

Synthesis of *meso-meso* Linked Hybrid Porphyrin Arrays by Pd-Catalyzed Cross-Coupling Reaction

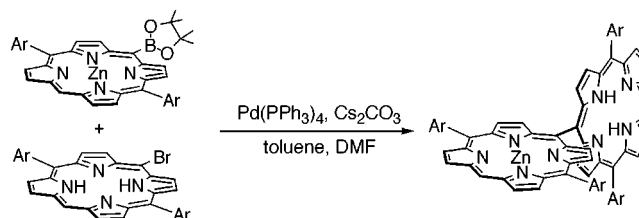
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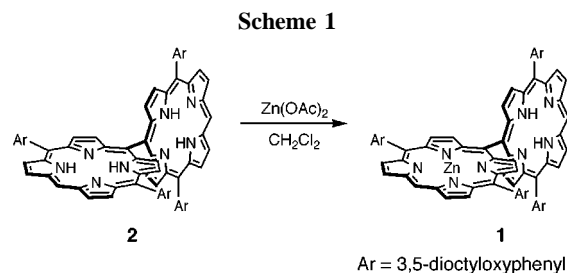
ABSTRACT



meso-meso linked porphyrin arrays of a variety of compositions and connectivities have been prepared by Pd-catalyzed cross-coupling reaction in a manner complementary to Ag^I-promoted oxidative coupling.

Covalently linked multiporphyrinic molecules have been attracting continuous attention in relation to the understanding and duplication of electron and/or energy transfer in natural photosynthetic systems,¹ as well as the development of novel functional materials.² Among these, *meso-meso* linked porphyrin arrays possess a unique position in that they are directly linked and are favorable for achieving rapid energy- and electron-transfer reactions owing to a short center-to-center distance (ca. 8.4 Å), large Coulombic interaction, and a nearly orthogonal conformation that minimizes conjugation of neighboring porphyrins, making a *state-to-state* dynamic energy- and/or electron-transfer process feasible without causing serious electronic delocalization.^{3,4} In line with this expectation, the singlet–singlet excitation energy transfer proceeds with a rate of (0.55 ps)⁻¹ in Zn^{II}-free base hybrid diporphyrin **1** in THF.⁵ Ag^I-salt promoted oxidative *meso-meso* coupling reaction of 5,15-diaryl Zn^{II}-porphyrins has been shown to be particularly effective in making homoge-

neous porphyrin arrays, which was highlighted by the synthesis of a discrete 128-mer with ca. 133 000 Da molecular weight and 0.1 μm molecular length in its straight form.^{3c} Unfortunately, however, this method is not applicable to the preparation of hybrid diporphyrins such as **1**, which was therefore prepared in 6% yield from partial metalation of **2** (Scheme 1). The low yield was due mainly to

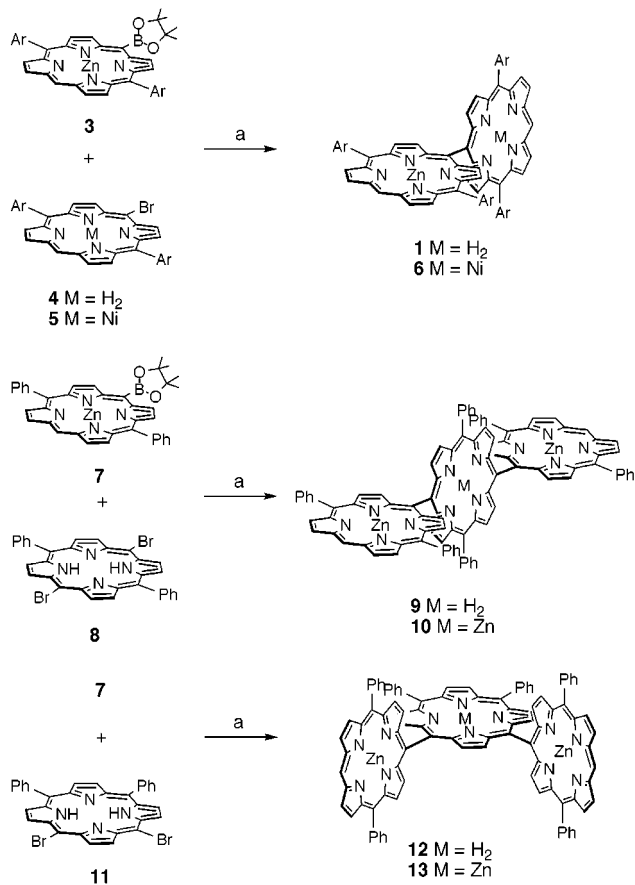


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nonselective metalation and very similar chromatographic eluting properties of **1**, **2**, and bis-Zn^{II} diporphyrin.

Scheme 2 shows a Pd-catalyzed coupling strategy for the synthesis of *meso-meso* coupled hybrid porphyrin arrays.^{6,7} Porphyrin boronate **3** was prepared in 90% yield from *meso-*

Scheme 2^a

^a (a) Pd(PPh₃)₄, Cs₂CO₃, toluene, DMF, 80 °C, 3 h; Ar = 3,5-diocetylxyphenyl.

bromoporphyrin **4** by coupling with pinacol borane.⁸ Cross-coupling of **3** and **4** was carried out in a mixture of toluene and DMF⁹ in the presence of a catalytic amount (~10 mol %) of Pd(PPh₃)₄ and 1.5 equiv of Cs₂CO₃ at 80 °C under an

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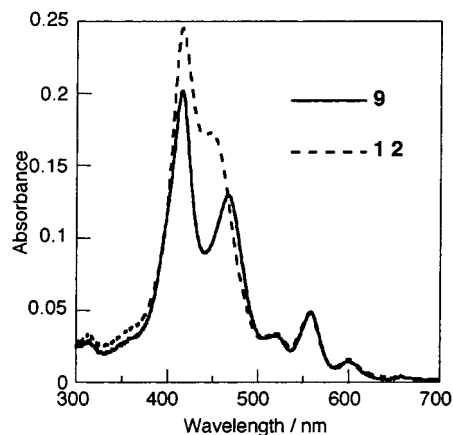


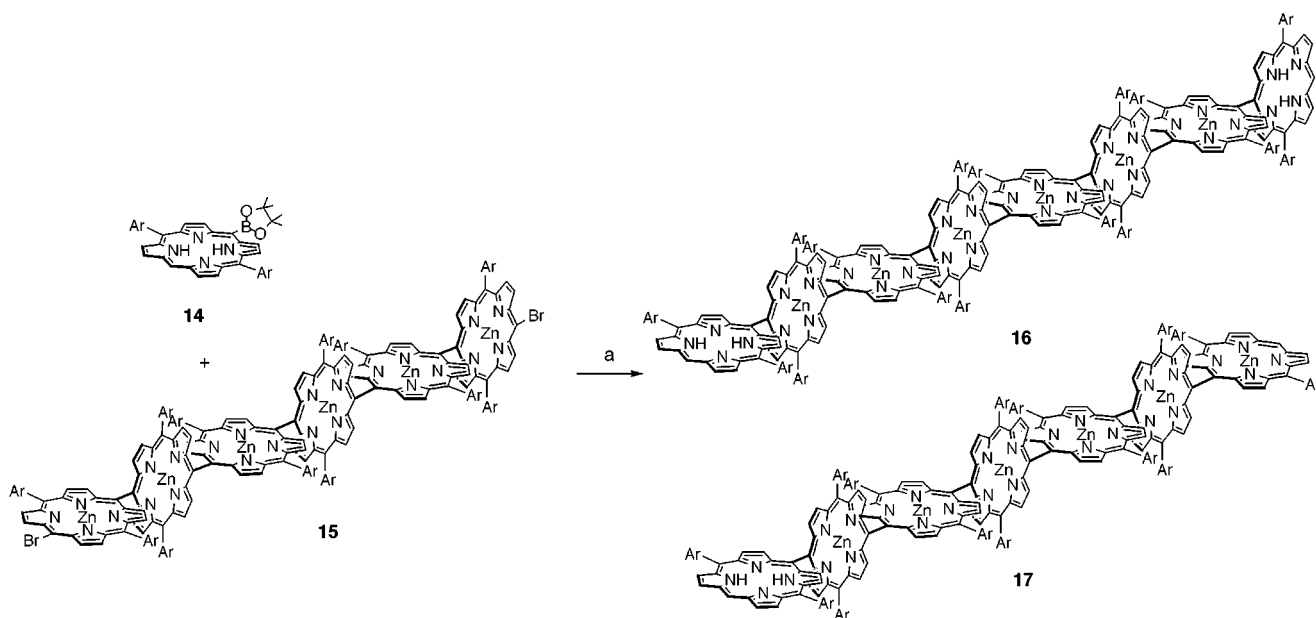
Figure 1. UV-vis spectra of linear and bent-shaped zinc^{II}-free base hybrid porphyrin arrays in THF.

inert atmosphere to give **1** in 62% yield. In marked contrast to the partial metalation route, isolation of **1** was easy by size-exclusion chromatography (SEC) owing to a molecular weight difference between the diporphyrin product and the starting materials. The Zn^{II}-free base hybrid **1** thus prepared exhibited properties identical with those of the previous diporphyrin product prepared from the partial metalation of **2**. Similarly Zn^{II}-Ni^{II} hybrid diporphyrin **6** was prepared in 57% yield. Linear and bent hybrid triporphyrin arrays **9** and **12** were prepared from the coupling reaction of **7** with **8** and **11** in 45% and 46% yields, respectively. Virtually no scrambling of metalated porphyrin sites during the coupling reaction is notable, since this method allows the synthesis of porphyrin arrays with metalated sites in a predictable manner, which are quite useful for studies on photoinduced energy- and/or electron-transfer reactions.

Taking advantage of no scrambling of this coupling, *meso,meso'*-dibromo-hexa-Zn^{II}-porphyrin **15** was reacted with free base porphyrin boronate **14** under the same conditions, to give porphyrin octamer **16** (11%) and heptamer **17** (32%) (Scheme 3). The products **16** and **17** displayed the parent mass at *m/z* = 8167 (calcd for C₅₁₂H₆₆₂N₃₂O₃₂Zn₆ = 8169) and 7198 (calcd for C₄₄₈H₅₇₈N₂₈O₂₈Zn₆ = 7196), respectively, by MALDI-TOF mass measurements. Analysis of their ¹H NMR spectra revealed the location of free base porphyrins as shown in Scheme 3 (Supporting Information). Concurrent debromination that led to formation of **17** restricted this application.

The absorption spectrum of **1** is given by a sum of the spectra of the Zn^{II}-Zn^{II} dimer and free base-free base dimer rather than the sum of the spectra of the Zn^{II} monomer and free base monomer, indicating that the electronic state of *meso-meso* linked porphyrin is strongly perturbed by the exciton coupling not only in the S₂-state but also in the S₁-state.⁵ Here it is noteworthy that an orthogonal conformation

(9) In the preliminary experiment, treatment of **3** and **4** with Pd(PPh₃)₄ as catalyst and K₂CO₃ as base in toluene gave the desired dimer **1** only in low yields (<10%).

Scheme 3^a

^a (a) Pd(PPh₃)₄, Cs₂CO₃, toluene, DMF, 80 °C, 5 h, Ar = 3,5-dioctyloxyphenyl.

prevents electronic delocalization of the Zn^{II}-porphyrin and free base porphyrin, thus allowing a *state-to-state* energy transfer in **1** in THF.⁵

A similar energy transfer is also suggested for both **9** and **12**, since the fluorescence emission is coming only from the free base porphyrin even upon irradiation at 556 nm, which corresponds to the predominant excitation of the peripheral Zn^{II}-porphyrins. The effect of the molecular connectivity, e.g., straight versus bent, on the energy transfer rate is an intriguing issue,¹⁰ which is now being studied by using ultrafast photophysical measurements. The effect of the molecular connectivity is evident for the absorption spectra (Figure 1) in that the Soret band is clearly split in **9** but is

only modestly split in **12**. The absorption spectra of all Zn^{II} complexes of the trimers **10** and **13** display a more distinct measurable difference in the coupling strength in the Soret band, $\Delta E \approx \sim 3200$ and 2400 cm⁻¹, respectively (Figure 2). It is appropriate to place two transition dipole moments of each porphyrin unit as shown in Figure 3.¹¹ When we postulate the nearly orthogonal conformations for the neighboring *meso-meso* linked porphyrins, which have recently been confirmed by the X-ray analysis of a straight *meso-meso* linked triporphyrin,¹² it is expected that the exciton coupling of three transition dipoles ($M_{X1} + M_{X2} + M_{X3}$) is possible but the other interactions should be zero in **10**, while

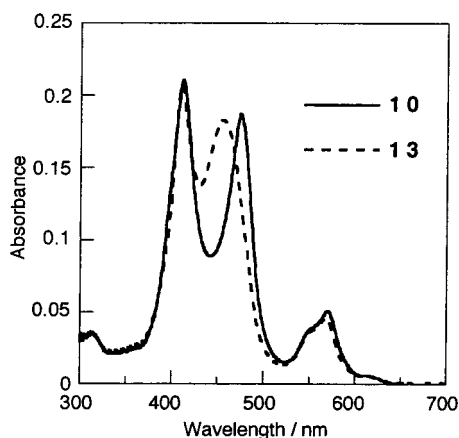


Figure 2. UV-vis spectra of linear and bent-shaped all-zinc^{II} porphyrin arrays in THF.

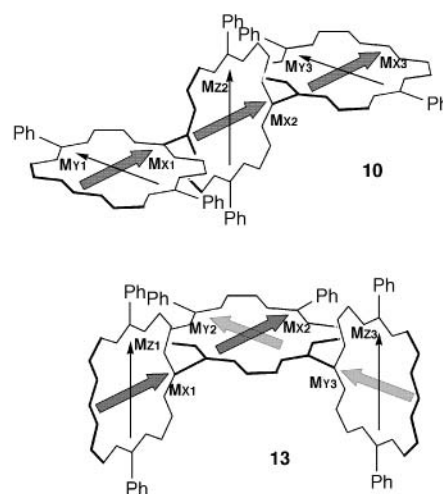


Figure 3. Schematic representations of transition moments in the linear- and bent-shaped porphyrin trimers.

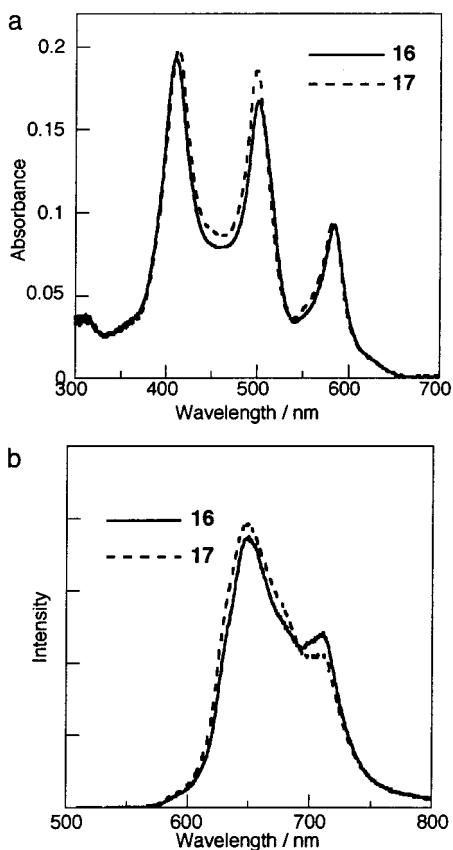


Figure 4. UV-vis and fluorescence spectra of *meso-meso* linked zinc^{II}-free base hybrid porphyrin long arrays in THF. (a) UV spectra of **16** and **17**, and (b) fluorescence spectra of **16** and **17** upon excitation at 411 nm.

the degenerate two exciton couplings ($M_{X_1} + M_{X_2}$ and $M_{Y_2} + M_{Y_3}$) are possible but the other interactions should be zero in **13**.¹³ Noninteracting transition dipoles would result in an unperturbed Soret band at the same position as the porphyrin

monomer. It is likely that the ratio of interacting (parallel) to noninteracting (perpendicular) components is reflected on the relative oscillator strength of split Soret bands.

In the steady-state fluorescence spectra of **16** and **17** in THF, the fluorescence emissions come predominantly from the free base porphyrin in both cases, indicating the efficient energy transfer from the photoexcited Zn^{II}-porphyrin array to the free base porphyrin end (Figure 4). These properties are interesting in light of use as a photonic molecular wire, since the excitation energy widely captured by a Zn^{II}-porphyrin array is efficiently transmitted unidirectionally to a free base porphyrin.

In conclusion, *meso-meso* linked hybrid porphyrin arrays can be prepared by Pd-catalyzed coupling reaction in a manner complementary to Ag^I-promoted oxidative coupling of Zn^{II}-porphyrins. Optical properties of *meso-meso* linked triporphyrins are indeed sensitive to their connectivity. This strategy is useful for the preparation of hybrid porphyrin arrays with definite composition and unique molecular shape.

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Supporting Information Available: Experimental procedures and characterization data for new compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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