



Controlled morphology of self-assembled microstructures via solvent-vapor annealing temperature and ambipolar OFET performance based on a tris(phthalocyaninato) europium derivative



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ABSTRACT

A novel homoleptic sandwich-type tris[2,3,9,10,16,17,23,24-octa(naphthoxy)phthalocyaninato] europium triple-decker complex $\text{Eu}_2[\text{Pc}(\text{ONh})_8]_3$ (**1**), having a low-lying LUMO energy level of -4.0 eV and relatively narrow HOMO–LUMO separation of 1.13 eV, was designed and successfully synthesized. The OFET devices fabricated from this compound using a solution-based quasi-Langmuir–Shäfer (QLS) method display air-stable ambipolar performance with the carrier mobilities of $(2.5 \pm 0.5) \times 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for holes and $(2.3 \pm 0.3) \times 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for electrons, indicating its ambipolar semiconducting nature. Upon the *o*-dichlorobenzene (DCB) solvent vapor annealing at the temperature of 60, 80, 100, and 120 °C, a fine combination of the “oriented attachment” with Ostwald ripening process under controlled SVA environments leads to the growth of the first two-dimensional (2D) micro-sheet microstructures with tunable morphology including the fragment-like irregular polygons, quasi-four-corner sheets, squares, and clovers, respectively, from the nanoparticles of the pristine QLS film. This in turn results in the tunable OFET device performance with the carrier mobilities changing as a result of the morphologies and crystallinities. The best result was achieved for the most crystalline 2D squares-based devices with the carrier mobilities of $0.11 \pm 0.03 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for holes and $0.06 \pm 0.02 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for electrons.

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1. Introduction

Ambipolar semiconductors that exhibit balanced hole accumulation for negative gate bias and electron accumulation for positive gate bias in a single-component active layer are highly desired due to their application in large-area manufacturing of complementary integrated circuits and light-emitting FETs [1–3]. For the purpose of realizing high-performance ambipolar transport with balanced mobility and robust air stability for solution-processable organic semiconductors, great efforts have been paid through the combination of a series of multiple approaches including developing novel narrow-energy-gap organic semiconductors (energy gap < 2.0 eV), tuning the HOMO and LUMO energy levels to match

the Fermi levels of environmentally stable electrode (Au or Ag), and carefully optimizing the device fabrication and interface engineering [4,5]. Inspired by the disclosing of the ambipolar semiconducting nature of bis(phthalocyaninato) lanthanide compounds $\text{M}(\text{Pc})_2$ ($\text{M} = \text{Tm}, \text{Lu}$) with the hole mobility of 10^{-3} to $10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and electron mobility of 10^{-4} to $10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in vacuum at the early 1990s [6], extensive investigations were carried out over a series of small molecular π -conjugated systems, revealing the ambipolar properties of rubrene, acene, thiophene, diketopyrrolopyrrole, and phthalocyanine [7–12]. Among which, phthalocyanines (Pcs) have received particular attention due to their high thermal and chemical stabilities in combination with synthetic versatility which lends a large chance in tuning the molecular and electronic structures [13]. For example, combination of *p*-type CuPc and *n*-type F_{16}CuPc with both good stability and high mobility yielded the air-stable ambipolar transistors with the best device performance at that time like the electron and hole mobilities of 0.05 and $0.07 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively [14]. However, the lack of solution-processability for both unsubstituted and F-

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substituted phthalocyaninato copper complexes retards their industrial application potentials in low-cost electronics. Design and synthesis of novel phthalocyanine derivatives for ambipolar semiconducting application with good solution-processability has therefore become a great challenge thereafter [15]. This in turn results in the unravelling of the intrinsically air-stable ambipolar nature of a series of peripherally phenoxy/naphthoxy-functionalized phthalocyanine-containing heteroleptic tris(phthalocyaninato) rare earth complexes [16–18]. The OTFTs fabricated from these compounds through the solution-based methods exhibited carrier mobilities of $0.014\text{--}1.7\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ for holes and $0.01\text{--}1.3\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ for electrons [17–22]. Nevertheless, further efforts are necessary towards further improving the device performance through optimizing the morphology and crystallinity of corresponding nano/microstructures of the semiconductor layer for the purpose of realizing their practical industrial applications.

On the other hand, the solvent vapour annealing (SVA) technique is well known to be able to effectively increase the molecular ordering over large distances (*i.e.* crystallinity) and lower the density of defects (*i.e.* polycrystalline domain boundaries) of organic films [23–25]. Immersing the pristine organic thin films of OFETs in an atmosphere saturated with the vapor of a solvent in which the organic molecules are soluble indeed significantly improves the device performance [26–28]. For example, after the DCE-vapour-annealing, the carrier mobility of the *n*-type OFETs with an *N,N*-dialkyl-substituted-(1,7&1,6)-dicyanoperylene-3,4:9,10-bis(dicarboximide) derivative as active layer got significantly increased to $0.5\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ from $0.02\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ for the pristine ones together with significantly enhanced stability [28]. However, clear relationship between the specific geometrical structures/thin-film crystallinity and OFET performance optimized via SVA method has still not yet been clarified due to the thus far less accumulation of corresponding results in this direction [29].

In this paper, a homoleptic sandwich-type tris[2,3,9,10,16,17,23,24-octa(naphthoxy)phthalocyaninato] europium triple-decker complex $\text{Eu}_2[\text{Pc}(\text{ONh})_8]_3$ (**1**), Scheme 1, was designed and prepared. Electrochemistry revealed its potential ambipolar semiconducting nature, which is verified by the device performance fabricated from this compound using the solution processed quasi-Langmuir-Shäfer (QLS) method [30]. In particular, *o*-

dichlorobenzene (DCB) solvent vapour annealing (SVA) over the pristine QLS film at 60, 80, 100, and 120 °C induces a systematic change in the morphology and crystallinity of the microstructures. This in turn becomes responsible for the tuned ambipolar OFET performance of the phthalocyaninato rare earth triple-decker complex.

2. Experiment

2.1. Chemicals and measurements

Anhydrous 1,2,4-trichlorobenzene (TCB) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) were purchased from Aldrich. Dichloromethane for voltammetric studies was freshly distilled from CaH_2 under an atmosphere of nitrogen. The precursors for synthesis of the target triple-decker compound, $\text{Eu}(\text{acac})_3 \cdot n\text{H}_2\text{O}$ [31], 4,5-bis(naphthoxy)-1,2-dicyanobenzene [32], $\text{H}_2\text{Pc}(\text{ONh})_8$ [33], and $\text{Eu}[\text{Pc}(\text{ONh})_8]_2$ [34], were prepared according to the literature methods. All other reagents and solvents were used as received. Detail informations of the experimental measurements including UV-vis, ^1H NMR, MALDI-TOF, Electrochemistry, SEM, XRD and OFET devices were detailed in Supplementary data.

2.2. Synthesis and characteristic of triple-decker $\text{Eu}_2[\text{Pc}(\text{ONh})_8]_3$

A mixture of $\text{Eu}(\text{acac})_3 \cdot n\text{H}_2\text{O}$ (10 mg), $\text{H}_2\text{Pc}(\text{ONh})_8$ (20 mg), and $\text{Eu}[\text{Pc}(\text{ONh})_8]_2$ (36.4 mg) in anhydrous 1,2,4-trichlorobenzene (TCB) (3 mL) was refluxed for 4 h under a slow stream of nitrogen. After being cooled to room temperature, 10 mL *n*-hexane was added to the mixture. The precipitate was filtered off and then washed with *n*-hexane and methanol. The residue left was chromatographed on a silica gel (200–300 mesh) column with CHCl_3 as eluent. Repeated chromatography followed by recrystallization from CHCl_3 and *n*-hexane gave pure compound as a blue powder [16–18]. Yield: 9.7 mg (32.5%). The detailed synthetic routes are shown in Scheme S1 (Supplementary data). ^1H NMR (400 MHz, CDCl_3 , δ): 12.71 (s, 8 H, Pc-H_α), 9.46 (s, 16 H, $\text{Pc}^*\text{-H}_\alpha$), 8.76–8.74 (d, 8 H, $\text{Pc-Nh-H}_{\beta 1}$), 8.17–8.15 (d, 16 H, $\text{Pc}^*\text{-Nh-H}_{\beta 1}$), 8.11–8.08 (d, 8 H, $\text{Pc-Nh-H}_{\beta 2}$), 8.07–8.05 (d, 16 H, $\text{Pc}^*\text{-Nh-H}_{\beta 2}$), 7.89–7.87 (d, 8 H, $\text{Pc-Nh-H}_{\beta 3}$), 7.85–7.83 (d, 16 H, $\text{Pc}^*\text{-Nh-H}_{\beta 3}$), 7.77–7.75 (m, 24 H, $\text{Pc-Nh-H}_{\beta 4}$, $\text{Pc}^*\text{-Nh-H}_{\beta 4}$), 7.72–7.03 (m, 24 H, $\text{Pc-Nh-H}_{\beta 5}$, $\text{Pc}^*\text{-Nh-H}_{\beta 5}$), 7.48–7.44 (t, 16 H, $\text{Pc-Nh-H}_{\beta 6}$), 7.40–7.37 (t, 16 H, $\text{Pc}^*\text{-Nh-H}_{\beta 6}$), 7.31–7.26 (t, 16 H, $\text{Pc-Nh-H}_{\beta 7}$), 6.98–6.95 (t, 16 H, $\text{Pc}^*\text{-Nh-H}_{\beta 7}$); MALDI-TOF MS: an isotopic cluster peaking at m/z 5253, Calcd for $\text{C}_{336}\text{H}_{193}\text{Eu}_2\text{N}_{24}\text{O}_{24}$, $[\text{M}]^+$, 5253, Fig. S1 and Fig. S2 (Supplementary data).

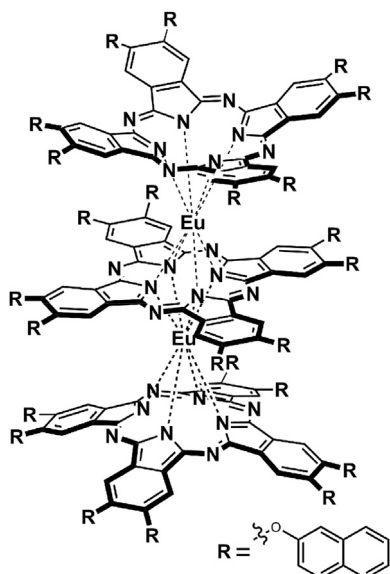
2.3. Preparation of the self-assembled film of the triple-decker using SVA method

The quasi-Langmuir-Shäfer (QLS) method was employed to prepare the pristine QLS film for **1** according the published procedure [30]. Then baked pristine QLS film on a hot plate under DCB vapor for 30 min by releasing 20 μL of solvent in the Petri dish (diameter: 9.5 cm, height: 1.5 cm, volume: 106.3 cm^3) and sequentially SVA-processed for different exposure temperatures from 60 to 120 °C at a temperature gradient of 20 °C under each solvent-vapour condition resulted in the SVA self-assemblies [28].

3. Result and discussion

3.1. Molecular design, synthesis and electrochemistry

Inspired by the success tuning over the semiconducting nature of heteroleptic tris(tetrapyrrole) rare earth complexes using the phenoxy/naphthoxy groups [17,18], in the present case totally



Scheme 1. The schematic molecular structure of $\text{Eu}_2[\text{Pc}(\text{ONh})_8]_3$ (**1**).

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