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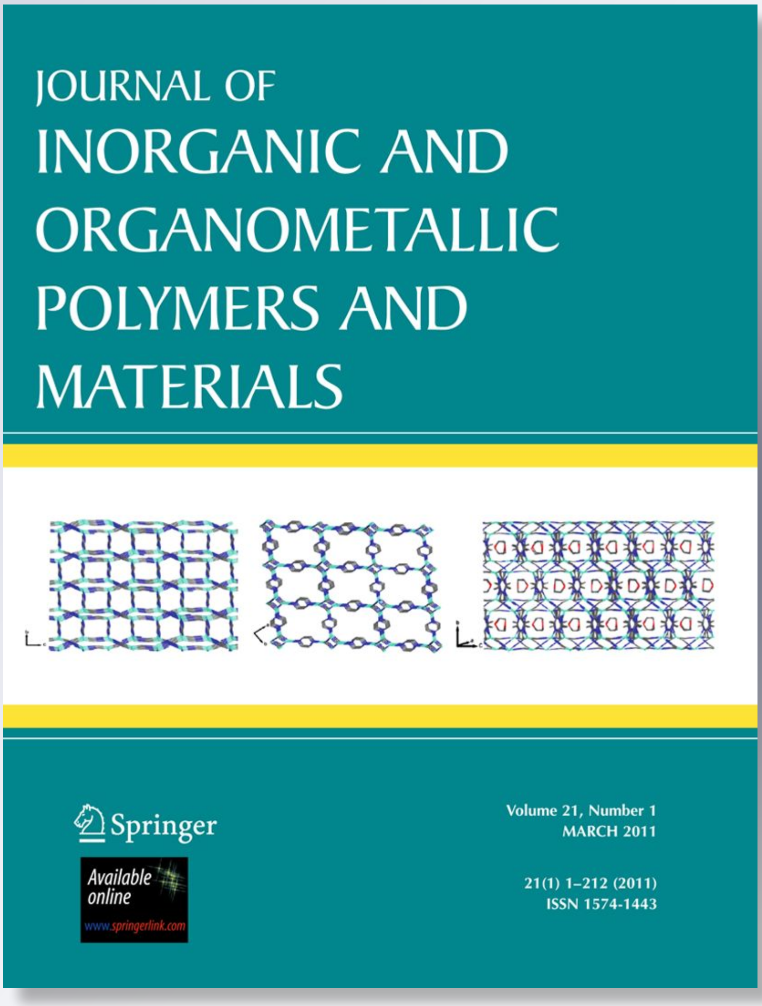

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Controllable Self-assembly of Sandwich-type Mixed (phthalocyaninato)(porphyrinato) Rare Earth Triple-Decker Complexes

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Abstract Two novel sandwich-type mixed (phthalocyaninato)(porphyrinato) rare earth complexes $Tb_2[TClPP]_2$ Pc (**1**) and $Tb_2[TClPP]$ Pc_2 (**2**) [Pc = phthalocyaninate, TClPP = meso-tetrakis (4-chlorophenyl) porphyrinate] have been fabricated into nanostructures by a solution-based method. Their self-assembly properties have been comparatively studied by electronic absorption spectroscopy, transmission electron microscope (TEM), X-ray diffraction (XRD) techniques and current–voltage (I–V) measurements. Due to the different number of porphyrin and phthalocyanine ligands interference, the self-assembly of the two molecules results in totally different morphologies in aggregate: one-dimensional (1D) nanoribbon from **1** vs. two-dimensional (2D) nanosheet from **2**. The electronic absorption measurements indicated that *J*-type aggregates have been formed with the increasing red-shifted degree from nanoribbons to nanosheets depending on the competition and cooperation between the inter-molecular π–π interaction and van der Waals for different compounds. Examination by XRD revealed that in the nanostructures of **1** and **2**, a dimeric supramolecular structure was formed through an intermolecular π–π interaction and van der Waals between two sandwich-type molecules, which as the building block self-assembles into the target nanostructures. In addition, the nanosheets from **2** were revealed to show excellent semiconducting properties with the conductivity of 3.0×10^{-3} S m^{-1} in air due to readily π-stacks with adjacent planar molecules enhanced by higher ordered crystalline molecular arrangement.

Keywords Phthalocyanine · Porphyrin · Rare earth · Sandwich complex · Self-assembly

1 Introduction

The controlled self-assembly of functional dyes into targeted nanoscaled architectures at interfaces represents one of the major goals of supramolecular chemistry and material science, given the perspective of the potential applications of these systems in nanotechnology [1–4]. Extensive investigations have revealed that self-assembly of conjugated molecular systems depends mainly on the inter-molecular π–π interaction in cooperation with other non-covalent interactions, forming nanostructures with different morphology [5, 6].

Associated with their potential applications in materials science and molecular electronics, sandwich-type phthalocyaninato and/or porphyrinato rare earth complexes have attracted great attention [7, 8]. The presence of two or three tetrapyrrole rings in one molecule with sandwich molecular structure of these compounds provides much more possibilities to tune the inter-molecular interactions [9, 10]. It is therefore worth to investigate the self-assembling properties of sandwich tetrapyrrole rare earth complexes in terms of both potential applications and theoretical importance. For example, solution-processed self-assemblied films of amphiphilic tris(phthalocyaninato) rare earth triple-deckers $[Pc(15C5)_4]M[Pc(15C5)_4]M[Pc(OC_8H_{17})_8]$ (M = Eu, Tb, Lu) have been revealed to display an excellent FET performance [11]. Very recently, highly sensitive, stable and reproducible responses to O_3 gas are obtained for self-assembling nanostructures of $Eu_2[Pc(15C5)_4]_2[Pc(OC_{10}H_{21})_8]$ complex [8].

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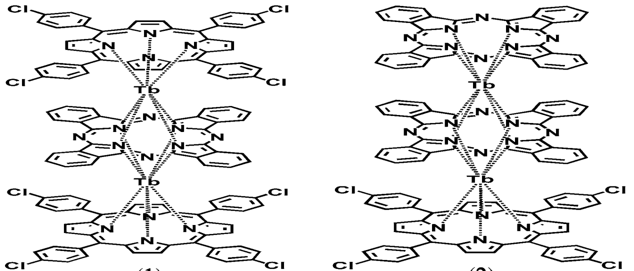
(1) (2)

Fig. 1 Schematic molecular structures of $Tb_2(TClPP)_2Pc$ (**1**) and $Tb_2(TClPP)Pc_2$ (**2**)

In the past few years, great efforts have also been devoted to these elaborately designed sandwich tetrapyyrole derivatives containing various functional group(s) for the purpose of fabricating ordered nanostructures [7]. For example, nanotubes of sandwich-type (phthalocyaninato)(pophyrinato) europium(III) double-decker complex were successfully fabricated using the template method by Jiang and coworkers [12]. The self-assembly properties of a series of mixed (phthalocyaninato)(porphyrinato) europium triple-decker complexes having different numbers of hydroxyl groups at the meso-attached phenyl groups of the porphyrin ligand have also been comparatively and systematically studied by Jiang and coworkers [9]. In the present paper, we describe self-assembly properties of two novel sandwich-type mixed (phthalocyaninato)(porphyrinato) rare earth complexes, namely $Tb_2(TClPP)_2Pc$ (**1**) and $Tb_2(TClPP)Pc_2$ (**2**) [Pc = dianion of phthalocyanine, TClPP = tetrakis (4-chlorophenyl) porphyrinate], Fig. 1. Introduction of different number of porphyrin and phthalocyanine ligands in the triple-decker molecules leads to the formation of nanostructures with different morphology, clearly revealing the effect of π–π interaction, van der Waals, and metal–ligand coordination in tuning the intermolecular interaction between sandwich-type molecules in the self-assembly process. The present study, representing part of our continuous efforts towards understanding the relationship between synergistic interplay among noncovalent interactions such as the π–π interaction and metal–ligand coordination bonding on controlling and tuning the morphology of self-assembled nanostructures of tetrapyrrole derivatives, will provide information helpful on preparing self-assembled nanostructures with controlled molecular packing conformation and morphology through molecular modification.

2 Results and Discussion

2.1 Electronic Absorption Spectra

The absorption spectra of the mixed ring sandwich complexes **1** and **2** in $CHCl_3$ solution and the aggregates formed in aqueous solution by a phase transfer method [13] are shown in Fig. 2. In line with that of analogous $M_2(TClPP)_2Pc$ and $M_2(TClPP)Pc_2$ (M = Sm, Gd, Dy) [14], the strong absorptions at about 343–353 and 414–419 nm can be attributed to the Soret bands of Pc and TClPP, respectively, while the absorptions at 494–738 nm to their Q bands. The electronic absorption spectra of the aggregates for two compounds are also recorded and given in Fig. 2(dashed line), which are significantly different from the spectra of corresponding compounds in $CHCl_3$ solution. All absorption peaks for the aggregate states of two molecules are broadened and red-sifted. Obvious band broadening was observed due to the significant intermolecular interaction in the self-assembled nanostructures. On the basis of Kasha's exciton theory [15], red-shifts in the main absorption bands of **1** and **2** upon aggregation indicated the formation of *J*-aggregates between the neighboring triple-decker molecules. More striking shifts of absorption spectra observed for the aggregates of **2** than those of **1** indicate that stronger intermolecular interactions exist in aggregates in the same order, revealing the effect of number of porphyrin and phthalocyanine ligands on tuning the inter-molecular interaction of triple-decker molecules and in turn molecular packing conformation. As see below such a different molecular packing conformation results in a different dimensional preference for the growth of the molecular assembly.

2.2 X-ray Diffraction Patterns

The quality of self-assembly nanostructures can be further assessed using X-ray diffraction (XRD) technique. In the low angle range of the XRD diagram, Fig. 3a, the XRD diagram of the self-assembly nanostructure formed from **1** shows a comparatively weak refraction peak at $2\theta = 4.54°$ (corresponding to 1.94 nm) along with one stronger refraction at 6.26° (1.41 nm), which are ascribed to the refractions from the (100) and (010) planes related to the distances between triple-decker molecules [9]. As can be seen from Fig. 4a, the dimensional size for a triple-decker molecule of $Tb_2(TClPP)_2Pc$ (**1**) is 1.49 nm (length) × 0.70 nm (width) using PCMODEL for windows Version 6.0, Serena Software. According to the XRD results and the simulated triple-decker molecular structure, one unit cell consisting of two triple-decker molecules is given for compound **1**, Fig. 4b. Obviously, a higher relative intensity in (010) plane obtained for nanostructures of **1** implies a favorable growing orientation along *b*-axis (the direction perpendicular to tetarpyrrole rings) during the self-assembly process, which is well-reflected by transmission electron microscope (TEM) observation as detailed below.

As shown in Fig. 3b, in the low angle range of the XRD diagram, the nanostructures formed from **2** show two well-

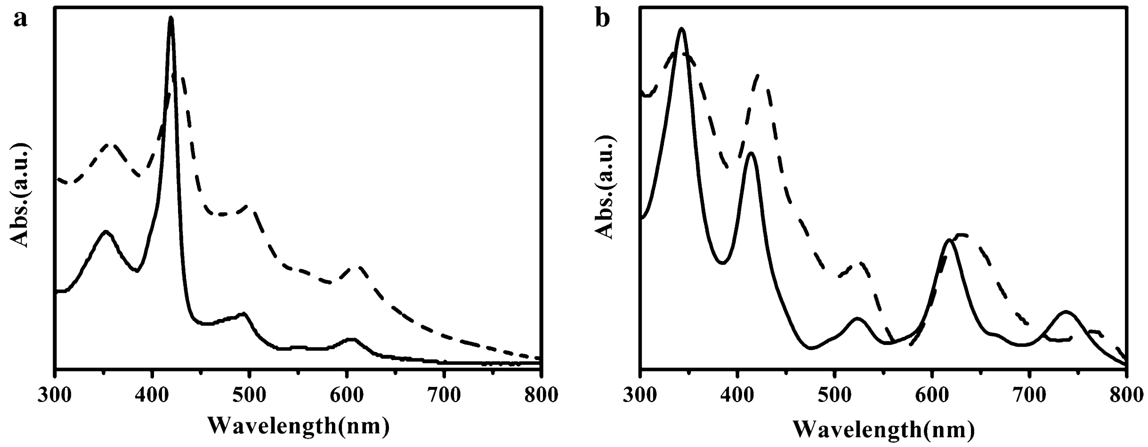

Fig. 2 Electronic absorption spectra in solution (*solid line*) and the aggregates on the SiO_2 surface (*dashed line*) of **1** (**a**) and **2** (**b**)

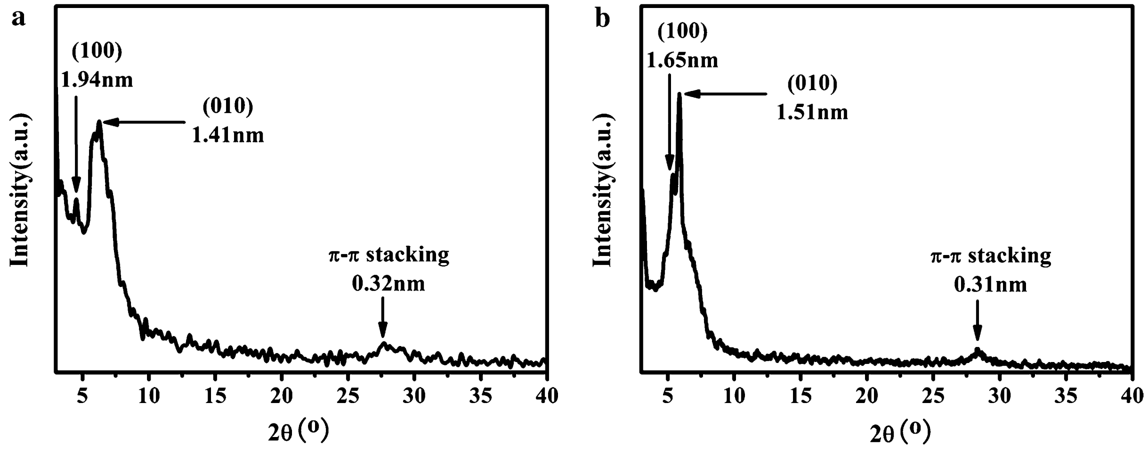

Fig. 3 XRD profiles of the aggregates of **1** (**a**) and **2** (**b**)

defined sharp peaks at 1.65 and 1.51 nm, respectively, originating from the (100) and (010) planes [16]. According to the energy-optimized conformation of the molecule (Fig. 4c), these diffraction results could be assigned to the refractions from a rectangular lattice with the cell parameter of $a = 1.65$ nm, $b = 1.51$ nm, Fig. 4d. Comparing with XRD pattern of aggregate state of $Tb_2(TClPP)_2Pc$ (**1**), a reduced stacking distance between neighboring triple-decker molecules along the direction parallel to the tetarpyrrole rings was obtained for that of $Tb_2(TClPP)Pc_2$ (**2**), implying that intermolecular edge-to-edge interactions grow stronger with the increase of the number of phthalocyanine rings. This is in good accordance with the electronic absorption spectroscopic analysis results as detailed above. It is worth noting that, in the wide angle region, the XRD patterns of the nanostructures from **1** and **2** present additional refractions at 0.32 and 0.31 nm respectively. These correspond mainly to the π–π stacking distances between tetrapyrrole cores of neighboring triple-decker molecules along the direction perpendicular to the tetarpyrrole rings [4, 9, 17].

2.3 TEM Observation

The foregoing XRD studies consistently suggest that the molecular assembly of **1** should grow up to some one-dimensional aggregate, whereas the molecular assembly of **2** should grow up to some two-dimensional aggregate. It is interesting to know whether these microscopic edge-to-edge and π–π stacking patterns are really reflected by the macroscopic superstructures. Fig. 5a shows a TEM image of aggregates of **1**. It is clearly seen from this TEM picture that triple-decker molecules of **1** self-assemble into ribbonlike aggregates with over 20 μm length and ca. 150 nm width. As displayed in Fig. 5b, on the other hand, self-assembly of triple-decker molecules of **2** results in a two-dimensional sheetlike morphology with ca. 6 μm length and ca. 0.85 μm width. One may conclude, therefore, that

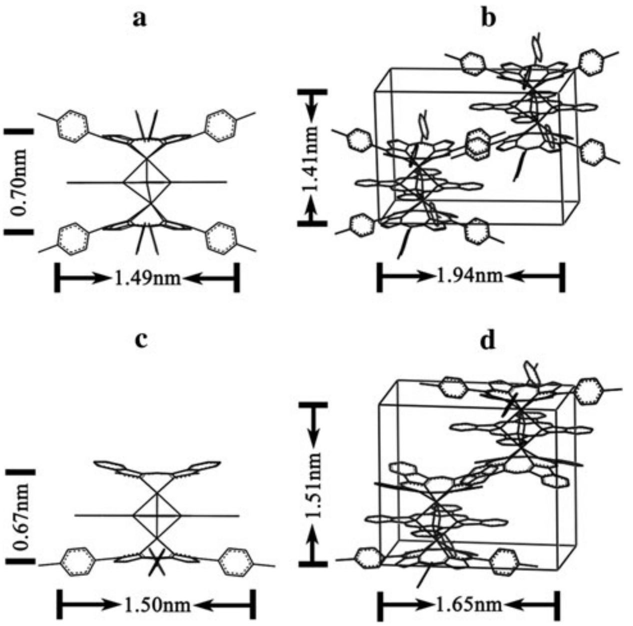

Fig. 4 Schematic representation of the unit cell in the aggregate of **1** (**a**–**b**) and **2** (**c**–**d**)

the microscopic packing modes identified by spectroscopic and XRD studies are rigorously reproduced in the macroscopic structures as detected by TEM.

2.4 I–V Properties

The electrical conductivity characterization of the nanostructures of two compounds based on a direct current–voltage (I–V) measurement was performed on insulating SiO_2 substrates with ITO interdigitated electrodes. Figure 6 shows the I–V properties of nanosheets fabricated from **2**, and corresponding cast films of **2** is also included for the purposes of comparative study. For the devices measured, the conductivity of the nanosheets and cast films extracted from the quasilinear region at high bias (up to 100 V) was about 3.0×10^{-3} and 2.4×10^{-4} S m^{-1}, respectively. Comparing with that of the cast films, the improved conductive capability of nanosheets of **2** might be attributed to both readily π-stacks with adjacent molecules and higher ordered crystalline molecular arrangement. Especially, unexpectedly good conductivity of ca. 3.0×10^{-3} S m^{-1} for the nanosheets is achieved, which is about 1 order of magnitude higher than that measured for polymer nanowires (e.g., polythiophene) [18], suggesting the great potential applications in electronic devices. However, we failed to obtain valuable I–V curve of nanoribbons from **1**, implying that molecular structures play a critical role for electrical conductivity of materials. Phthalocyanine rings of **2** have more extended π electronic conjugation than porphyrin rings of **1**, which should favor charge transport and result in better conductivity of **2** than that of **1** [19].

3 Experimental

The sandwich-type mixed (phthalocyaninato)(porphyrinato) rare earth triple-decker complexes, $Tb_2[TClPP]_2Pc$ (**1**) and $Tb_2[TClPP]\ Pc_2$ (**2**), were synthesized previously [14]. All other reagents and solvents were of reagent grade and used as received.

The nanostructures of **1** and **2** were fabricated by using the solution-based method according to the following procedure [8]. 4.0 mL of chloroform solution (0.30 mg mL^{-1}) was put into a cylindrical container, then a little water was slowly added without cover the air/$CHCl_3$ interface completely. After complete evaporation of $CHCl_3$, the densely packed nanostructures remained on the water surface, the nanostructures can be easily transferred from the water surface onto the carbon-coated grid and SiO_2 substrates by horizontal lifting for the TEM observation, electronic absorption spectra and XRD measurements. Residual water on the substrates was removed with a stream of nitrogen. For I–V measurement, this process was repeated several times until the channels of ITO interdigitated electrodes were covered completely.

Electronic absorption spectra were recorded on a Hitachi U-4100 spectrophotometer. X-ray diffraction (XRD) measurements were carried out on a Rigaku D/max-γB X-ray diffractometer. TEM images were measured on a JEOL-

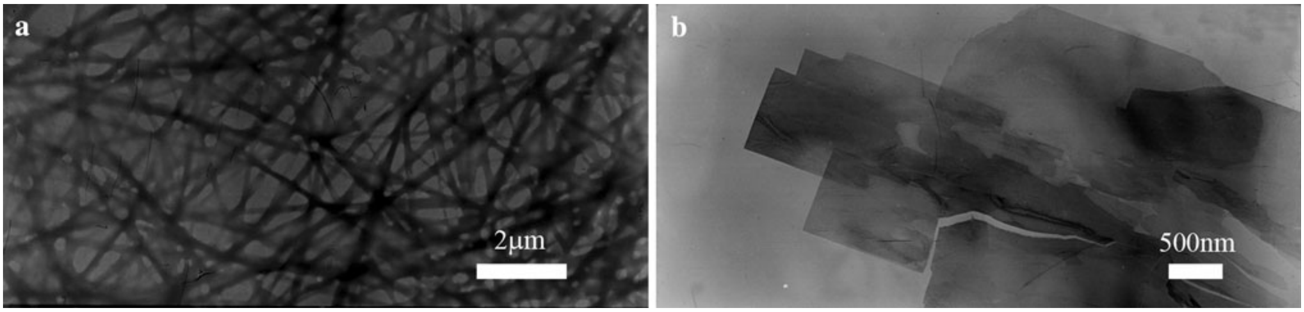

Fig. 5 TEM images of nanostructures of **1** (**a**) and **2** (**b**)

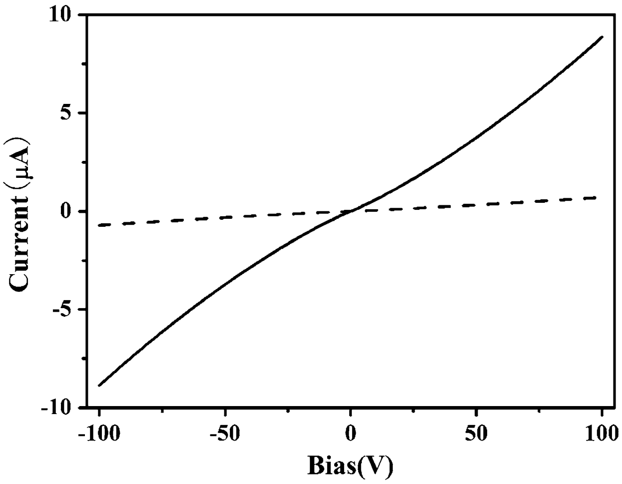

Fig. 6 Representative I–V characteristics of nanosheets (*solid line*) and cast films (*dashed line*) of **2**

100CX II electron microscope operated at 100 kV. The interdigitated array electrode is composed of 10 pairs of ITO electrode digits (fingers) deposited onto a glass substrate with the following dimensions: 125-μm electrode width, 75-μm spacing, 5850-μm overlapping length, and 20-nm electrode thickness. The conductivity, σ, can be calculated according to the equation reported by Ref [18]. The I–V characteristics were obtained with a Keithley 4200 semiconductor characterization system at room temperature in air.

4 Summary

In summary, we have investigated the self-assembly properties of two mixed (phthalocyaninato) (porphyrinato) rare earth triple-decker complexes having different number of porphyrin and phthalocyanine ligand. Competition and cooperation between the inter-molecular π–π interaction, van der Waals, and metal–ligand coordination for different compounds leads to different molecular packing conformation and in turn different nanostructure morphology in the self-assembly process.

The present result represents the continuous effort toward realization of controlling and tuning the morphology of self-assembled nanostructures of sandwich tetrapyrrole rare earth complexes through molecular design and synthesis. They are believed to be helpful in opening new possibilities for construction of molecular-based nano- and optoelectronics.

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