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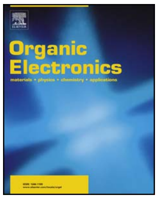

Polymorphism in the self-assembled nanostructures of a tris (phthalocyaninato) europium derivative: Phase-dependent semiconducting and NO_2 sensing behaviour

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ABSTRACT

A new trifluoroethoxy-substituented tris(phthalocyaninato) europium complex $Eu_2[Pc(OCH_2CF_3)_4]_3$ {$[Pc(OCH_2CF_3)_4]$ = 2(3),9(10),16(17),23(24)-tetrakis(2,2,2-trifluoroethoxy)phthalocyaninate}, is designed and synthesized. Introduction of trifluoroethoxy substituents at the phthalocyanine periphery within the triple-decker complex ensures their good solubility in conventional organic solvents. Significantly, depending on the fluorine-participated multiple hydrogen bonding and the π–π interactions in different solvent systems (*i.e. n*-hexane and water), the self-assembly of the $Eu_2[Pc(OCH_2CF_3)_4]_3$ molecules results in well controlled morphologies (nano-bowling bowls, nanobelts and nano-particles) with totally different phases (χ, β and α phases). Furthermore, the sensitivity to NO_2 at varied concentrations in the range of 20–1600 ppb, follows the order of nano-bowling bowls in χ phase (SA-1) » nanobelts in β phase (SA-2) > nano-particles in α phase (SA-3), revealing the effect of both phase structure and morphology on sensing performance of the $Eu_2[Pc(OCH_2CF_3)_4]_3$. In particular, SA-1 displays unexpected high percent current change of 6.52% to NO_2 gas as low as 20 ppb at room temperature, representing thus far the best result of the room-temperature NO_2 gas sensing performance in terms of the lowest detection limit with largest response. The present work not only represents the first observation of χ, β and α polymorphs for the sandwich-type triple-decker tetrapyrrole-based rare earth complexes, but more importantly provides an efficient strategy to obtain high performance organic semiconductor-based gas sensors through molecular design and solvent-triggered phase transformations.

1. Introduction

Inorganic materials including oxides, metals, alloys, and ionic salts usually possess different phases and therefore exhibit significant different optical, electrical, and magnetic properties [1,2]. This is also true for the carbon material with rich phase forms of amorphous carbon, graphite, diamond, fullerene, carbon nanotube, graphene, and graphdiyne [3]. However, except a few of the liquid crystal molecular materials [4] and recently interest-concentrated ferroelectric materials [5,6], the relationship between the physical properties and phase states for the molecular materials without liquid crystalline properties is still far from being established due to the great difficulty in obtaining and maintaining the well-defined chemical composition of molecular materials in a relatively large temperature range. Thanks for the large π conjugated electronic structure of phthalocyanines, the polymorphic properties of the same molecular species in particular unsubstituted phthalocyanines have been found with a variety of UV–visible absorption spectra depending on a slight difference in the π electronic interaction among stacked planar molecules [7–12]. This in turn results in the few reports on the preliminary investigation over the phase states of phthalocyanine compounds [7–12]. As early as in 1980, the stable β phase, metastable α phase, and stable χ phase of ZnPc crystallines were claimed to be fabricated from ZnPc powder upon solvent annealing in vapor of the various alcohols at constant temperatures, 45 and 55 °C

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[7]. This was followed by the preparation of the PbPc film in either triclinic β phase or monoclinic α phase state using CVD method through controlling the substrate temperature as well as the deposition rate [8]. By means of a similar method, both α- and β-phase CuPc films with different morphology were fabricated in late years, showing phase-dependent NO_2 gas sensitivity and *p*-type OFET performance associated with their internal structures [9,10]. Interestingly, by utilizing the simple milling at 400 rpm for 100 h, the stable β phase FePc was successfully transformed into the metastable α phase [11]. Very lately, both the α- and β-phase films of the tetra(3-nitro-5-*tert*-butyl)phthalocyaninato copper complex were fabricated by LB technique at different compressing pressure [12]. Aging the film naturally for 3 days led to the successful transformation from the β-phase to the χ-phase [12]. Among the large family of the phthalocyanines, sandwich-type bis/tris(phthalocyaninato) rare earth semiconducting materials have been intensively studied due to their great application potentials in organic field-effect transistors (OFETs) [13–18], sensors [19–23], and single molecule magnets (SMMs) [24–28]. Although two polymorphs (*i.e.* α- and β-phases) have been already reported for bis(phthalocyaninato)neodymium complex [29,30], studies on phase behaviour of sandwich-type phthalocyanines, especially tris(phthalocyaninato) rare earth complexes, and corresponding phase-dependent functionality has never been explored yet due likely to their weak intermolecular interactions. Therefore, incorporation of suitable functional substituents onto the phthalocyanine periphery, those are able to enhance the intermolecular interactions of sandwich phthalocyanines, is high desired to obtain the different polymorphic forms in order to determine the relationship between the type of phase and the alignment behaviour and thus for phase-functionality relationship studies.

In the present work, trifluoroethoxy groups with both hydrophobic and lipophobic nature have been introduced onto the phthalocyanine periphery, yielding novel tris(phthalocyaninato) europium complex $Eu_2[Pc(OCH_2CF_3)_4]_3$ {$[Pc(OCH_2CF_3)_4]$ = 2(3),9(10),16(17),23(24)-tetrakis(2,2,2-trifluoroethoxy)phthalocyaninate}, Scheme 1. Fine tuning intermolecular multiple F···H—C hydrogen bonding and the π–π interactions among neighbouring triple-decker molecules by using different solvents, leads to three different polymorphic forms (α, β and χ phases) in self-assembled nanostructures of the triple-decker complex. Meanwhile solvent-triggered transformations in the resulting self-assembled nanostructures are also observed for the first time from χ phase to β phase and α phase. Significantly, their phase-dependent semiconducting and NO_2 gas sensing behaviour are revealed. In particular, the sensor of the nano-bowling bowls in the form of χ phase displays unexpected high sensitivity. Consequently, the phase-functionality relationship of sandwich phthalocyaninato rare earth semiconducting molecular is clarified for the first time.

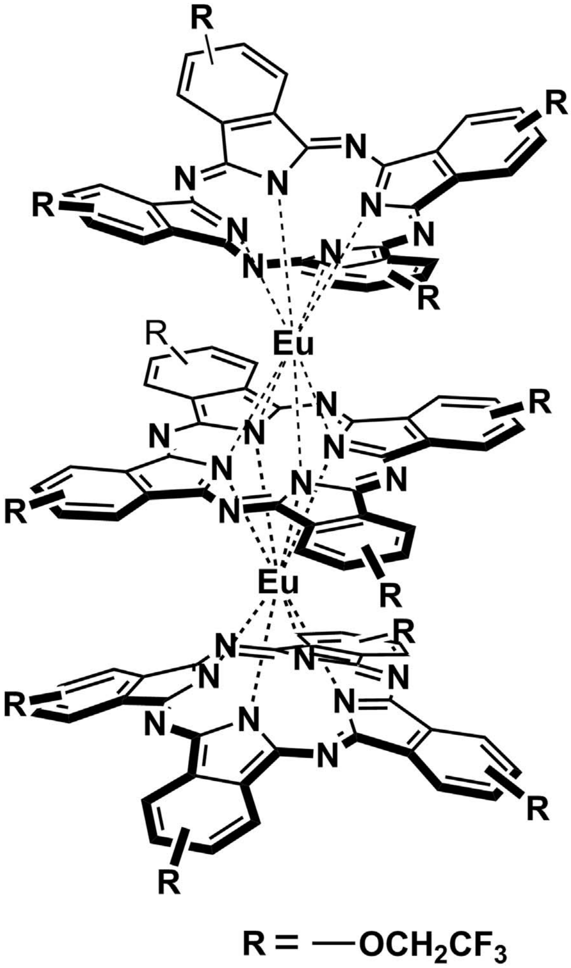
2. Experimental section

2.1. Chemicals

All the reagents and solvents were purchased from Aldrich. CH_2Cl_2 for DPV studies was freshly distilled from CaH_2 under nitrogen [2,13–18,31,32]. Column chromatography was carried out on silica gel (Merck, Kieselgel 60, 200–300 mesh) with the indicated eluents. The compounds of 4-(2,2,2-trifluoroethoxy)phthalonitrile and 2(3),9(10),16(17),23(24)-tetrakis(2,2,2-trifluoroethoxy) phthalocyanine were prepared according to the published procedures [13].

2.2. Measurements

Electronic absorption spectra were recorded on a Hitachi U-3900 UV–visible spectrophotometer. Fourier transform infrared (FT-IR) spectra were recorded as KBr pellets using Bruker Tensor II spectrometer with 2 cm^{-1} resolution. PerkinElmer Diamond TG/DTA Analyzer was used for thermogravimetric analysis. The fundamental electrical and sensor measurements were performed using a Keysight B2910A precision source/measure unit with an incorporated direct current voltage supply. X-ray diffraction (XRD) experiments were carried out on Rigaku D/max-γB X-ray diffractometer with copper (Kα) radiation. SEM images were measured using a JEOL JSM-6700F field-emission scanning electron microscopy. Electrochemical measurements were conducted using a CHI760D voltammetric analyzer. Three-electrode system was used to obtain DPV curve according to the reported procedure [13,14]. The desired NO_2 concentration was produced by diluting a mixture NO_2/N_2 (50 ppm NO_2, from Qingdao Ludong Gas., Ltd, China) with dry N_2 using two CS200 Mass Flow Controllers (total mass flow: 0.1 L min^{-1} for NO_2 and 2 L min^{-1} for diluent gas N_2).



Scheme 1. Schematic molecular structure of $Eu_2[Pc(OCH_2CF_3)_4]_3$.

2.3. Preparation of self-assembled nanostructures of $Eu_2[Pc(OCH_2CF_3)_4]_3$

The chloroform solution (0.1 mM) of $Eu_2[Pc(OCH_2CF_3)_4]_3$ was injected into *n*-hexane to form a binary solvent of chloroform/*n*-hexane (1:5 v:v). After being kept at room temperature for 3, 6, 9, 12, and 24 h, the aggregates precipitated were then transferred to different substrates (SiO_2/Si, ITO/glass etc.) by pipette for microstructural characterization and sensing measurements. The QLS film was fabricated by means of a solution-based quasi-Langmuir–Shäfer (QLS) method reported previously [33].