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Prepared Chiral Nanorods of a Cobalt(II) Porphyrin Dimer and Studied Changes of UV–Vis and CD Spectra with Aggregate Morphologies under Different Temperatures

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Novel porphyrin dimer ligand and cobalt complexes by directly bridging with L-glutamic acid have been prepared and characterized. The intensities of circular dichroism and UV–vis spectra that change the aggregate morphologies of the porphyrin dimer under different temperatures have been investigated.

The self-assembly porphyrins have attracted extensive interest of many researchers because of their potential applications in electronic devices and biomimic chemistry. Porphyrin can offer several remarkable features for molecular self-assembly.[1−3] First, it has a large flat, conjugated central tetrapyrrole macrocycle, the peripheral of which can be decorated with both hydrophobic and hydrophilic groups; second, it can offer intermolecular $\pi-\pi$ interaction (a significant driving force for the self-assembly of a number of materials),[4−6] which can promote the assembly of porphyrin. With the appropriate selection of substituents, noncovalent self-assembly can occur via intermolecular electrostatic interaction, hydrogen bonding, and metal coordination. In recent years, a wide variety of nanometer-sized self-assembly structures using porphyrin have been reported.[7,8]

In our study, we synthesized a novel chiral cobalt porphyrin dimer by directly bridging with L-glutamic acid and prepared the nanorods of the dimer using liquid−solid−solution technologies.[9−11] We further investigated that the aggregate morphologies of the porphyrin dimer transformated from H-aggregate to J-aggregate with an increase of the temperature under the same experimental conditions. The diameter of the aggregate porphyrin dimer was controlled by a tunable solution temperature. The procedure to prepare nanorods of a cobalt(II) porphyrin dimer was initiated by dissolving 14.86 mg of porphyrin dimer in 10 mL of *N*,*N*-dimethylformamide (DMF), which was then equally divided into five parts. Each was vigorously stirred under different designated temperatures (a, 273 K; b, 298 K; c, 308 K; d, 318 K; e, 328 K). As followed, the aqueous sodium chloride solution with 0.01 mol/L was added slowly to each of the five solutions, and then the system was treated for 12 h. After the addition of 6 mL of $CHCl_3$, each of the five solutions was divided into two phases: a and b retain purple-red in the below solution and colorless in the above solution; c−e also retain purple-red in the below solution and light red in the above solution. For c−e, a suspension appeared in the above solution that suggested that the metallorporphyrin was dispersed into the mixture of DMF and water, and this can be explained by chloroform volatilization as the temperature of the system is increased or the solubility of the aggregate porphyrin dimer declines in chloroform.

The intermolecular aggregates were promoted by intermolecular $\pi-\pi$ stacking, hydrophobic and hydrophilic groups of the molecule, and intermolecular electrostatic interactions at the interface of the two phases. Because of hydrogen and metal−metal bonding, the cobalt(II) porphyrin dimers adopted a head-to-tail (J-aggregate) or face-to-face

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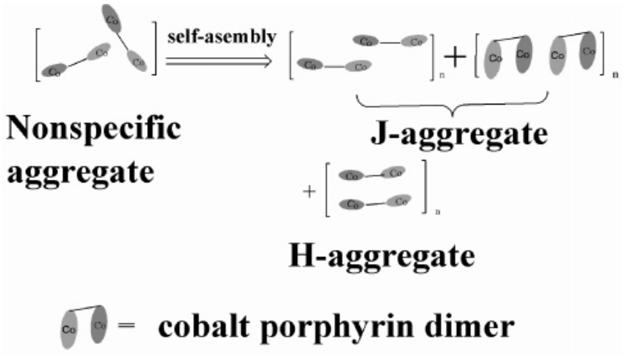

Figure 1. Module strategy used to assemble a one-dimensional porphyrin by intermolecular interaction. The basic module is a cobalt porphyrin dimer.

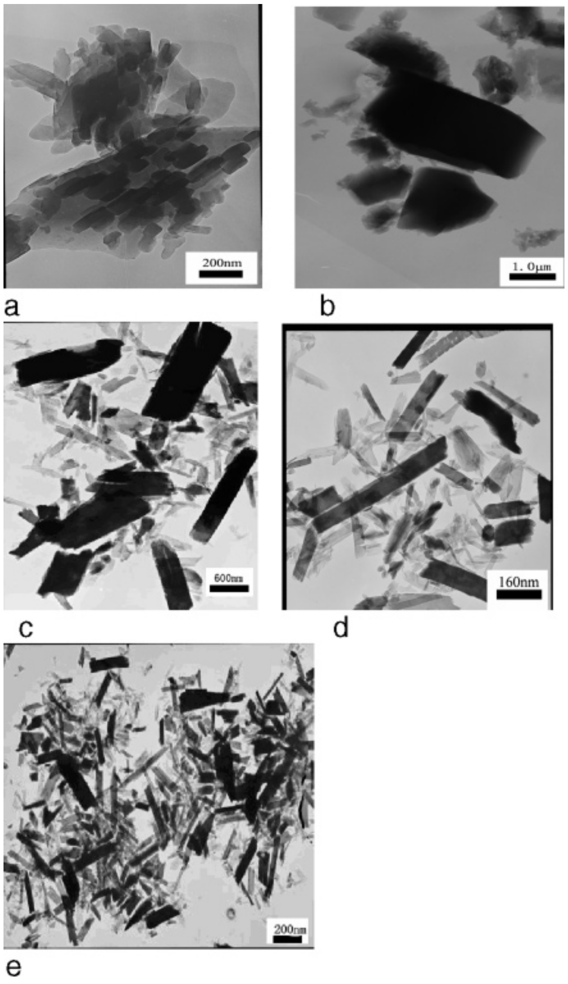

Figure 2. TEM images of porphyrin nanorods at different temperatures: (a) 273 K; (b) 298 K; (c) 308 K; (d) 318 K; (e) 328 K.

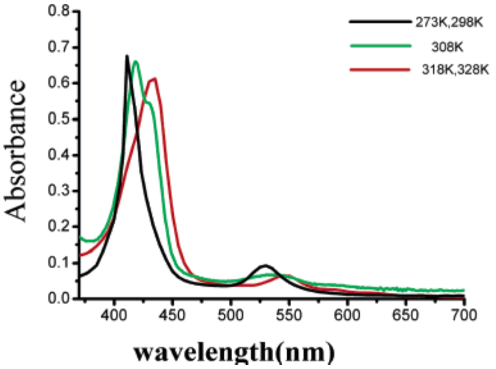

Figure 3. Electronic absorption spectra of cobalt porphyrin dimer nanorods in DMF at different temperatures: (a) 273 K; (b) 298 K; (c) 308 K; (d) 318 K; (e) 328 K.

(H-aggregate) arrangement. Therefore, a rod nanostructural porphyrin dimer was formed[12] (Figure 1).

Figure 2 shows transmission electron microscopy (TEM) images of nonarod products formed at different temperatures. Their shapes change from disordered stacking to ordered aggregates, and the configurations of the aggregates transform from fractal, big brick to rodlike particles as the temperature is increased. The reason is that the J-aggregate is stable in thermodynamics, while the H-aggregate is stable in dynamics, so the increase of temperature promotes the formation of the J-aggregate. Besides, the diameters of the porphyrin rods change from micron to nanometer, and the diameter size distributions of the nanorods change from inhomogeneous to homogeneous (Figure 2e) with an increase of the temperature.

The exciton theory developed by Kasha predicts the occurrence of hypsochromic or bathochromic shifts for the relevant absorption bands, in the case of H-type (face-to-face) or J-type (side-by-side) interactions, respectively. So, the UV−vis and circular dichroism (CD) spectra of the porphyrin dimer were measured. The UV−vis spectra of c−e demonstrated significant diversity compared with the spectra of the corresponding porphyrin solution of a and b. Because of the lack of a strong electronic coupling of the chromophores in the nonaggregate form, there was no change in the UV−vis spectra of a and b. Figure 3 presents the optical spectra of the aggregate morphologies of a cobalt porphyrin dimer under different temperatures. The absorption spectra between b and a and also d and e were identical, respectively. Also, the Soret band was red-shifted from 409 nm of a and b to 435 nm of d and e. The Soret band of the middle c was found to be split. We speculated that this resulted for the following two reasons: first, the porphyrin dimer transforms from H-aggregate to J-aggregate as the temperature of the stock solution increases; second, the Co ion in the center of the porphyrin ring transforms from Co^{2+} to Co^{3+}, which produces a Co−Co covalent bond between the two cobalt porphyrinic dimers. However, we cannot offer further evidence. On the other hand, all of the Soret bands of c−e were found to broaden the arrangement of macrocycles in aggregates that generally fell into two types: “J” (edge-to-edge) and “H” (face to face). The split, broadened, red-shifted Soret bands, as well as the Q bands in the optical spectra, presented both types of interactions in the nanorods.[13,14] The results were consistent with other nanoscale porphyrin

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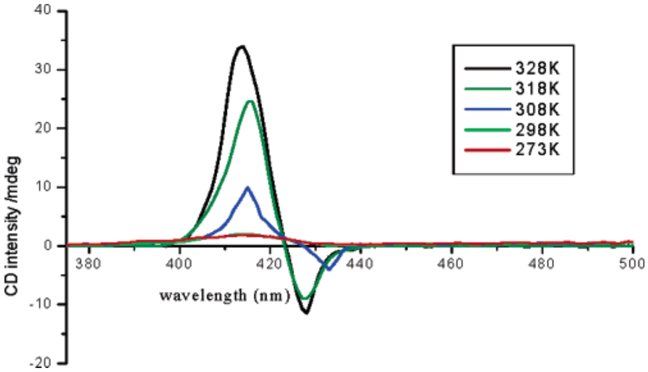

Figure 4. CD spectra of cobalt porphyrin dimer nanorods in DMF at different temperatures: (a) 273 K; (b) 298 K; (c) 308 K; (d) 318 K; (e) 328 K.

aggregates and were well-understood to be indicative of electronic coupling of the chromophores.[15]

We measured the CD spectra of nanorods of a cobalt porphyrin dimer and discussed their tendency to change the aggregate morphologies under different temperatures. The bisignate CD curves are evidence for dipole−dipole, long-range electronic interaction between the two porphyrin chromophores.[16] It is known that such an interaction depends on the interchromophoric distance and twist, as well as the conformational rigidity around the porphyrin−L-glutamic acid linkage.[17]

As shown in Figure 4, a weak single CD band at 414 nm for b and a appeared, assigned to the CD induced by the chiral amino acids or the side-chain amino groups of the L-glutamic acid residues, not the exciton-coupled CD. The CD spectrum of the cobalt porphyrin dimer in c shows a small bisignate curve with a positive band at 414 nm and a negative band at 433 nm. The split Cotton effects were assigned to the exciton-coupled CD between two porphyrin chromophores that arose from L-glutamic acid.[18] While the CD spectra of d and e show a stronger bisignate curve with a positive band at 414 nm and a negative band at 428 nm (blue shift, $\Delta = 5$ nm relative to c), the CD signal grew stronger, which can be attributed to the enhancement of both the dihedral angle of the two porphyrin chromophore planes by metallation and the intramolecular exciton coupling interaction between the two cobalt porphyrins.[19,20] The conversion from H-aggregate to J-aggregate as the temperature is increased can lead to both of the enhancements mentioned above.

In this study, we prepared the nanorods of a chiral porphyrin dimer by adjusting the temperature of the solution; we also investigated the UV−vis and CD spectral variations with changes of the morphologies of the aggregates at different temperatures. According to our results, as the temperature increases, the configurations of the aggregates transform from fractal, big brick into rodlike particles. Under appropriate conditions, the higher the temperature, the smaller the diameter of the nanorods. Furthermore, UV−vis and CD spectra of the morphological change of the aggregate porphyrin dimer were investigated.

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Supporting Information Available: Molecular structure, MS and IR spectra, and ^{1}H NMR and UV−vis data for the porphyrin dimer. This material is available free of charge via the Internet at http://pubs.acs.org.

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