



# Flexible, ambipolar organic field-effect transistors based on the solution-processed films of octanaphthoxy-substituted bis(phthalocyaninato) europium



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## ABSTRACT

A new sandwich-type bis(phthalocyaninato) europium complex  $[\text{Pc}(\text{OAr})_8]\text{Eu}[\text{Pc}(\text{OAr})_8]$  [ $\text{Pc}(\text{OAr})_8 = 2,3,9,10,16,17,23,24$ -octanaphthoxy phthalocyanine], was synthesized and fabricated into organic field-effect transistors devices on a flexible plastic substrate by using a simple solution-based quasi-Langmuir-Shäfer method. Ambipolar transport has been obtained in  $[\text{Pc}(\text{OAr})_8]\text{Eu}[\text{Pc}(\text{OAr})_8]$ -based thin film transistors with the carrier mobilities to  $0.10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  for holes and  $0.01 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  for electrons, respectively. The energy levels of the highest occupied molecular orbital ( $-4.63 \text{ eV}$ ) and the lowest unoccupied molecular orbital ( $-3.41 \text{ eV}$ ) were obtained based on electrochemical studies of this double-decker complex. These values just simultaneously meet the energy levels required for *p*-type and *n*-type natures of organic semiconductors, suggesting the ambipolar organic semiconducting nature of this double-decker complex. Organized film microstructures and *J*-type molecular stacking mode for the double-decker complex in the quasi-Langmuir-Shäfer film are revealed. This study constitutes the first attempt to fabricate low-cost, flexible ambipolar phthalocyanine-based organic field-effect transistors by using simple solution-processing methods.

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## 1. Introduction

Organic electronic devices manufactured by solution-based methods have attracted tremendous interest due to their great potential for the creation of a new paradigm in the fabrication process of low-cost, large area, flexible electronic and optoelectronic devices, such as organic light-emitting diodes (OLEDs), organic photovoltaics (OPVs), organic field-effect transistors (OFETs), and organic memory devices and sensors [1–6]. OFETs are fundamental building blocks of integrated circuits (ICs) and drivers for active-matrix flat-panel displays. Accordingly, they are promising candidates to replace the vacuum-processed amorphous inorganic ICs. Recently, several research groups have reported the fabrication of flexible *p*-type OFETs employing oligothiophene [7], pentacene [8], and polythiophene derivatives [9,10] as the active semiconductor layer, and various polymeric insulators as the gate dielectric layer, with the mobility in the range of

$0.01\text{--}0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ . Compared with highly developed flexible *p*-type OFETs, high-performance *n*-type or ambipolar flexible OFETs in particular those constructed by solution-processable organic small molecules as the active semiconductor layer still remain rare [11]. Recently, an ambipolar OFET based on solution-processable pentacene as the semiconductor layer deposited on flexible plastic substrates with parylene-C as the dielectric material with the mobilities up to  $0.09 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  for holes and  $0.03 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  for electrons was reported [8], which induces further incentive toward the fabrication of complementary circuits with enhanced performance and device operation [12]. For the fabrication of flexible OFETs, the poly(ethylene terephthalate) (PET) is a good candidate as a flexible substrate due to the advantages with regard to clarity, coefficient of thermal expansion, chemical resistance, moisture absorption, and low-cost [13–15], while poly(methylmethacrylate) (PMMA) is usually chosen as a dielectric layer because of its low electrical leakage and good chemically compatible with a range of organic semiconductors [16–18]. So far, mainly flexible OFET devices fabricated on PET plastic substrates with PMMA as the gate dielectric layers have been investigated. For example, Chen and co-workers reported fabricating flexible graphene FETs using a 600 nm

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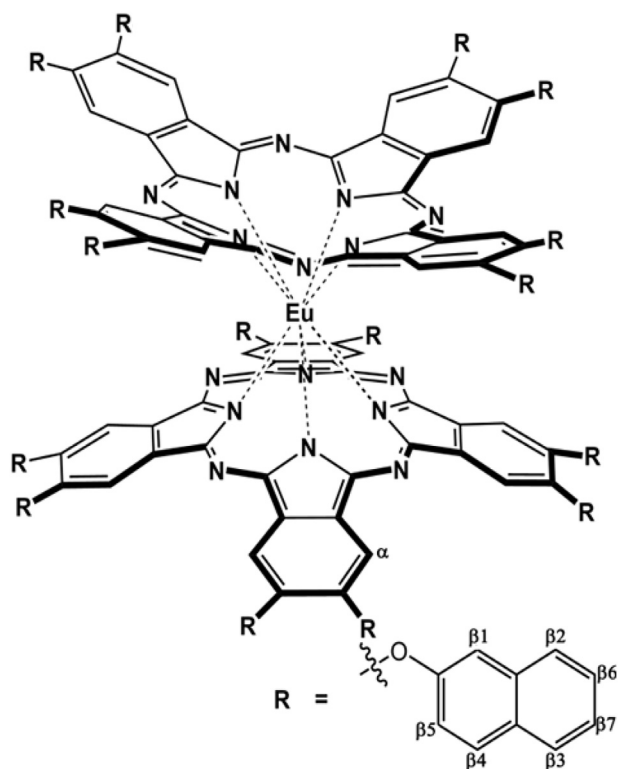
thick PMMA gate dielectric, via transferring mechanically exfoliated graphene flakes to a PET plastic substrate for device assembly [19]. Huang and co-workers investigated the properties of pentacene based OFETs using PMMA as the gate dielectric layer and found larger grain sizes and better crystalline quality of the pentacene thin films on PMMA as compared to  $\text{SiO}_2$ , which translated to superior electrical performance [20]. Khim and co-workers developed a simple wire-bar-coating process for deposition of ambipolar conjugated polymer and insulating PMMA gate dielectric films in OFET arrays [18]. Phthalocyanines have been intensively studied as good molecular semiconductor materials because of their large conjugated  $\pi$  system, unique electronic characteristics, and high thermal and chemical stability [21–24]. By using different techniques, a large number of phthalocyanine (Pc) compounds have been fabricated into OFET devices [24–27]. Bisphthalocyanines represent a special class of phthalocyanine based molecular materials, which are sandwich complexes of rare earth elements ( $\text{LnPc}_2$ ) and stable radical molecules. After the first report of ambipolar OFETs based on thermally-evaporated thin films of  $\text{MPC}_2$  ( $\text{M} = \text{Tm}, \text{Lu}$ ) in 1990 [28], sandwich-type bis(phthalocyaninato) rare earth complexes have been subjected to extensive investigations because of their radical nature and possible applications in gas sensors, photovoltaic and organic electronic devices [23,29–33]. In light of these pioneering works, we report in this paper the design and synthesis of a new bis(phthalocyaninato) europium complex,  $[\text{Pc}(\text{OAr})_8]\text{Eu}[\text{Pc}(\text{OAr})_8]$  (**1**) [ $\text{Pc}(\text{OAr})_8 = 2,3,9,10,16,17,23,24$ -octanaphthoxy phthalocyanine], Scheme 1. With a special sandwich structure and strong intermolecular  $\pi$ - $\pi$  interactions between the phthalocyanine rings; this molecular material is expected to be an intrinsic semiconductor [34,35]. A novel flexible OFET device is constructed with the solution-based quasi-Langmuir-Shäfer (QLS) film [36] of

$[\text{Pc}(\text{OAr})_8]\text{Eu}[\text{Pc}(\text{OAr})_8]$  as the active layer, spin-coated poly(-methylmethacrylate) (PMMA) as the dielectric layer and poly(-ethylene terephthalate) (PET) as the flexible substrate, Fig. 1a. The high-performance ambipolar transport has been obtained in the single component  $[\text{Pc}(\text{OAr})_8]\text{Eu}[\text{Pc}(\text{OAr})_8]$  thin film-based transistors, with carrier mobilities up to  $0.10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  for holes and  $0.01 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  for electrons, respectively. This work constitutes the first attempt to fabricate low-cost, flexible ambipolar phthalocyanine-based OFETs by using the simple solution-processing methods.

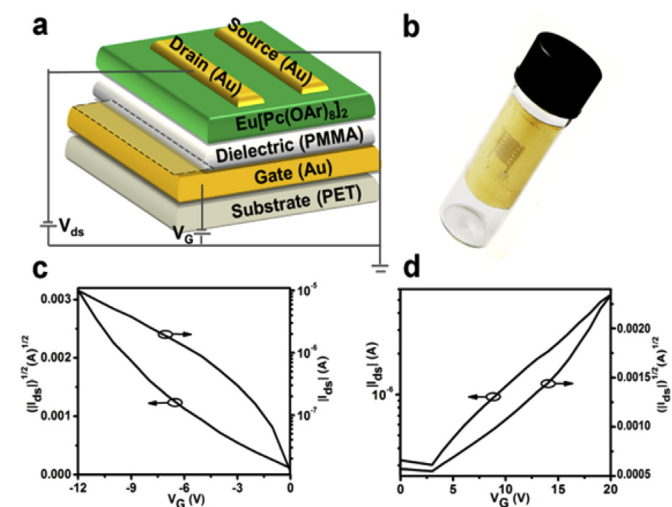
## 2. Experiment

### 2.1. Measurements

$^1\text{H}$  NMR spectrum was recorded on a Bruker DPX 400 spectrometer in  $\text{CDCl}_3/[\text{D}_6]\text{DMSO}$  (1:1) in the presence of ca. 1% (by volume) hydrazine hydrate. Spectrum was referenced internally with residual DMSO ( $\delta = 2.49$  ppm). MALDI-TOF mass spectrum was taken on a Bruker BIFLEX III ultra-high-resolution Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer with alpha-cyano-4-hydroxycinnamic acid as matrix. Electrochemical measurement was carried out with a CHI760D voltammetric analyzer. The cell comprised inlets for a glassy carbon disk working electrode of 3.0 mm in diameter and a silver-wire counter electrode. The reference electrode was  $\text{Ag}/\text{Ag}^+$  ( $0.01 \text{ mol L}^{-1}$ ), which was connected to the solution by a Luggin capillary, whose tip was placed close to the working electrode. It was corrected for junction potentials by being referenced internally to the ferrocene/ferrocene ( $\text{Fc}^+/\text{Fc}$ ) couple [ $E_{1/2}(\text{Fc}^+/\text{Fc}) = 0.50 \text{ V vs. SCE}$ ]. Typically, a  $0.1 \text{ mol L}^{-1}$  solution of  $[\text{Bu}_4\text{N}][\text{ClO}_4]$  in  $\text{CH}_2\text{Cl}_2$  containing  $0.5 \text{ mmol L}^{-1}$  of sample was purged with nitrogen for 5 min, then the voltammogram was recorded at ambient temperature. Electronic absorption spectra were recorded on a Hitachi U-4100 spectrophotometer. The X-ray diffraction experiment was carried out on a Bruker D8 FOCUS X-ray diffractometer. AFM images were collected under ambient conditions using the tapping mode with a NanoscopeIII/Bioscope scanning probe microscope from Digital instruments.



**Scheme 1.** Schematic structure of bis(phthalocyaninato) europium complex  $[\text{Pc}(\text{OAr})_8]\text{Eu}[\text{Pc}(\text{OAr})_8]$  (**1**) ( $\alpha$  and  $\beta 1$ - $\beta 7$  are the labels of the protons).



**Fig. 1.** (a) Schematic diagram of the QLS-film based OFET with a top-contact bottom-gate structure on a PMMA/PET substrate; (b) Digital camera image of a top-contact flexible OFET device; Transfer characteristics ( $|I_{\text{dsb}}|^{1/2}$  vs.  $V_{\text{g}}$ ) of (c) *p*-type and (d) *n*-type OFET devices based on the QLS film of **1** deposited on PMMA/PET flexible substrate with Au top contacts.

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