereas those between *meso*–β linkages are shown to be smaller with values from 47.5° to 74.9°, to give a large cavity inside the rings.

Furthermore, we extended this cyclization strategy in a stepwise manner to construct even larger assemblies such as the bridged heptameric porphyrin array **15** (Scheme 1). Cross-coupling reaction of **2** with an excess amount of **7** gave 2,18-bisporphyrinyl porphyrin **13** in 45% yield, which was then brominated by *N*-bromosuccinimide (NBS) to afford **14** quantitatively. Formation of **15H** proceeded smoothly by the 2:1 Suzuki–Miyaura coupling of **14** with **8**.[4a] The parent ion peak was detected at *m*/*z* 5169.3 (calcd for $(C_{364}H_{402}N_{28})^+$: 5169.2 ($[M]^+$)) for **15H**. In spite of the large molecular size, the $^1$H NMR spectra of **15H** and **15Z** are both clear, exhibiting relatively sharp signals (see the Supporting Information). Typically, the $^1$H NMR spectrum of **15Z** showed two singlet signals at $\delta = 8.38$ and 8.20 ppm due to the *meso*-protons, and two singlet signals at $\delta = 10.3$ and 10.0 ppm due to the pyrrolic β-protons. These data well support the expected structures. Finally, the structure of **15Z** was unambiguously confirmed by single-crystal X-ray diffraction analysis (Figure 3b).[7] To the best of our knowledge, this is the largest single-crystal structure among the covalent porphyrin arrays so far reported. The absorption spectrum of **15Z** is similar to that of **9Z** except for the red-shifted and intensified lower-energy Soret band. The red shift of the emission spectrum of **15Z** is not so large (645 nm) relative to that of **9Z**.

In summary, we have achieved the designed synthesis of directly *meso*–β doubly linked porphyrin rings by Suzuki–Miyaura cyclization. Excitation energy hopping processes in light-harvesting complexes depend mainly on the strength of exciton coupling governed by interconnection length and relative configuration between adjacent moieties. Thus, these directly linked porphyrin rings are suitable to examine the relationship between the photoexcited dynamics and molecular structure. Detailed photophysical studies on these porphyrin rings are actively in progress in our laboratories and will be reported in due course.

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[7] **9Z**: $C_{245.33}H_{290.35}N_{16}O_{8.89}Zn_4$, $M_w = 3867.24$, triclinic, space group $P\bar{1}$ (no. 2), $a = 14.067(5)$, $b = 20.108(5)$, $c = 23.151(5)$ Å, $\alpha = 112.617(5)$, $\beta = 94.271(5)$, $\gamma = 103.263(5)°$, $V = 5786(3)$ Å$^3$, $Z = 1$, $T = 90(2)$ K, $D_{calcd} = 1.093\ g\,cm^{-3}$, $R_1 = 0.0960$ $(I > 2\sigma(I))$, $R_w = 0.2865$ (all data), GOF = 1.038; **10Z**: $C_{224}H_{252}N_{16}O_4Zn_4$, $M_w = 3493.9$, triclinic, space group $P\bar{1}$ (no. 2), $a = 16.1435(14)$, $b = 16.1435(14)$, $c = 36.901(3)$ Å, $\alpha = 76.753(2)$, $\beta = 79.419(2)$, $\gamma = 75.156(2)°$, $V = 12\,402.5(19)$ Å$^3$, $Z = 2$, $T = 90(2)$ K, $D_{calcd} = 0.936\ g\,cm^{-3}$, $R_1 = 0.0795$ $(I > 2\sigma(I))$, $R_w = 0.2416$ (all data), GOF = 0.960; **11**: $C_{316}H_{344}N_{24}Ni_4$, $M_w = 4712.91$, triclinic, space group $P\bar{1}$ (no. 2), $a = 20.382(3)$, $b = 30.277(5)$, $c = 31.868(5)$ Å, $\alpha = 87.907(3)$, $\beta = 72.501(3)$, $\gamma = 84.926(3)°$, $V = 18\,681(5)$ Å$^3$, $Z = 2$, $T = 90(2)$ K, $D_{calcd} = 0.838\ g\,cm^{-3}$, $R_1 = 0.0865$ $(I > 2\sigma(I))$, $R_w = 0.2387$ (all data), GOF = 0.768; **15Z**: $C_{373.28}H_{408.73}N_{28}O_{5.45}Zn_7$, $M_w = 5832.35$, triclinic, space group $P\bar{1}$ (no. 2), $a = 20.161(3)$, $b = 24.440(4)$, $c = 24.481(3)$ Å, $\alpha = 117.747(3)$, $\beta = 98.540(3)$, $\gamma = 104.177(2)°$, $V = 9854(2)$ Å$^3$, $Z = 1$, $T = 90(2)$ K, $D_{calcd} = 0.983\ g\,cm^{-3}$, $R_1 = 0.0981$ $(I > 2\sigma(I))$, $R_w = 0.2705$ (all data), GOF = 0.767. The contributions to the scattering arising from the presence of the disordered solvents in the crystals of **10Z**, **11**, and **15Z** were removed by use of the utility SQUEEZE in the PLATON software package.[11] CCDC 761907 (**9Z**), 761904 (**10Z**), 761905 (**11**), and 761906 (**15Z**) 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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