Highly planar amphiphilic porphyrins

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ABSTRACT

A first synthesis of an asymmetric and amphiphilic β-substituted porphyrin is reported. The porphyrin can be integrated into various types of nanostructures with the amphiphilic characters in hydrophilic solvents. The one-dimensional integration may induce a magnetic interaction between the central metals.

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The supramolecular integration of porphyrin and its derivatives has attracted great attention because of the relevance to the natural photosynthetic systems, where a large number of chromophores such as chlorophylls and carotenoids are spatially aligned in protein environment and the mutual distances are completely controlled.[1] In order to obtain well-defined porphyrin aggregates,[2] not only covalent bonding[3] but also metal coordination,[4] hydrogen-bonding,[5] and van der Waals interaction[6] have been utilized and the obtained integrated structures have been employed for application in the fields of sensors, field-effect transistors, and photovoltaic cells.[2b,7] For these years, amphiphilic motives with rigid π-cores have been well employed to obtain excellent optoelectronic properties associated with the characteristic nanostructures.[8] Recently, Tashiro and co-workers have reported interesting liquid crystalline properties of amphiphilic fully fused porphyrin dimer, associated with electrical conductivity.[8h] In this Letter, we have developed an asymmetrically β-substituted amphiphilic porphyrin, which is much planar and less bulky in order to accomplish densely packed nanostructures and hence induce strong intermolecular interactions between the metal centers. The Cu[II]-complex of the amphiphilic porphyrin 1-Cu shows a H-aggregate in a polar solvent and the precipitate obtained from the solution may exhibit magnetic interaction between closely packed central metals.

The synthesis of the target porphyrin has been accomplished by the condensation reaction of alkyl-tethered and triethyleneglycol(TEG)-tethered dipyrromethanes.[9] In contrast to the synthesis of *meso*-aryl-type porphyrin, that of asymmetrically substituted β-alkyl-type porphyrin has not been well explored.[10] Herein, several conditions were examined for the condensation reaction of two different dipyrromethanes (Scheme 1, Table 1 and Supplementary Figures). The first condition was the condensation between

TEG-tethered dipyrromethane 6 and alkyl-tethered α,α′-diformyl-dipyrromethane in the presence of trifluoroacetic acid (TFA) as the acid catalyst and the subsequent oxidation by *p*-chloranil.[10c] This reaction resulted in the formation of the mixture of the target free-base porphyrin 1-H$_2$ and the isomers, which were obtained from the scrambling reaction during the condensation. Considering a proposed reaction mechanism (Fig. 1),[11] the obtainable isomers from this reaction should be only one, 2-H$_2$. Actually, the ^{1}H NMR spectrum of the product in CDCl$_3$ displayed signals ascribable to only two species (Fig. S1). The ratio of 1-H$_2$ and 2-H$_2$ (2/1) was 7.9 and the total yield of the porphyrins was 1.9%.[12] For the second condition, we employed *p*-toluenesulfonic acid as the catalyst and Zn(OAc)$_2$·2H$_2$O as the template for the condensation reaction and subsequently oxidized the condensation products in air.[10a] With this condition, we obtained the target zinc porphyrin 1-Zn and the isomer 2-Zn, whose isomeric ratio was 0.88 with the total porphyrin yield of 3.1%. The third condition was the condensation between TEG-tethered dipyrromethane 6 and alkyl-tethered α,α′-dihydroxy-methyl-dipyrromethane with acetic acid as the catalyst and the subsequent oxidation by *o*-chloranil,[13] and then, the total yield of the porphyrins was 1.9% and the ratio of 2/1 was 6.0. In these three reaction conditions, we had not been able to obtain satisfactory isomeric ratios and the total yield of porphyrins.

Recently, Lindsey and co-workers have reported a new method for the syntheses of asymmetrically *meso*-substituted porphyrins, where an imino-derivative of diformyl-dipyrromethane was employed.[14] The fourth condition was the modified condensation of Lindsey's method, where a TEG-tethered dipyrromethane 6 and an alkyl-tethered α,α′-dipropylimino-dipyrromethane 15 were condensed in the presence of Zn(OAc)$_2$·2H$_2$O in refluxing toluene (Scheme 1). As a result of this reaction, much improved isomeric ratio of 2/1 (= 0.18) was obtained and the total yield of porphyrins reached 12%. We investigated the temperature and solvent effects on the reaction (Table 1). At first, three solvents with almost similar dielectric constants (benzene: bp = 80 °C and ε_r = 2.3, toluene:

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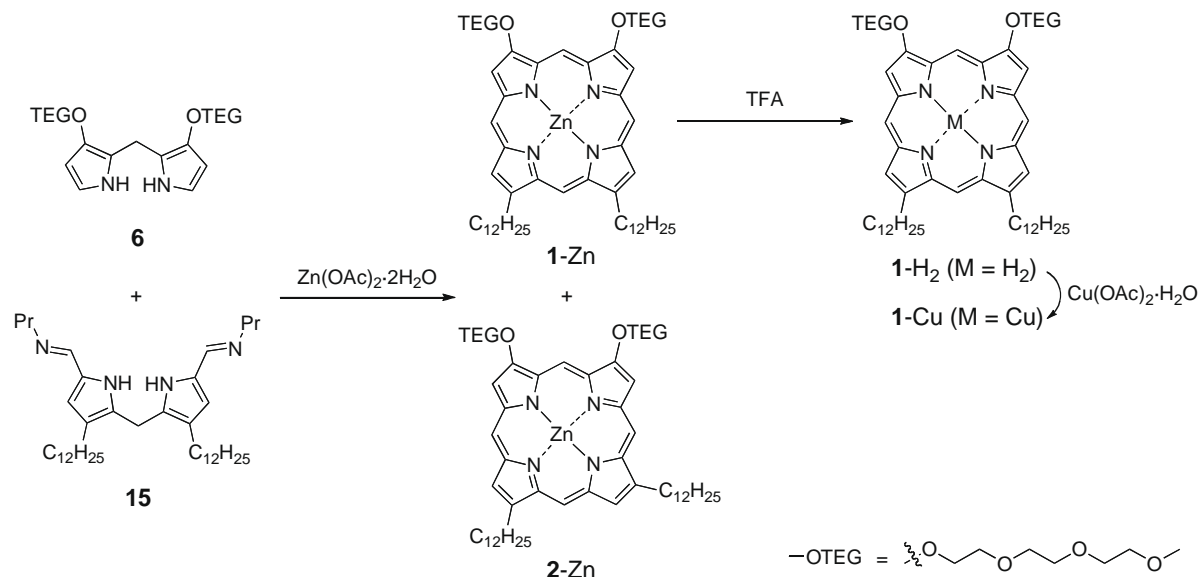
Scheme 1. Syntheses of amphiphilic β-alkylporphyrins.

Table 1
The total reaction yields of the porphyrin isomers and the isomeric ratios between **1**-Zn and **2**-Zn from the procedure in Scheme 1 at the concentration of the substrate with 10 mM

Entry	Solvent	ε_r	bp	Yield	**2/1**
1	Toluene	2.4	111	12	0.18
2	Xylene	2.3–2.6	138–145	14	0.65
3	Benzene	2.3	80	8.0	0.10
4	EtOH	25	79	4.7	0.23
5	1,2-Dichloroethane	10	84	2.1	0.72
6	Cyclohexane	2.0	81	12	0.05

bp = 111 °C and ε_r = 2.4, and xylene: bp = 138–145 °C and ε_r = 2.3–2.6) were employed at each boiling point to confirm the temperature effect on the condensation (entries 1–3), and the lower reaction temperature afforded a better isomeric ratio of **2/1**. When the polarity of the solvents was varied, a less polar solvent afforded a better isomeric ratio of **2/1** (entries 3–6).[15] The best result was achieved by the condensation in cyclohexane (bp = 81 °C, ε_r = 2.0), where the isomeric ratio of **2/1** reached 0.05 and the total yield of porphyrins was 12%. In the proposed mechanism of the scrambling reaction (Fig. 1), ionic intermediates or transition species would participate in the pathway, and they
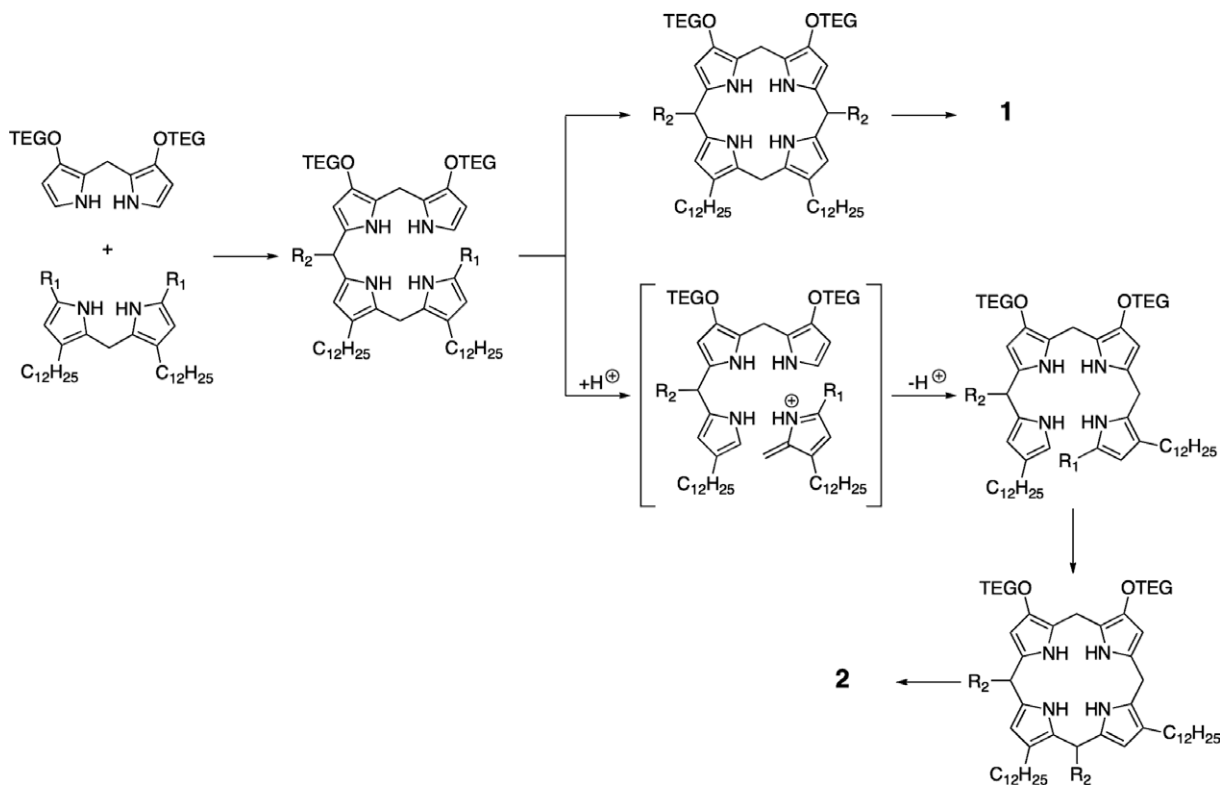

Figure 1. A plausible reaction mechanism of the scrambling in the porphyrin condensation.

might be destabilized in less polar solvents. Therefore, less polar solvents such as cyclohexane can afford better isomeric ratios. Lower reaction temperature may also assist the better isomeric ratios by hampering the pathways of the scrambling reactions.

For the preparative synthesis, the condensation was done under the same condition as in entry 6 with 0.24 mmol of each of the dipyrromethane derivatives, and 44.8 mg of the porphyrin mixture was obtained in 18% yield, at **2/1** isomeric ratio of 0.03. The isolation of the target porphyrin **1**-Zn from the isomeric mixture was accomplished by repeated recrystallizations from the solution in CH_2Cl_2–MeOH mixed solvent. As a result, the isomeric mixture of 44.8 mg afforded 22.5 mg of the target **1**-Zn to be pure at NMR level. The characterization of the target porphyrin has been done by ^{1}H and ^{13}C NMR spectroscopies and HR FAB-MS spectrometry.[9] The central zinc atom was demetallated under the acidic condition with TFA in CH_2Cl_2 and the free-base porphyrin **1**-H_2 was obtained in 98% yield. The insertion of copper was carried out by refluxing the solution of **1**-H_2 in the presence of $Cu(OAc)_2 \cdot H_2O$ to give the target compound **1**-Cu quantitatively.

The supramolecular integration of the obtained porphyrins **1**-H_2 and **1**-Cu has been examined under several different conditions by employing the amphiphilic properties of the porphyrins. The UV–Vis spectral changes were observed on adding H_2O to the solution of the free-base porphyrin **1**-H_2 in THF at the concentration of 1.1×10^{-4} M (Fig. S5(a)). The Soret absorption band of **1**-H_2 shows bathochromic shift at 42 nm. Similar behaviors were observed for the absorption experiments of **1**-H_2 on cooling the hot MeOH solution (1.2×10^{-4} M). On the other hand, when H_2O was added to the solution of **1**-Cu in THF at the concentration of 4.9×10^{-5} M, the Soret absorption of **1**-Cu at 397 nm displayed clear hypsochromic shifts with a peak (λ_{max}) at 392 nm in THF–H_2O = 1:9 mixed solvent. In general, Kasha's exciton theory tells that a hypsochromic shift of the optical absorption indicates face-to-face H-aggregation of the chromophores.[16] In contrast to the changes in THF–H_2O experiments of **1**-Cu, the Soret absorption of **1**-Cu exhibits only a decrease of the absorbance and no wavelength shifts in the experiment on cooling the hot MeOH solution.

The shapes of the nanostructures of the integrated porphyrin have been observed by scanning and transmission electron microscopies (SEM and TEM) (Fig. 2). When the suspension of free-base porphyrin **1**-H_2 precipitated from the hot MeOH solution was casted on an HOPG substrate, SEM observation revealed fiber-like structures with diameters between 75 and 550 nm and lengths of over 25 μm (Fig. 2b). The TEM images of the same sample of **1**-H_2 displayed that the rod structure consisted of the bundles of narrower wires with the diameter of 25 nm (Fig. 2f). Precipitate of **1**-H_2 from THF–H_2O also showed 1D-rod structures (Fig. 2a). The precipitate of **1**-Cu obtained from THF–H_2O showed short rod-like structures with a diameter of around 11 nm and a length in the range of 140–310 nm as estimated by the SEM and TEM observations (Fig. 2c and g). The SEM image of the precipitate of **1**-Cu obtained from a hot MeOH solution afforded a helical ribbon-structure without chiral selectivity (Fig. 2d). The XRD analysis[9] of the precipitate of **1**-Cu from THF–H_2O solution has revealed that the molecules are packed in a *monoclinic* unit cell with the dimensions of a = 67.71(4), b = 3.546(3), and c = 24.62(2) Å and β = 96.72(7)°, and the π-stacked 1-D chains are aligned on the *b*-axis with the π-stacking distance of 3.55 Å. On the basis of an optimized structure of **1**, the observed cell parameters *a* and *c* can be assumed twice as large as the molecular length between the paraffinic and the TEG ends and the molecular width, respectively. Despite the clearly distinctive appearance with the SEM and TEM observations, the precipitate of **1**-Cu obtained from a hot MeOH solution displayed an almost identical XRD pattern with that from THF–H_2O solution.[17]

We have investigated the thermal magnetic behaviors of **1**-Cu with SQUID measurements in order to confirm the intermolecular
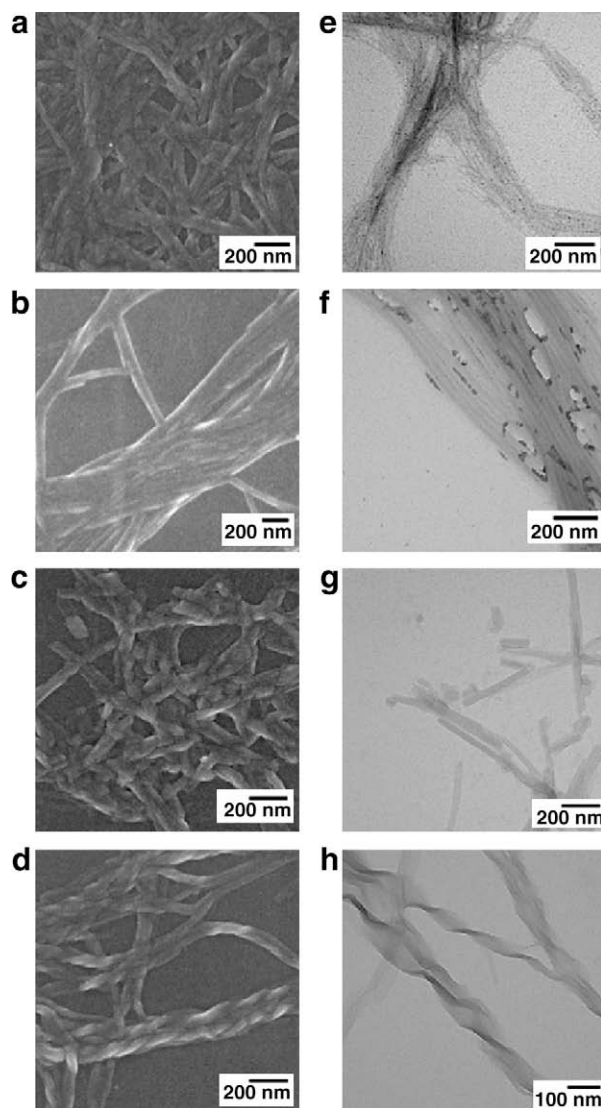
Figure 2. SEM and TEM images of the precipitates of (a) and (e) **1**-H_2 from a THF–H_2O solution, (b) and (f) **1**-H_2 from a hot MeOH solution, (c) and (g) **1**-Cu from a THF–H_2O solution, and (d) and (h) **1**-Cu from a hot MeOH solution.

metal–metal interaction induced by the supramolecular integration (Fig. 3). The magnetic susceptibility of the precipitate obtained from THF–H_2O solution shows a bent on decreasing temperature, which indicates the weak magnetic interaction between the Cu(II) centers. The Curie–Weiss plot of the susceptibility between 4 and 300 K affords the Weiss constant as −0.22 K. Reflecting the same packing mode, the precipitate of **1**-Cu obtained from a hot MeOH solution shows a similar magnetic behavior with that from a THF–H_2O solution.[9]

In conclusion, we have succeeded in the synthesis of a highly planar and amphiphilic β-alkylporphyrin and investigated the temperature and solvent effects on the condensation reaction for the porphyrin synthesis. Suppressing the scrambling problem is of great importance for synthesizing asymmetric porphyrins, and thus the proposed solution here will contribute to the future development of porphyrin chemistry and the material application. We have confirmed the supramolecular integration of the porphyrin complexes under amphiphilic conditions. The SEM images elucidated the morphology dependence on the precipitation solvents. In addition, the precipitates of Cu(II)-complex **1**-Cu obtained from THF–H_2O or hot MeOH solution exhibit weak magnetic
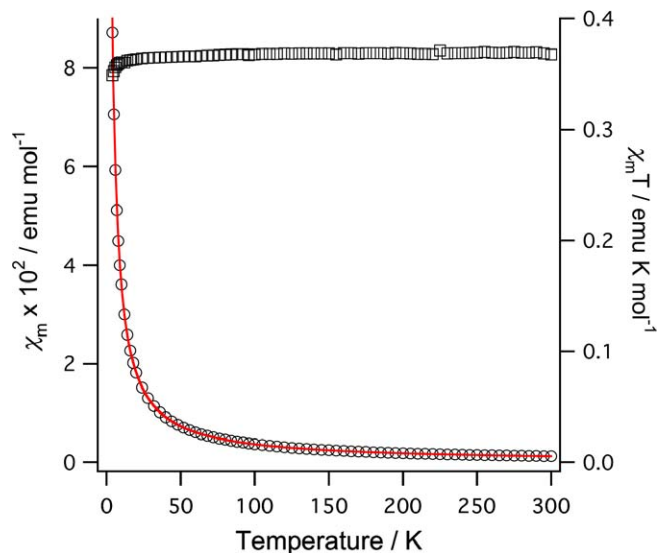
Figure 3. Temperature dependences of the magnetic susceptibility χ_m and $\chi_m T$ of the precipitate of **1**-Cu obtained from THF–H_2O mixed solvent. The red line indicates the best fit of the magnetic susceptibility χ_m to Curie–Weiss law.

interactions between the central copper atoms. The induction of intermolecular magnetic interaction between metal centers with soft-material systems is rare. The detailed magnetic studies for other paramagnetic complexes in the same amphiphilic porphyrin are currently underway.

Acknowledgments

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2009.10.001.

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