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Efficient synthesis of benzene-centered cyclic porphyrin hexamers

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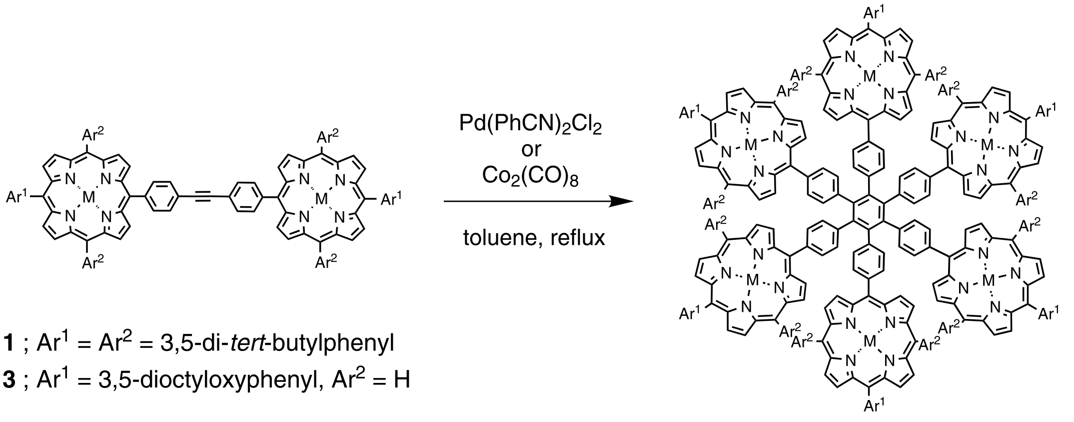
Abstract—Palladium- and cobalt-catalyzed trimerization of diphenylethynyl-bridged diporphyrin gave benzene-centered cyclic porphyrin hexamers. © 2002 Elsevier Science Ltd. All rights reserved.

Covalently linked porphyrin arrays have been pursued as models for studies on electron- or energy-transfer reactions to mimic the key processes in natural photosynthesis.[1] Elucidation of the ring structure of bacterial light harvesting antenna LH2[2] has stimulated experimental and theoretical studies on these interesting bacteriochlorophyll aggregates.[3] Model studies have been similarly activated, resulting in developments of a variety of discrete cyclic porphyrin arrays.[4] In this paper, we describe the synthesis of benzene-centered cyclic porphyrin arrays by palladium- and cobalt-catalyzed trimerization reactions of diphenylethynyl-bridged diporphyrins. Here we also report that cyclic porphyrin hexamers can serve as effective chiral amplifiers when complexed with a chiral amine in a manner that a chiral geometrical constrain arising from the coordination is transmitted to the chiral conformation of the whole array.



1 ; $Ar^1 = Ar^2$ = 3,5-di-*tert*-butylphenyl
3 ; Ar^1 = 3,5-dioctyloxyphenyl, Ar^2 = H

2 ; $Ar^1 = Ar^2$ = 3,5-di-*tert*-butylphenyl
4 ; Ar^1 = 3,5-dioctyloxyphenyl, Ar^2 = H

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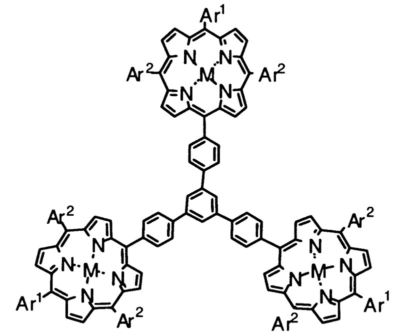
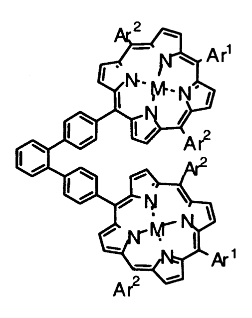
Transition metal catalyzed trimerization of di-substituted acetylenes has proven successful in preparation of a variety of hexa-substituted benzenes.[5] Our first trial to trimerize diphenylethynyl-bridged diporphyrin **1-H$_2$**[6] under the reported reaction conditions (Pd(PhCN)$_2$Cl$_2$, toluene, 80°C, 40 h)[7] failed due to easy transmetallation to mono- and bis-Pd(II)-diporphyrins. We, therefore, changed the reactant to **1-Pd**, which provided, under the similar conditions for 1 week, hexameric porphyrin array **2-Pd** in 3.4% yield. The molecular weight of **2-Pd** has been determined by MALDI-TOF MS to be $m/z = 6397$ (calcd for $C_{414}H_{450}N_{24}Pd_6 = 6393$) and its ^1H NMR spectrum is quite simple and shows that the six porphyrins are equivalent, featuring four doublets due to the β-protons at 8.73, 8.67, 8.55, and 7.96 ppm, two doublets due to the 1,4-phenylene spacer at 8.37 and 8.15 ppm, and aromatic signals due to the *meso*-3,5-di-*tert*-butylphenyl substituents with a 2:1 ratio. It is worth noting that only the *ortho*-aromatic protons in Ar^2 experience extensive broadening, probably due to the crowding of the Ar^2-substituents in the hexameric porphyrin array. Similarly, the trimerization of **1-Ni** (1 week, 50°C) gave hexamer **2-Ni** ($m/z = 6109$, calcd for $C_{414}H_{450}N_{24}Ni_6 = 6105$) in 3.3% yield along with the recovery of **1-Ni** (61%). As has been observed for **2-Pd**, the ^1H NMR spectrum of **2-Ni** showed the similar broadening for the same particular aromatic protons in Ar^2.

With a view of steric congestion around the Ar^2-substituents as a main cause for the low yields of **2-Pd** and **2-Ni**, we changed a reactant to **3-Ni**, which, under the same conditions, afforded porphyrin hexamer **4-Ni** (MALDI-TOF MS, $m/z = 4722$; calcd for $C_{294}H_{306}N_{24}Ni_6O_{12} = 4720$) in 30% yield and the yield was improved to 70% under the modified conditions (using threefold amount of Pd(II)-catalyst, a shorter reaction time (12 h)) and the similar trimerization of **3-Cu** afforded the corresponding hexamer **4-Cu** ($m/z = 4747$; calcd for $C_{294}H_{306}N_{24}Cu_6O_{12} = 4742$) in a better yield of 87%. The hexamer **4-Cu** was quantitatively demetallated with H_2SO_4 in trifluoroacetic acid to give free-base hexamer **4-H$_2$** ($m/z = 4377$; calcd for $C_{294}H_{306}N_{24}Cu_6O_{12} = 4377$), which was metallated with Zn(OAc)$_2$ to afford **4-Zn** ($m/z = 4757$; calcd for $C_{294}H_{306}N_{24}Cu_6O_{12} = 4748$).

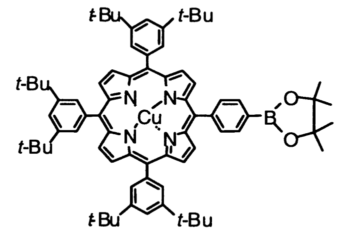
In the next step, we examined the Co$_2$(CO)$_8$-catalyzed cyclotrimerization reaction that gave **4-Cu** from **3-Cu** in 70% yield. Remarkably, the Co$_2$(CO)$_8$-catalyzed cyclotrimerization reaction has been found to be effective also for sterically demanding 5,10,15-triaryl substituted diporphyrin substrates **1-Pd**, **1-Ni**, and **1-Cu**, giving **2-Pd**, **2-Ni**, and **2-Cu** in 78, 71, and 82% yields, respectively. Zinc complex **2-Zn** was prepared quantitatively from **2-Cu** under the same conditions used for **4-Cu**. As reference molecules, 1,3,5-triphenylene-bridged triporphyrin **5-Zn** and 1,2-phenylene diporphyrin **6-Zn** were prepared by Suzuki coupling reaction of boronate Cu(II) porphyrin **7-Cu** with 1,3,5-tribromobnzene and 1,2-diiodobenzene followed by demetallation and zinc insertion.



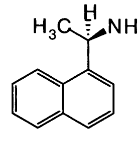
5 ; Ar^1 = Ar^2 = 3,5-di-*tert*-butylphenyl



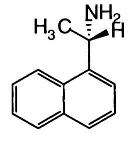
6 ; Ar^1 = Ar^2 = 3,5-di-*tert*-butylphenyl



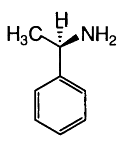
7-Cu



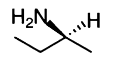
(R)-1-(1-naphthyl)ethylamine **8**



(S)-1-(1-naphthyl)ethylamine **8**



(R)-1-phenylethylamine **9**



(S)-2-butylamine **10**

As an interesting use of the cyclic porphyrin hexamers, we have examined the host–guest interaction of **2-Zn** and **4-Zn** with chiral amines. As shown in Fig. 1, the addition of an excess amount of optically active (1-naphthyl)ethylamine (**8**) to **2-Zn** and **4-Zn** caused

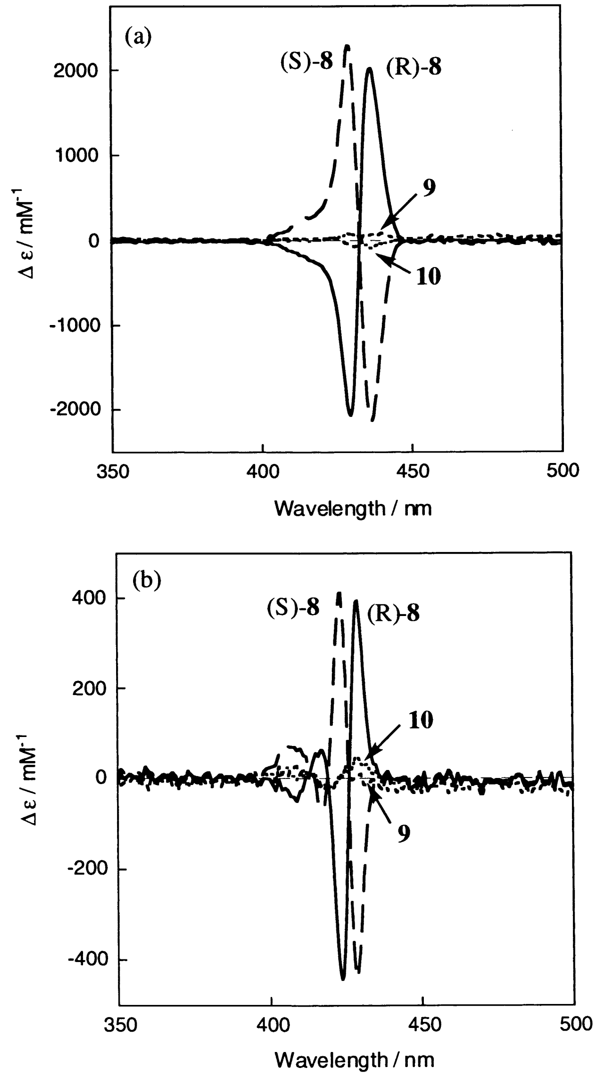


Figure 1. CD spectra of **2-Zn** (a) and **4-Zn** (b) in the presence of **8**–**10** in toluene at 298 K; [**2-Zn**, **4-Zn**] = 5.0×10^{-7} M, [**8**–**10**] = 1.0×10^{-3} M.

strong bisignate Cotton effects at the Soret band in the CD spectra, whereas the addition of chiral amines such as phenylethylamine (**9**) and 2-butylamine (**10**) led to only weak Cotton effects. The induced CD signals are, judging from the position, considered to be arising from the interaction of the dipole moments of the neighboring porphyrins held in a chiral arrangement.[8,9] The large CD intensity observed with **8** suggests that the porphyrin macrocycles are held in the similar arrangement with respect to a chiral sense. Since the present cyclic porphyrin hexamers are essentially achiral, the complexation with the chiral amines, (*R*)-**8** and (*S*)-**8**, results in the transcription of point chirality of the amines into an overall chiral, most probably helical, propeller-like conformation of the array, which may be brought about through the partially overlapping geometry of the hexamer. The fact that no significant Cotton effect has been detected for the trimer **5-Zn** and the dimer **6-Zn** indicate the importance of a consecutive cyclic arrangement for the strong Cotton effect. This view may be supported from the observed stronger Cotton effects for **2-Zn** than **4-Zn**, in that the former array is sterically more demanding due to the additional two *meso*-aryl substituents.

In summary, we found the efficient synthetic routes to the benzene-centered cyclic hexamer via the transition metal catalyzed reaction from the diphenylethynyl-bridged diporphyrins. The array thus prepared has been shown to serve as a chiral amplifier toward optically active amine. The study on very fast excitation energy hopping around the array is now actively in progress in our laboratories and will be reported elsewhere.

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