



Solution-processable ambipolar organic field-effect transistor based on Co-planar bisphthalocyaninato copper



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ABSTRACT

A soluble binuclear phthalocyaninato copper (II) complex, $\text{Cu}_2[\text{Pc}(\text{COOC}_8\text{H}_{17})_6]_2$ (**1**), with planar molecular structure and extended conjugation system, has been designed and synthesized. By fusing two phthalocyanine rings side by side and introducing electron withdrawing groups at periphery positions, the energy levels of HOMO and LUMO have been tuned successfully into the range of an air-stable ambipolar organic semiconductor required as revealed by the electrochemical studies. With the help of a solution-based quasi-Langmuir–Shäfer (QLS) method, thin solid films of this compound were fabricated and organic field effect transistors (OFETs) based on these QLS thin solid films were constructed. Because of the promising electrochemical properties as well as the high ordered packing structure of the molecules in the thin solid films, the OFETs performed excellent ambipolar operating properties, with the electron and hole mobility in air as high as 1.7×10^{-1} and $2.3 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively. For comparison purpose, mononuclear compound $\text{Cu}[\text{Pc}(\text{COOC}_8\text{H}_{17})_6]$ (**2**) was comparatively studied. The QLS thin solid films of this compound possess similar ordered structure with that of $\text{Cu}_2[\text{Pc}(\text{COOC}_8\text{H}_{17})_6]_2$ (**1**), but the OFETs based on the thin solid films of this compound can only show n-type properties under nitrogen atmosphere with an extremely small electron mobility of $1.6 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. This result suggests that extension on the conjugation system of an aromatic compound with multiple electron withdrawing groups can tune the molecule into an air stable ambipolar organic semiconductor.

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1. Introduction

The development of solution-processable organic semiconductors for the thin-film organic field effect transistors (OFETs), which exhibit high carrier mobility and good ambient stability, is crucial to realizing low-cost and mechanically flexible printed electronics [1–4]. During the past decade, intensive researches towards developing novel semiconductor materials especially those possessing π -conjugated electronic structure including conjugated polymers, oligomeric thiophenes, linear fused acenes, perylenes, and phthalocyanines have yielded a number of transistors with either hole or electron as the charge car-

rier [5–14]. But ambipolar OTFTs, which allow dual operation at both p and n channel, are highly desired for practical applications in integrated circuits like high gain complementary metal-oxide-semiconductor inverters and light emitting devices [15–18].

Phthalocyanines (Pcs) with planar or nearly planar molecular structures and a large network of π -electrons have been among the most promising semiconducting materials for OFETs due to their excellent thermal and chemical stabilities and good semiconducting properties. Pcs employed as semiconductors in OFETs can be divided into two categories based on their molecular structures. The first group of phthalocyanines are the commercially available unsubstituted monomeric phthalocyaninato metal complexes (MPC, M = Cu, Co, Fe, Mn, Ni, Zn, etc.) [5]. Among which, CuPc is the most widely used material for

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OFETs with hole transfer mobilities in the range of 10^{-5} – $1.0 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [19,20]. The second group of Pcs used in OFETs are the substituted phthalocyanines with reasonable solubilities in conventional organic solvents and can be processed with solution methods, such as amino-(tri-*tert*-butyl)phthalocyaninato copper [21], hydroxydecyloxy-(tri-*tert*-butyl) phthalocyaninato copper [22], and sandwich-type bis/tris(phthalocyaninato) rare earth double/triple-decker complexes bearing substituents at the peripheral positions [23]. Most of the Pcs used in OFETs present p-type semiconducting properties with hole as the major charge carriers. Because n-type of OFETs are important for the implementation of complementary circuits, which have low power consumption, high operating speeds, and an increased device lifetime, but n-type organic semiconductors have significantly lagged behind their p-type counterparts [10,11,24]. As a result, design and synthesis of n-type or ambipolar phthalocyanine based semiconductors with acceptable performance and robust air stability has become an fascinating area in the past decade. Pioneer work of Bao and co-workers in this field demonstrated that the CuPc can be changed successfully into air stable n-type semiconductor by introducing sixteen fluorine atoms on the periphery positions of the phthalocyanine ring (copper hexadecafluorophthalocyanine, F_{16}CuPc) with mobility as high as $0.03 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [25]. Since then F_{16}CuPc becomes a widely applied n-type semiconductor in different OFETs with different structures [26–28]. However, because F_{16}CuPc cannot dissolve in conventional organic solvents, and therefore, the OFETs based on this material are all fabricated by vacuum deposition techniques. Very recently, solution processable monomeric phthalocyaninato copper and “sandwich” type phthalocyaninato rare earth metal complexes have been successfully changed into n-type or ambipolar semiconductors by attaching electron withdrawing groups [29]. The ambipolar semiconductors are particularly important because they can be fabricated into ambipolar OFETs based on only one semiconducting component, which ensures a simple device structure and low-cost fabrication, have therefore attracted great research interest [30,31]. However, the ambipolar semiconductors with reasonable semiconducting properties are still rare, the design and synthesis of novel ambipolar solution processable phthalocyanine semiconductor remain a challenge for phthalocyanine chemists and material scientists.

For organic semiconductors with conjugated electronic structure, the energy of the lowest unoccupied molecular orbitals (LUMOs), that are necessary for ensuring effective electron injection and stable electron transport under ambient conditions, should locate below -4.0 eV , while that of the highest occupied molecular orbitals (HOMOs) should align with the work function of air-stable electrodes (Au: 5.1 eV) for the purpose of diminishing the hole injection barrier [32–34]. Hence, the key problem in searching for good ambipolar organic semiconductors should be tuning the energy levels of HOMO and LUMO, and meanwhile reaching a delicate balance between solubility in conventional organic solvents and efficient molecular packing behavior in solid state. In the present paper, we designed a novel bisphthalocyaninato copper complex,

$\text{Cu}_2[\text{Pc}(\text{COOC}_8\text{H}_{17})_6]_2$ (**1**), Scheme 1. Carboxylate groups are introduced to the bisphthalocyanine periphery positions, which on one the hand can improve the solubilities of this bisphthalocyanine compound in conventional organic solvents, on the other hand they are electron withdrawing groups and can lower the energy levels of LUMO and are expected to tune the semiconducting nature of phthalocyaninato copper complexes from p-type to n-type [29]. Most importantly, the extra large π -conjugation network is expected to increase the energy of HOMO significantly [35], and then makes it matches with the work function of Au electrode. Moreover, the extended π system could enhance the π - π interactions between neighbor molecules in solid state and thus could improve the carrier mobility. To the best of our knowledge, this represents the first experimental effort towards developing organic semiconductors based on bisphthalocyaninato metal complexes. More importantly, this work proves that extending on the conjugation system of molecule will be powerful approach to tune the semiconducting properties of phthalocyanines.

2. Experimental section

2.1. General methods

Electronic absorption spectra and polarized UV–vis absorption spectra were recorded on a SHIMADZU UV-2450. X-ray diffraction experiments were carried out on a Rigaku D/max-gB X-ray diffractometer. MALDI-TOF mass spectra were taken on a Bruker BIFLEX III instrument. Substrates for the thin solid film deposition were successively cleaned with pure water, acetone, and ethanol. Electrochemical measurements were carried out with a chenhua-760 voltammetric analyzer. The cell comprised inlets for a glassy carbon working electrode of 2.0 mm in diameter and a silver wire counter electrode. The reference electrode was Ag/Ag^+ (a solution of 0.01 M AgNO_3 and 0.1 M TBAP in acetonitrile), 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 ferrocenium/ferrocene Fc^+/Fc couple. Typically, a 0.1 M solution of $[\text{NBu}_4][\text{ClO}_4]$ in CH_2Cl_2 containing 0.5 M of sample was purged with nitrogen for 10 min , and then the voltammograms were recorded at ambient temperature. The scan rates were 20 and 10 mV s^{-1} for cyclic voltammetry (CV) and differential pulse voltammetry (DPV), respectively.

2.2. OFET device fabrication

The thin solid films were deposited by the solution-based quasi-Langmuir–Shäfer (QLS) method [36]. Before the film deposition, surface treatment with HMDS for SiO_2/Si substrates was performed according to literature method [37]. OTFT devices were fabricated on a HMDS treated Si/SiO_2 (300 nm thickness, capacitance $C_0 = 10 \text{ nF cm}^{-2}$) substrate by evaporating gold electrodes onto the QLS films of Cu_2BPc employing a shadow mask.

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