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Design, synthesis, and aggregation behavior of sandwich mixed (phthalocyaninato)(porphyrinato) europium triple-deckers: Effect of substituent on tuning the intermolecular interaction

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ABSTRACT

Two new sandwich mixed (phthalocyaninato)(porphyrinato) europium triple-decker (TDMAPP)$Eu_2[Pc(OPh)_8]_2$ (**1**) and (TPyP)$Eu_2[Pc(OPh)_8]_2$ (**2**) were designed and synthesized. The self-assembled aggregates of **1** and **2** were fabricated by means of a solution-based quasi-Langmuir–Shäfer (QLS) method. Both structures and properties of the aggregates of **1**–**2** were comparatively studied by UV–vis absorption spectroscopy, atomic force microscopy (AFM), X-ray diffraction (XRD) techniques and current–voltage (I–V) measurements. Experimental results indicated that the molecules of **1** in the self-assembled aggregates adopted a typical *J*-type (edge-to-edge) aggregation mode, whereas those of **2** took a "face-to-face" conformation and "edge-on" orientation, implying the effect of side-group substituents on tuning the intermolecular stacking. XRD and AFM characterization clearly showed evidence for the formation of highly textured film structures with controlled molecular orientations within the self-assembled aggregates of **1**, while a dimeric supramolecular structure was revealed and thus as the building block self-assembles into the target the net-like nanostructures for the aggregates of **2**. In addition, the highly ordered film of **1** showed good semiconducting property with a conductivity of ca. $2.35 \times 10^{-5}\ S \cdot cm^{-1}$, which is more than ca. 1 order of magnitude higher than those of **2**, closely related to micro-structures and morphology found for the self-assembled aggregates.

Sandwich phthalocyaninato and/or porphyrinato metal complexes have attracted increasing research interest in areas of molecular devices because of their unique optical and electronic properties associated with the extended π networks along the axis perpendicular to the macrocycle planes [1–3]. For most of the applications, the properties of the molecular devices are closely related to the micro-structures and morphologies of molecular materials. Great progress has been achieved in the past decade toward controlling and tuning the morphology of nanostructures formed from π-conjugated molecular systems via introducing different functional groups onto the peripheral positions of conjugated molecules [4–6], and/or developing new fabrication techniques to obtain a highly ordered super-molecular aggregate [6,7]. By introducing different side chains onto the imide positions of the perylenetetracarboxylic diimide (PDI) ring to tune the π–π interaction between perylene systems, PDI nano-assemblies with different structure and morphology have been prepared by several research groups [8]. Using a solution based on self-assembling method, the sandwich (phthalocyaninato)(porphyrinato) europium triple-decker molecules with different numbers of hydroxyl groups onto the meso-substituted phenyl groups of porphyrin ligand have been fabricated into one-dimensional (1D) nanoribbons, two-dimensional (2D) nanosheets and nanoleaves by Jiang and co-workers [4]. Obviously, the presence of three tetrapyrrole rings in one molecule with a sandwich molecular structure of these compounds provides much more possibilities to tune the intermolecular interactions due to the versatile possible substitution positions in different tetrapyrrole rings. It is therefore worth of investigating the self-assembling properties of sandwich tetrapyrrole rare earth complexes in terms of both potential applications and theoretical importance. However, to the best of our knowledge, a comparative investigation of the self-assembled nanostructures, morphology, and conductivity of resulting nanostructures obtained at air–water interface by using a simple solution-based method between different sandwich phthalocyaninato and/or porphyrinato rare earth complexes with symmetrical substituents at phthalocyanine and/or porphyrin periphery is still rare. The main challenge of self-assembly of tetrapyrrole rare earth triple-decker derivatives lies in controlling and optimizing the strong π–π interaction between the phthalocyanine and/or porphyrin planes in cooperation with the hydrophilic/hydrophobic interactions between the side groups linked at phthalocyanine and/or porphyrin periphery. In other words, self-assembling triple-decker molecules into well-defined nanostructures represents a balance between molecular stacking and solubility. As part of our continuous effort to construct sandwich triple-decker tetrapyrrole metal complexes into ordered

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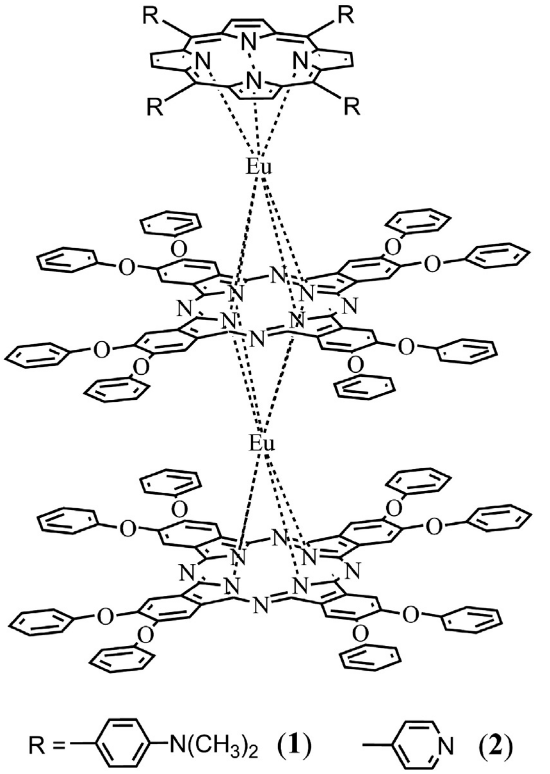

Scheme 1. Schematic molecular structure of the sandwich mixed (phthalocyaninato)(porphyrinato) europium (TDMAPP)$Eu_2[Pc(OPh)_8]_2$ (**1**) and (TPyP)$Eu_2[Pc(OPh)_8]_2$ (**2**).

structures [3,4,9–14], in this paper, two new sandwich mixed (phthalocyaninato)(porphyrinato) europium complexes, (TDMAPP)$Eu_2[Pc(OPh)_8]_2$ (**1**) and (TPyP)$Eu_2[Pc(OPh)_8]_2$ (**2**) [TDMAPP = dianion of 5,10,15,20-tetrakis(4-N,N-dimethylaminophenyl) porphyrin; TPyP = dianion of 5,10,15,20-tetrakis(4-pyridyl) porphyrin; $Pc(OPh)_8$ = dianion of 2,3,9,10,16,17,23,24-octa(phenoxy) phthalocyanine], Scheme 1, were prepared. A simple solution-based quasi-Langmuir–Shäfer (QLS) process allows us to prepare highly ordered film-structure for **1** and well-defined 3D networks for **2**. In particular, the film of **1** exhibited excellent conductivities. The investigation presented here demonstrates direct correlation between the maximized conductivity and the optimized molecular stacking as well as the morphology of the self-assembled nanostructures of the triple-decker molecules.

Two new sandwich mixed (phthalocyaninato)(porphyrinato) europium complexes, (TDMAPP)$Eu_2[Pc(OPh)_8]_2$ (**1**) and (TPyP)$Eu_2[Pc(OPh)_8]_2$ (**2**), Scheme 1, were prepared according to a published procedure [15, 16]. Satisfactory ^1H NMR spectroscopic data in $CDCl_3$, MALDI-TOF mass spectra, element analysis and FT-IR data were obtained for compounds **1** and **2** after repeated column chromatographic purification and recrystallization (see Supplementary data). With two kinds of different substituents attached to the meso-positions of the porphyrin ligand, these compounds exhibited good solubility in common organic solvents, making them possible to fabricate them into supramolecular structures by solution processing. Supermolecular self-assembled aggregates of (TDMAPP)$Eu_2[Pc(OPh)_8]_2$ (**1**) and (TPyP)$Eu_2[Pc(OPh)_8]_2$ (**2**) were prepared by a solution-based QLS method [9,17]. To obtain information about the supermolecular structures of **1–2**, electronic absorption spectra of the samples in solution and in aggregates were recorded, Fig. 1. As shown in Fig. 1a, (TDMAPP)$Eu_2[Pc(OPh)_8]_2$ (**1**) in CH_2Cl_2 solution displays an intense main Q band at 644 nm and the two Soret bands at 359 and 438 nm, respectively, which are analogous to those reported for mixed (phthalocyaninato)(porphyrinato) rare earth complexes [4, 18]. However, after being fabricated into aggregates, both of the main Q bands and two Soret bands of **1** were broadened and red-shifted to 652 nm, 362 and 443 nm, respectively, Fig. 1a. On the basis of Kasha's exciton theory [19], red-shifts of the main absorption bands of **1** upon aggregates implied that the (TDMAPP)$Eu_2[Pc(OPh)_8]_2$ molecules are enforced to adopt the *J*-aggregation mode in the nanostructures. On the other hand, in comparison with the spectrum of **2** in CH_2Cl_2 solution, the Soret absorption bands of **2** upon aggregates blue-shifted from 359 and 411 nm to 348 and 397 nm, respectively, while the Q bands red-shifted from 625 and 683 nm to 640 and 711 nm, as shown in Fig. 1b. The point-dipole model of Kasha provides a rationale for the observed band shifts [19]. The extreme cases are represented by a head-to-tail arrangement of the dipoles, which results in a red-shifted absorption band (*J*-aggregate), and a parallel arrangement of the dipoles (*H*-aggregate) with a blue-shifted absorption band. The red and blue shifted bands observed in the present case for aggregates of **2** appear to represent an intermediate case that is conventionally thought of as a slipped cofacial stack with an “edge-on” configuration between adjacent Pc/Por chromophores of **2** [20]. The difference of absorption spectra observed between compounds **1** and **2** revealed the effect of substituent groups of porphyrin 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. As shown in Fig. 2a, the X-ray diffraction (XRD) diagram of self-assembled aggregates of **1** deposited on SiO_2/Si substrate shows four well-defined diffraction peaks at 2θ = 3.66°, 7.50°, 15.18° and 23.04°, which are ascribed to the diffractions from the (001), (002), (004) and (006) planes, respectively. The fact that all diffraction scans exhibit single dominant Bragg progressions indicated clearly the formation of highly textured multilayer assemblies and the long range molecular ordering across the assemblies [10]. The average *d*-spacing calculated according to the Bragg equation is about 2.35 nm, which corresponds to a periodic distance of **1** along the direction of the

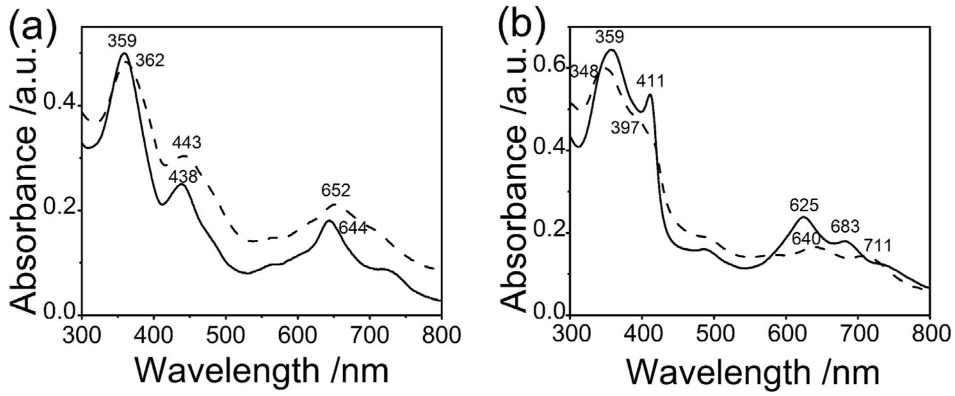

Fig. 1. UV–vis absorption spectra of (TDMAPP)$Eu_2[Pc(OPh)_8]_2$ (a) and (TPyP)$Eu_2[Pc(OPh)_8]_2$ (b) in CH_2Cl_2 solution (solid line) and self-assembled aggregates obtained by QLS method (dashed line).

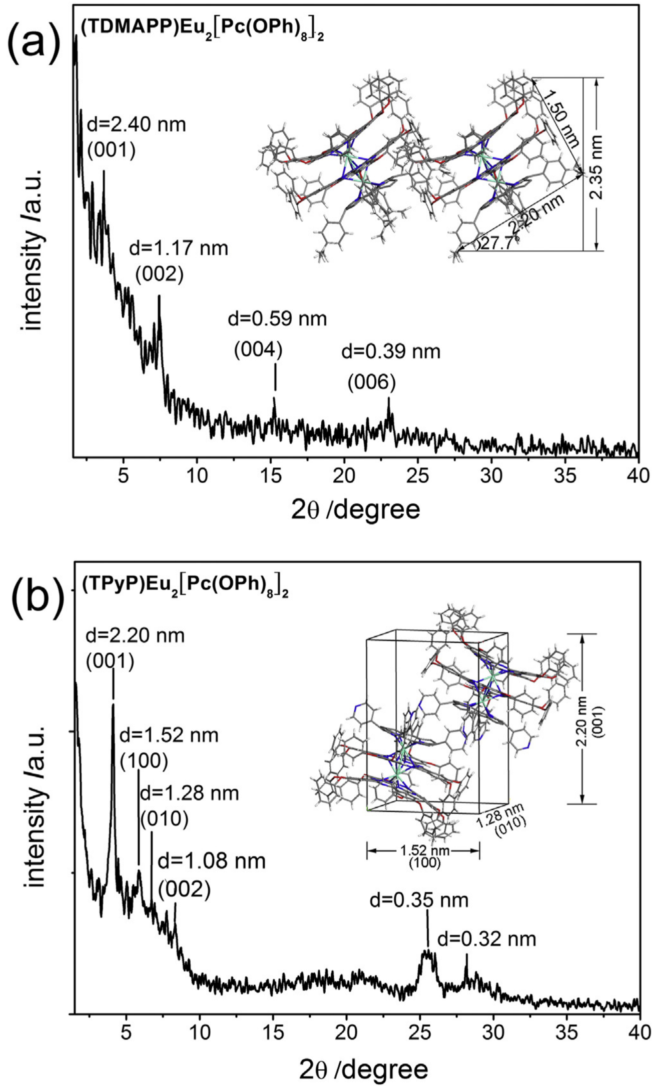

Fig. 2. X-ray patterns and schematic packing mode (inset) for the self-assembled aggregates of (TDMAPP)$Eu_2[Pc(OPh)_8]_2$ (a) and (TPyP)$Eu_2[Pc(OPh)_8]_2$ (b).

substrate surface normal. Considering the dimensional size for a triple-decker molecule **1** of 2.20 nm (either length or width) and 1.50 nm (thickness) by using PCMODEL for windows Version 6.0, Serena Software [4,11], the molecules of **1** take an "edge-on" configuration on the surface of the substrate and the orientation angle between the phthalocyanine ring in the triple-decker molecule and substrate surface of 27.7° is deduced (inset of Fig. 2a). This result is obviously in good accordance with that deduced from UV–vis spectroscopic measurement, therefore confirming the *J* aggregate mode nature for the self-assembled multilayer of **1** [3,12]. In contrast to **1**, as shown in Fig. 2b, XRD diagram of self-assembled aggregates formed from **2** shows a strong diffraction peak at $2\theta = 4.08°$ (corresponding to 2.20 nm) along with one relative weaker second-order diffraction at 1.08 nm, which are ascribed to the diffractions from the (001) and (002) planes. In addition, the XRD pattern also displays two well-defined peaks at 1.28 and 1.52 nm, respectively, originating from the (010) and (100) planes. This means that there exists very regular repetition of the nanostructure along the long axis of the phthalocyanine/porphyrin as well as the direction perpendicular to the phthalocyanine/porphyrin rings. According to the energy-optimized conformation of the molecule **2**, these diffraction results could be assigned to the diffractions from a rectangular lattice with the cell parameter of a = 1.52 nm, b = 1.28 nm, c = 2.20 nm (inset in Fig. 2b). Although the water (as a poor solvent) provides limited solubility for both **1** and **2** thus facilitate the molecular aggregation, the stronger solvent–molecule interaction between water and the pyridyl groups from **2** may induce the formation of a dimeric supramolecular structure through the formation of intermolecular hydrogen bonds between hydroxyl groups of water and the pyridyl groups of triple-decker molecules of **2**. Furthermore, in the wide angle region, the XRD pattern of the self-assembled aggregates of **2** presents two diffractions at $2\theta = 28.14°$ and 25.38° (corresponding to 0.32 nm and 0.35 nm) respectively, which can be attributed to the π–π stacking distance between phthalocyanine–phthalocyanine and porphyrin–porphyrin cores, respectively [4,21]. Obviously, the difference in XRD pattern for the aggregates between **1** and **2** should attribute to their different substituents at the meso-positions of the porphyrin ligand and in turn result in different favorable growing orientations of nanostructures of **1** and **2**. The morphologies of the self-assembled aggregates of **1** and **2** were observed by atomic force microscopy (AFM), Fig. 3. As revealed, the self-assembled aggregates of **1** show uniform small grain crystallites with approximately 235 nm in diameter, giving a root-mean-square (R_{rms}) roughness value of 2.15 nm, typical of a particularly smooth surface film-structure without large grain boundaries and special separation, Fig. 3a. This is in good contrast to the disconnected net-like domains with large gaps and cracks between aggregate domains ($R_{rms} = 17.2$ nm) observed for the aggregates of **2**, Fig. 3b. One may conclude, therefore, that the microscopic packing modes identified by UV–vis spectroscopic and XRD studies are rigorously reproduced in the macroscopic structures as detected by AFM. Unlike the situation for the self-assembled aggregates of **1**, the discontinuity in the self-assembled aggregates of **2** will surely add negative effect on the electrical conductivity as detailed below.

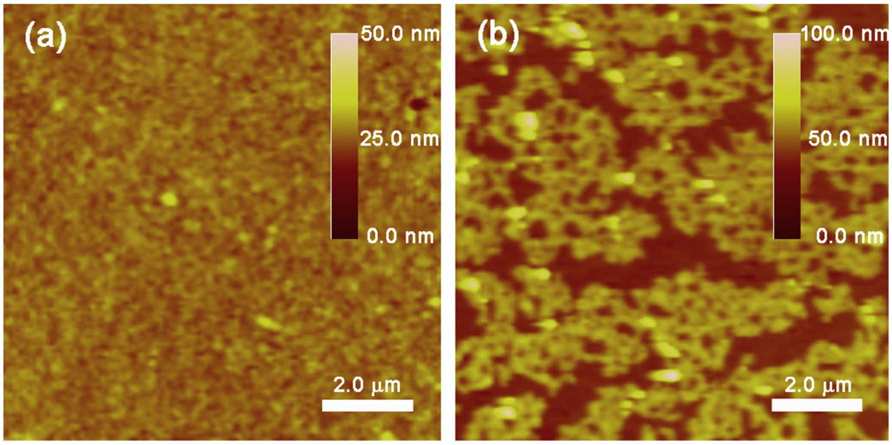

Fig. 3. AFM images for the self-assembled aggregates of (TDMAPP)$Eu_2[Pc(OPh)_8]_2$ (a) and (TPyP)$Eu_2[Pc(OPh)_8]_2$ (b).

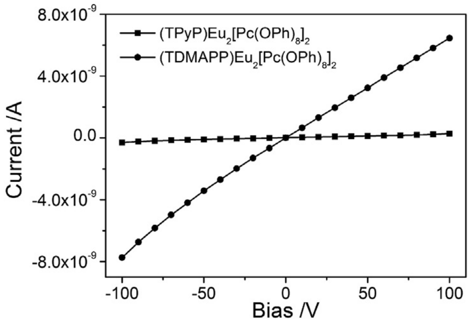

Fig. 4. I–V curves measured on the self-assembled aggregates of **1** (solid circles) and **2** (solid squares).

The uniform aggregates of sandwich mixed (phthalocyaninato)(porphyrinato) europium triple-deckers with well-defined nanostructures would be promising candidates for applications in electronic devices [4,13,14]. To demonstrate the potentials of the self-assembled aggregates of **1** and **2**, the current–voltage (I–V) measurements were performed on SiO_2 substrates with ITO interdigitated electrodes, Fig. 4. The devices made from different nanostructural aggregates of both **1** and **2** exhibit similar Ohmic behavior but a significantly increased current response for the aggregates of **1** compared to those of **2**. According to the equation reported in the literatures [9], the electronic conductivity is calculated to be about $2.35 \times 10^{-5}\ S\cdot cm^{-1}$ and $8.53 \times 10^{-7}\ S\cdot cm^{-1}$ for the aggregates of **1** and **2**, respectively. Comparing with that of the aggregates of **2**, the dramatically improved conductivity of the aggregates of **1** might be attributed to both higher ordered molecular arrangement and less gaps and cracks on the microstructure, implying that the substituent groups play a critical role on tuning the intermolecular stacking, and then impact on electrical conductivity of materials.

In summary, the self-assembled aggregates with distinct morphologies and structures for (TDMAPP)$Eu_2[Pc(OPh)_8]_2$ (**1**) and (TPyP)$Eu_2[Pc(OPh)_8]_2$ (**2**) were prepared at air–water interface. Comparative investigation results reveal that the substituent groups play a critical role on tuning the intermolecular stacking, and in turn impact on electrical conductivity of materials. The result presented here represents the continuous effort toward realizing control over the aggregates of sandwich tetrapyrrole rare earth complexes through molecular design and synthesis. It will be valuable for the design and preparation of conjugated molecular-based nano-electronic and nano-optoelectronic devices with good performance due to the close relationship between the molecular ordering and dimensions of nanostructures and the performance of nanodevices.

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Appendix A. Supplementary material

Synthesis and characterization details of (TDMAPP)$Eu_2[Pc(OPh)_8]_2$ (**1**) and (TPyP) $Eu_2[Pc(OPh)_8]_2$ (**2**), Experimental section. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.inoche.2015.02.009.

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