



Self-assembly of sandwich-type (phthalocyaninato)(porphyrinato) europium double-decker complexes: Effects of hydrogen bonding on intermolecular stacking mode and morphology of self-assembled nanostructures



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ABSTRACT

Two novel sandwich-type (phthalocyaninato)(porphyrinato) europium double-decker complexes, namely Eu(Pc)[(NHC₈H₁₇)PP] (**1**) and Eu(Pc)[(NHC₈H₁₇)₄PP] (**2**), have been designed and synthesized. Their self-assembly properties, in particular the effect of the numbers of octylaminophenyl groups on the morphology of self-assembled nanostructures of these double-decker complexes, have been comparatively and systematically studied. Depending mainly on the hydrogen bond between one octylaminophenyl group at *meso*-attached phenyl group of porphyrin ligand in **1** and one aza-nitrogen atom of the phthalocyanine ring in the neighboring molecule of **1**, **1** self-assembled into nano-rods with *J*-type aggregation. In good contrast, introduction of four octylaminophenyl groups onto the *meso*-attached phenyl groups of the porphyrin ligand in **2**, induces more N–H···N hydrogen bonds between neighboring molecules of **2**, induces the formation of nano-sheets with *H*-type aggregation. These results clearly imply the effective influence of hydrogen bond numbers on the molecular stacking mode and the morphology of the assembled nanostructures.

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1. Introduction

Self-assembled nanostructures have attracted increasing research interests both in material and chemistry fields due to their potential application in catalysts, sensors, field-effect transistors, and photovoltaics [1–15]. Extensive investigations have revealed that self-assembly depends mainly on the competition and/or interplay of various non-covalent interactions including π – π , van der Waals, hydrogen bonding, hydrophilic/hydrophobic, electrostatic, and metal–ligand coordination. As a result, numerous artificial modified molecules with various functional groups have been synthesized for the purpose of introduction of non-covalent and in turn intermolecular stacking modes, morphologies and properties into these self-assembled systems. However, despite the vigorous developments in this field, understanding the effect of the synergistic interplay of different noncovalent interactions on controlling and tuning the morphology and functional properties of organic

self-assembled nanostructures is still a great challenge for material and chemical science.

As a typical representative of functional discotic molecular materials, sandwich phthalocyaninato and/or porphyrinato rare earth complexes have attracted great research interest as self-assembled building blocks over the past ten years owing to their rich optical, electronic, and magnetic properties [16–21]. Their sandwich molecular structure with two or three tetrapyrrole ligands connected by one or two rare earth metal ion(s) renders it possible to incorporate various functional groups onto the peripheral positions of one, two, or even three tetrapyrrole ligands, providing enough room to introduce various non-covalent interactions to tune the inter-molecular interaction of sandwich complexes and in turn the morphology of self-assembled nanostructures. For example, Jiang's group incorporated different numbers of hydroxyl groups onto the *meso*-substituted phenyl groups of the porphyrin ligand in mixed (phthalocyaninato)(porphyrinato) europium triple-decker complexes to tune the intermolecular interaction [22]. It was revealed that cooperation and/or competition between the intermolecular π – π interaction and additional introduced hydrogen bonding resulted in the formation

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of nanostructures with different morphologies. However, to the best of our knowledge, investigations about the self-assembled properties of the functional tetrapyrrole derivatives are rare. Fabrication of functional tetrapyrrole derivatives into a prerequisite nanostructure with desirable dimensions and morphology through intra-molecular modification and inter-molecular regulation still remains a great challenge in this field.

With either one idea in mind, in the present paper, we describe the design, synthesis, and the self-assembled properties of sandwich-type (phthalocyaninato)(porphyrinato) europium double-decker complexes with one or four octylaminophenyl groups attached at the *p*-position of the meso-attached phenyl group of the porphyrin ligand in the double-decker molecule, namely Eu(Pc)[(NHC₈H₁₇)PP] (**1**) and Eu(Pc)[(NHC₈H₁₇)₄PP] (**2**), Scheme 1. Introduction of different numbers of octylaminophenyl groups onto the meso-substituted phenyl groups of porphyrin ligand in the double-decker molecules lead to the formation of nano-rods for **1** and nano-sheets for **2**, clearly revealing the effect of hydrogen bonding numbers on the molecular stacking style and the morphology of self-assembled nanostructures.

2. Experimental

2.1. General information

n-Octanol was distilled from sodium under nitrogen before use. Column chromatography was carried out on silica gel (Merck, Kieselgel 60, 200–300 mesh) with indicated eluent. All other reagents and solvents were used as received. The compounds of H₂[(NH₂)PP] [23], Li₂Pc [24], and Eu(acac)₃·*n*H₂O [25] were synthesized according to the literature procedures. The double-decker complexes Eu(Pc)[(NHC₈H₁₇)PP] (**1**) and Eu(Pc)[T(NHC₈H₁₇)₄PP] (**2**) were prepared according to the reported procedure as detailed below [26–29].

2.2. Measurements

¹H NMR spectra were measured on a Bruker DPX 300 spectrometer (300 MHz) in CDCl₃-DMSO-*d*₆ (1:1) in the presence of ca. 10% (by volume) hydrazine hydrate. Spectra were referenced internally using the residual solvent resonances of CDCl₃ at 7.26 ppm and DMSO at 2.49 ppm relative to SiMe₄. Electronic absorption spectra were recorded on a Hitachi U-4100 spectrophotometer. MALDI-TOF mass spectra were taken on a Bruker BIFLEX III ultra-high resolution. Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer with α -cyano-4-hydroxycinnamic acid as matrix. Elemental analyses were performed by the Institute of

Chemistry, Chinese Academy of Sciences. Low-angle X-ray diffraction (XRD) measurements were carried out on a Rigaku D/max- γ B X-ray diffractometer with an Cu-K α sealed tube ($l = 1.5406 \text{ \AA}$) at 293 K. Fourier transform infrared spectra were recorded in KBr pellets with 2 cm⁻¹ resolution using an aALPHAT spectrometer. Transmission electronmicroscopic (TEM) images were measured on a JEOL-100CX II electron microscope operated at 100 kV. Scanning electron microscopic (SEM) images were obtained on a JEOL JSM-6700F. For SEM imaging, Au (1–2 nm) was sputtered onto the grids to prevent charging effects and to improve the image clarity.

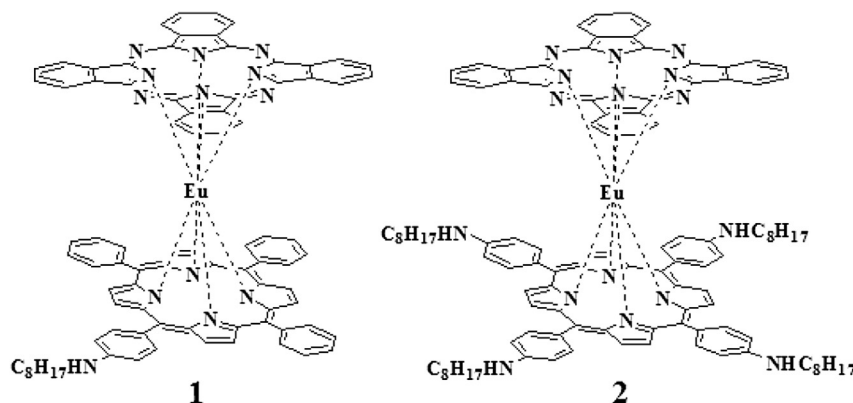
2.3. Nanostructures fabrication

The nanostructures of double-decker complexes **1** and **2** were fabricated by the phase transfer method according to the following procedure [30–34]. A minimum volume (30–50 mL) of concentrated toluene solution of double-decker complexes **1** and **2** (1 mM) was injected rapidly with a micro-injector into a large volume of methanol (2 mL) and subsequently mixed. After being kept at room temperature for 2 h, nanostructures were precipitated from the solution. Then one drop of the suspending solution was cast onto a grid (Cu with a carbon film) for TEM and SEM imaging. These procedures and results were reproducible under the experimental condition described above.

2.4. Materials

2.4.1. Preparation of Eu(Pc)[(NHC₈H₁₇)PP] (**1**)

A mixture of Eu(acac)₃·*n*H₂O (55.3 mg, 0.11 mmol) and H₂[(NH₂)PP] (43.7 mg, 0.10 mmol) in *n*-octanol (4 mL) was heated to reflux under nitrogen for 12 h. The mixture was cooled to room temperature, treated with Li₂Pc (52.3 mg, 0.10 mmol) and then refluxed for another 2 h. After a brief cooling, the mixture was evaporated under reduced pressure and the residue was subjected to chromatography on a silica-gel column with CHCl₃ as eluent. A small amount of unreacted metal-free H₂[(NH₂)PP] was collected as the first fraction, then the target mixed ring double-decker product Eu(Pc)[(NHC₈H₁₇)PP] (**1**) was collected as the second fraction. Repeated chromatography followed by recrystallization from CHCl₃-MeOH gave pure complex **1** (59.0 mg, 42%). ¹H NMR (300 MHz, CDCl₃, 25 °C): 1.05–2.12 (m, 15H, Por alkyl), 3.65–3.68 (m, 2H, Por alkyl), 5.32 (br, 1H, Por NH), 5.89 (br, 3H, Por *p*-Ph), 6.03 (br, 2H, Por *exo* *m*-Ph), 6.51 (br, 2H, Por *exo* *m*-Ph), 7.16–7.23 (m, 10H, Por *exo* *o*-Ph and Por- β), 7.30 (br, 2H, Por *exo* *o*-Ph), 8.12 (br, 2H, Por *endo* *m*-Ph), 8.59 (s, 8H, Pc- β), 8.70 (br, 2H, Por *endo* *m*-Ph), 10.43 (s, 8H, Pc- α), 10.59 (br, 2H, Por *endo* *o*-Ph), 10.92 (s, 2H, Por *endo* *o*-Ph). IR/cm⁻¹ (KBr): 3411 (w), 3052 (w), 2922 (m), 2849 (m), 2587 (w), 2445 (w), 2120



Scheme 1. Schematic molecular structures of Sandwich-type (Phthalocyaninato)(Porphyrinato) Europium Double-decker complexes Eu(Pc)[(NHC₈H₁₇)PP] (**1**) and Eu(Pc)[(NHC₈H₁₇)₄PP] (**2**).

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