



Single crystal structure, self-assembled nano-structure and semiconductor properties of a sandwich-type mixed (phthalocyaninato)(porphyrinato) europium triple-decker complex



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ARTICLE INFO

Article history:

Received 8 November 2014

Received in revised form

2 December 2014

Accepted 4 December 2014

Available online 16 December 2014

Keywords:

Phthalocyanine

Porphyrin

Rare earth

Sandwich complex

Self-assemble

Crystal structure

ABSTRACT

Sandwich-type (phthalocyaninato)(porphyrinato) europium triple-decker complex with butyloxy substituents at the peripheral-positions of the two phthalocyanine ligands in the triple-decker molecules $\text{Eu}_2[\text{Pc}(\beta\text{-OC}_4\text{H}_9)_8]_2(\text{TCIPP})$ (**1**) has been designed, synthesized, and characterized. Their self-assembly properties and in particular nano-structures formed have also been systematically investigated in a confirmed manner due to the available single crystal structure. Investigation reveals that introduction of butyloxy substituents at the peripheral-positions of the phthalocyanine ligands in the triple-decker molecule induces additional van der Waals interactions between neighboring triple-decker molecules. This in combination with the intermolecular $\pi\text{-}\pi$ interaction result in the formation of one-dimensional nanostructures with rod shaped morphology. In addition, current–voltage ($I\text{-}V$) measurement result indicates good semiconductor feature of the nanorods with the conductivity of $2.2 \times 10^{-5} \text{ Sm}^{-1}$.

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1. Introduction

Self-assembled nanostructures have created a wide range of ever more sophisticated molecular materials associated with their diverse applications. In particular, well-defined nanostructures self-assembled from functional molecular with a conjugated electronic molecular structure has attracted increasing research interests in both material and chemistry fields [1–8]. Among which, as a typical representative of functional discotic (disc-like) molecular materials with a rigid aromatic core, phthalocyanine and porphyrin derivatives, in particular their sandwich-type rare earth complexes have attracted great research interest over the past years owing to their fundamental importance as model systems for studying the charge and energy transport and due to their potential application in molecular electronic devices [9–16]. In the past decade, great efforts have been devoted to these elaborately designed sandwich tetrapyrrole rare earth complexes containing

various functional group(s) for the purpose of fabricating nanostructures with different morphologies due to their various potential applications. For example, Jiang and co-workers incorporated different numbers of hydroxyl groups onto the meso-substituted phenyl groups of porphyrin ligand in mixed (phthalocyaninato)(porphyrinato) europium triple-decker complexes, resulting in nanostructures with different morphologies [17]. However, it is must be pointed out that investigation of the formation mechanism as well as the molecular packing mode of self-assembled nanostructures of these sandwich tetrapyrrole rare earth complexes still remains a great challenge for chemists and material scientists. X-ray diffraction technique is a useful tool to investigate the internal structure of the self-assembled nanostructures. This, in combination with their available single crystal and molecular structure revealed by X-ray diffraction analysis, should render it possible to investigate the formation mechanism as well as the molecular packing mode of self-assembled nanostructures in a confirmed manner. However, few self-assembled nanostructures of sandwich tetrapyrrole rare earth complexes can give enough internal structural information by X-ray diffraction analysis due to their short range and relatively low molecular

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ordering nature of the self-assembled nanostructures associated with the limited dimension(s) in some direction(s) and rapid growing speed of self-assembled nanostructures formed before reaching the thermodynamic equilibrium. Examination of a large number of self-assembled nanostructures reported thus far indicates that self-assembled nanostructures of molecular materials seldom exhibit rich refraction peak(s) in their X-ray diffraction (XRD) patterns [18–26]. Quite a significant fraction of self-assembled nanostructures do not even give any XRD refraction peak [27–34]. In addition, obtaining the single crystal molecular structure always plays an important role. However, the single crystals of these sandwich tetrapyrrole rare earth complexes remain rare [35–38]. In particular, to the best of our knowledge, the mixed ring triple-deckers containing one porphyrin ligand are only limited to {(Pc)M(Pc)M[T(4-OCH₃)PP]} (M = Nd and Tb) [39,40], {(TCIPP)M[Pc(OPh)₈]M'[Pc(OPh)₈]} (M–M' = Dy–Dy, Y–Dy, Dy–Y, and Y–Y) [41], and {(Pc)Eu(Pc)Eu[TCIPP]} [42]. As a result, most self-assembled nanostructures of these sandwich tetrapyrrole rare earth complexes reported thus far were usually characterized only in terms of their morphology and dimension by means of various electronic microscopic techniques but without investigating the formation mechanism as well as the molecular packing mode of self-assembled nanostructures.

In the present paper, we describe the characterization of nanostructures fabricated from sandwich-type (phthalocyaninato)(porphyrinato) europium triple-decker complex with butyloxy substituents at the peripheral-positions of the two phthalocyanine ligands in the triple-decker molecule, namely Eu₂[Pc(β-OC₄H₉)₈]₂(TCIPP) (**1**). Their self-assembly properties and in particular nano-structures formed have also been systematically investigated in a confirmed manner due to the available single crystal structure. The present study represents part of our continuous effort for providing new examples of sandwich-type tetrapyrrole rare earth complexes towards the preparation of tetrapyrrole based nano-electronic devices with the desired structure and good performance.

2. Experimental

2.1. General information

1,2,3-trichlorobenzene (TCB) 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 (phthalocyaninato)(porphyrinato) europium triple-decker complex Eu₂[Pc(β-OC₄H₉)₈]₂(TCIPP) (**1**) was prepared according to the published procedure [43]. Satisfactory elemental analysis result was obtained for this newly prepared complex **1** after repeated column chromatography [Ana. Calcd (%) for C₁₇₂H₁₈₄N₂₀O₁₆.Cl₄Eu₂·CH₃OH: C, 63.64; H, 5.80; N, 8.58; found: C, 63.59; H, 5.81; N, 8.60]. Further MALDI-TOF mass spectra analysis indicated that the intense signal was the molecular ion (M)⁺ [MS: Calcd. for C₁₇₂H₁₈₄N₂₀O₁₆Cl₄Eu₂ 3233.2; found *m/z*. 3232.9].

2.2. Measurements

Electronic absorption spectra were recorded on a Shimadzu UV-1650 PC spectrometer. X-Ray diffraction (XRD) measurements were carried out on a Rigaku D/max-γB X-ray diffractometer. Transmission electron microscopic (TEM) images were collected on a JEOL-100CX II electron microscope operated at 100 kV. Scanning electron microscopic (SEM) images were obtained on a JEOL JSM-6700F. For TEM imaging, a drop of sample solution was cast onto a carbon copper grid. For SEM imaging, Au (1–2 nm) was sputtered onto these grids to prevent charging effects and to improve image clarity.

2.3. Nano-structure fabrication

The nano-structures of triple-decker complex **1** were fabricated by the phase transfer method according to the following procedure [44–48]. A minimum volume (30–50 μL) of concentrated chloroform solution of triple-decker complex **1** (1 mM) was injected rapidly with a micro-injector into a large volume of methanol (2 mL) and subsequently mixed. Then nanostructures were precipitated from the solution quickly. 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. X-ray crystallographic analyses

Crystal data and details of data collection and structure refinement are given in Table 1. Data were collected on a Bruker SMART CCD diffractometer with a Cu-Kα sealed tube (λ = 1.54178 Å) at 293 K, using a ω scan mode with an increment of 0.3°. Preliminary unit cell parameters were obtained from 45 frames. Final unit cell parameters were derived by global refinements of reflections obtained from integration of all the frame data. The collected frames were integrated using the preliminary cell-orientation matrix. The SMART software was used for collecting frames of data, indexing reflections, and determination of lattice constants; SAINT-PLUS for integration of intensity of reflections and scaling [49]; SADABS for absorption correction [50]; and SHELXL for space group and structure determination, refinements, graphics, and structure reporting [50]. CCDC 1031378 for the triple-decker complexes **1** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

3. Results and discussion

3.1. X-ray single crystal structure

The single crystals of the triple-decker complex **1** suitable for X-ray diffraction analysis were obtained by slow diffusion of MeOH

Table 1
Crystallographic data for triple-decker complex **1**.

Eu ₂ [Pc(β-OC ₄ H ₉) ₈] ₂ (TCIPP)	
Formula	C ₁₇₂ H ₁₈₄ N ₂₀ O ₁₆ Cl ₄ Eu ₂
<i>M_r</i>	3233.11
Crystal size (mm)	0.3 × 0.28 × 0.25
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	23.6331(6)
<i>b</i> (Å)	24.1297(5)
<i>c</i> (Å)	30.4005(12)
α (°)	90.00
β (°)	105.207(3)
γ (°)	90.00
<i>V</i> (Å ³)	16729.1(9)
<i>Z</i>	4
ρ _{calcd} (g cm ⁻³)	1.284
μ (mm ⁻¹)	6.429
<i>F</i> (000)	6712.0
2θ range (°)	7.32 to 140.84
Total no. of reflns	63,712
No. of indep reflns	31,116 (<i>R</i> _{int} = 0.0755)
Parameters	1938
Goodness of fit	1.089
<i>R_i</i> [<i>I</i> > 2σ (<i>I</i>)]	0.0888
<i>wR₂</i> [<i>I</i> > 2σ (<i>I</i>)]	0.2161

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