# High-Performance Air-Stable Ambipolar Organic Field-Effect Transistor Based on Tris(phthalocyaninato) Europium(III)

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Ambipolar organic field-effect transistors (OFETs) play a very important role in complementary metal oxide semiconductor (CMOS) logic circuits.[1] Ideal ambipolar OFET devices with high carrier mobility for both holes and electrons, good operational stability under ambient conditions, and solution processability, which ensures low-cost fabrication, have therefore attracted great research interest in the past decade.[2] Despite great efforts made in this direction, OFETs meeting all the above-mentioned requirements still remain rare. Effective methods thus far developed for fabricating ambipolar OFETs include blending two organic components[3] and modifying the gate insulator or electrodes.[4] However, the most attractive approach appears to be the utilization of a single-component organic semiconductor with suitable energy for both the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), balanced carrier mobility for both holes and electrons, and solution processability.[2a,5,6] To our knowledge, the best achievement of a solution-processed ambipolar OFET device fabricated using single-component molecular material was reported by Ribierre et al., with dicyanomethylene-substituted quinoidal quaterthiophene as the semiconductor with carrier mobilities of 0.07 and 0.007 $cm^2$ $V^{-1}$ $s^{-1}$ for holes and electrons, respectively.[7]

Phthalocyanines have been intensively studied as good molecular semiconductor materials because of their large conjugated π system, unique electronic characteristics, and high thermal and chemical stability. By using different techniques, a large number of phthalocyanine (Pc) compounds have been fabricated into OFET devices of either p-type or n-type and with mobility in the wide range of $1.1 \times 10^{-8}$ to 3.31 $cm^2$ $V^{-1}$ $s^{-1}$.[8] Following the pioneering work of Guillaud et al. on

thermally evaporated $M(Pc)_2$ (M = Tm, Lu) film-based OFETs with mobilities of $10^{-3}$–$10^{-4}$ and $10^{-4}$–$10^{-5}$ $cm^2$ $V^{-1}$ $s^{-1}$ for holes and electrons,[9] respectively, ambipolar devices with the largest mobilities of 0.3 and 0.03 $cm^2$ $V^{-1}$ $s^{-1}$ for holes and electrons, respectively, have been fabricated using either two kinds of phthalocyaninato metal complexes (CuPc as p-type and $F_{16}CuPc$ as n-type semiconductor) or a FePc single component by means of the vacuum/inert atmosphere-based deposition process in recent years.[10] However, air-stable ambipolar OFET devices fabricated from a single phthalocyanine derivative by a solution-processing technique with industrial application potential still remain undeveloped.

Investigations have revealed that the HOMO energy of good p-type OFET materials should align with the work function of the source–drain electrodes (Au: 5.1 eV) to decrease the hole injection barrier.[11] As for n-type molecular semiconductors, the LUMO energy for effective electron injection and stable charge transport under ambient conditions should locate below –4.1 to –4.0 eV.[2a] As a consequence, to achieve good performance and air-stable ambipolar OFET devices, molecular semiconductors simultaneously possessing appropriate HOMO (around the work function of a Au electrode, 5.1 eV) and LUMO (below –4.1 to –4.0 eV) energies with their gap in the range of ca. 1.0 eV are necessary. However, most probably associated with their intrinsic electronic structures, the HOMO–LUMO gap for most well-known molecular semiconductors, such as monomeric phthalocyanines, acenes, thiophenes, and perylene diimides, usually locates in the range far above than 1.0 eV, indicating that the injection of at least one carrier under ambient conditions was contact limited for the given electrode (such as Au).[5,6,12] This dilemma seems to be fixed only by tuning the conjugation extent of molecular semiconductors, since peripheral incorporation of either electron-donating or electron-withdrawing groups does not induce significant change in the HOMO–LUMO gap.[13]

By means of coordination bonding between metal ions and the phthalocyanine isoindole nitrogen atoms, two rare earth ions are able to connect three phthalocyanine ligands, forming sandwich-type tris(phthalocyaninato) rare earth complexes in which intense intramolecular π–π interaction exists between the three phthalocyanine chromophores.[14] It is worth noting that quite systematic studies have revealed good p-type OFET performance of sandwich-type tris(phthacyaninato) rare earth triple-decker complexes bearing peripheral electron-donating alkoxyl groups with hole mobility in the range of 0.014–0.60 $cm^2$ $V^{-1}$ $s^{-1}$.[12d,15] Their n-type OFET characteristics have, however, not yet been investigated, despite their potential in ambipolar OFET devices as revealed by their electrochemistry,

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where the first oxidation potential of 0.13–0.27 V and first reduction potential of −0.71 to −0.81 V (vs the saturated calomel electrode, SCE), correspond to a HOMO of −4.57 to −4.71 eV and a LUMO of −3.73 to −3.63 eV.[12d,15b,16] Obviously the HOMO energy level, −4.57 to −4.71 eV, of these tris(phthalocyaninato) rare earth triple-decker compounds, which aligns with the work function of a Au electrode (5.1 eV) for good p-type organic semiconductors, is responsible for the good p-type OFET behavior of these triple-decker complexes. In contrast, their LUMO energy in the range of −3.73 to −3.63 eV seems a bit of higher than the range of −4.0 to −4.1 eV necessary for good air-stable n-type organic semiconductors. As a consequence, incorporating suitable electron-withdrawing instead of electron-donating groups onto the phthalocyanine periphery in the triple-decker molecules, which could slightly lower the HOMO and in particular the LUMO energy, appears to be an effective approach to achieving air-stable ambipolar OFET devices.

In this Communication, a new sandwich-type tris{2,3,9,10,16,17,23,24-octakis[(*p*-fluoro)phenoxy]phthalocyaninato} europium triple-decker complex bearing peripheral electron-withdrawing groups $Eu_2[Pc(OPhF)_8]_3$ was designed, synthesized, and fabricated into an OFET device on a $SiO_2$/Si substrate with Au electrodes by means of the quasi-Langmuir–Schaefer (QLS) method.[17] In line with previous results,[12d,15] this triple-decker-based OFET device also displayed good p-type performance with hole mobility of 0.24 cm² V⁻¹ s⁻¹ in air. Nevertheless, good n-type behavior in air was also simultaneously revealed for the device with electron mobility of 0.042 cm² V⁻¹ s⁻¹. This is the first example of high-performance ambipolar OFETs that are solution processable, air stable, and based on a single phthalocyanine component.

The tris(phthalocyaninato) europium complex $Eu_2[Pc(OPhF)_8]_3$ was prepared according to a published procedure.[18] Its sandwich-type triple-decker nature was defined by matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry and $^1$H NMR (Figures S1 and S2 in the Supporting Information). This compound exhibited good solubility in common organic solvents, making it possible to fabricate it into devices by solution processing. Cyclic voltammetry (CV) measurement of $Eu_2[Pc(OPhF)_8]_3$ in $CH_2Cl_2$ reveals a few one-electron redox couples, with the first oxidation and first reduction potentials at +0.83 and −0.27 V (vs SCE), respectively, see Table S1 (Supporting Information) and **Figure 1**. Both the HOMO and LUMO energies at −5.27 and −4.17 eV thus derived for this triple-decker just locate in the HOMO and LUMO energy ranges that are necessary for good p- and n-type organic semiconductors, respectively, ensuring the facilitation of both hole and electron injection from the Au electrodes. This reveals the potential of this triple-decker compound in ambipolar OFET devices.

Ordered multilayers of $Eu_2[Pc(OPhF)_8]_3$ were easily prepared by the QLS method. The QLS layers were then deposited onto hexamethyldisilazane (HMDS)-treated $SiO_2$/Si substrates. The low-angle X-ray diffraction (XRD) pattern of the thin film exhibits one sharp diffraction peak at 1.91 nm (2θ = 4.62°), see Figure S3 (Supporting Information), which corresponds to the thickness of one layer of QLS film, suggesting a regular layered structure of this QLS film.[17,19] The orientation angle of the phthalocyanine ring with respect to the substrate of 58.3° was
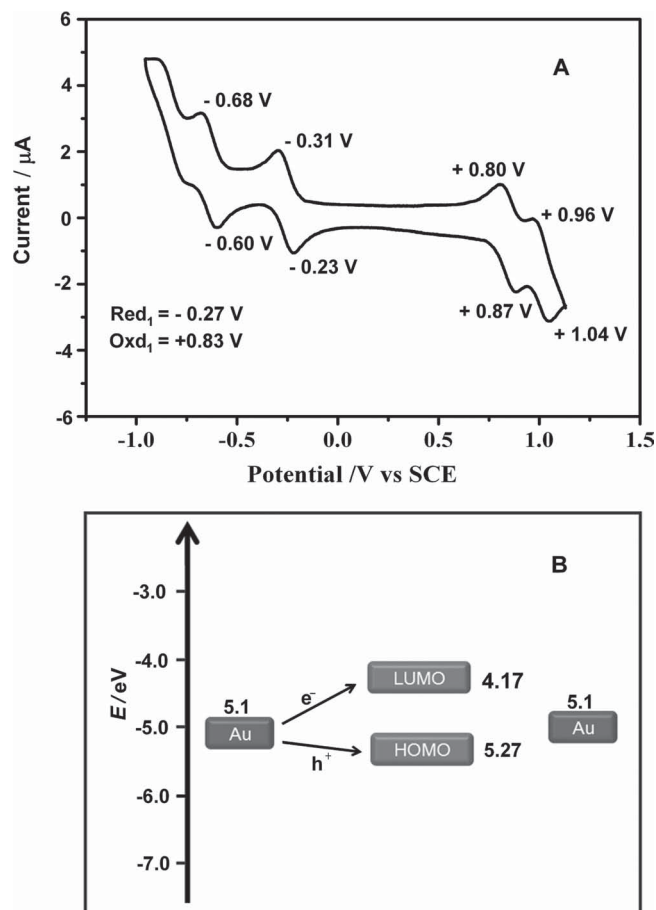


**Figure 1.** A) Cyclic voltammogram of $Eu_2[Pc(OPhF)_8]_3$ in $CH_2Cl_2$ containing 0.1 mol dm⁻³ [Bu₄N][ClO₄] at a scan rate of 20 mV s⁻¹. B) Energy level diagram exhibiting hole and electron injection from Au electrodes into organic material.

estimated by a polarized UV-vis technique according to a literature method[20] (Figure S4 and Table S2, Supporting Information), revealing the "edge-on" conformation of the triple-decker molecules in the film. This is in line with the calculated result (58.5°) based on the simulated triple-decker molecular dimension (2.24 nm)[21] and the above-mentioned low-angle XRD result (1.91 nm), see Figure S5 (Supporting Information). The morphology of the triple-decker QLS film was characterized by atomic force microscopy (AFM; Figure S6, Supporting Information). The image shows a high density of small grains approximately 300 nm in size, revealing a highly molecular microstructure of the film surface.

The triple-decker compound $Eu_2[Pc(OPhF)_8]_3$ displays a Q band at 664 nm in $CHCl_3$ solution, which is dramatically blue-shifted in comparison with that of the mononuclear 2,3,9,10,16,17,23,24-octakis(*p*-fluorophenoxy)phthalocyaninato zinc complex in the same $CHCl_3$ solution at 676 nm,[22] due mainly to the intense intramolecular π–π interaction between the three stacked Pc rings in the triple-decker molecules.[14] As shown in Figure S7 (Supporting Information), the Q band of the triple-decker compound in QLS film blue-shifts to 654 nm, indicating the formation of H-aggregates (face-to-face)[23] and
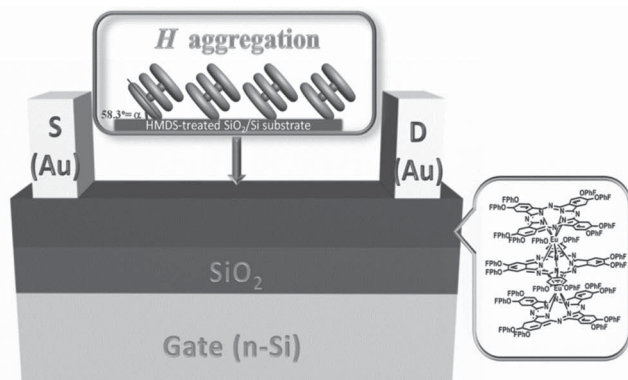
**Figure 2.** Schematic structure of the QLS-film-based OFET device (the insets show the schematic structure of H-aggregates and molecular structure of $Eu_2[Pc(OPhF)_8]_3$).
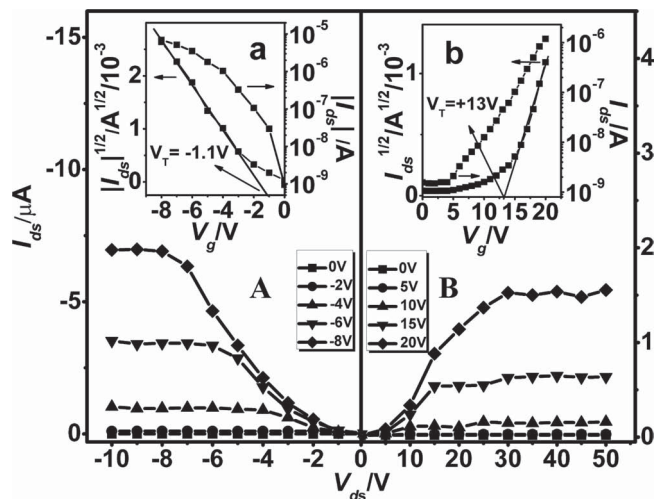


**Figure 3.** Output characteristics ($I_{ds}$ versus $V_{ds}$) and (insets) transfer characteristic ($|I_{ds}|^{1/2}$ versus $V_g$) of an ambipolar OFET device based on QLS films of $Eu_2[Pc(OPhF)_8]_3$ deposited on an HMDS-treated $SiO_2$/Si (500 nm) substrate with Au top contacts measured in air. Current–voltage output plots with various $V_g$: A for p-channel and B for n-channel. Insets: The transfer characteristics of OFETs at $V_{ds} = -10$ V for p-channel (a) and $V_{ds} = +40$ V for n-channel (b).

strong interaction between neighboring molecules in one layer (**Figure 2**). The strong intramolecular $\pi$–$\pi$ stacking in the triple-decker molecule,[24] together with intense intermolecular face-to-face interaction in the H-aggregates of the QLS film, is believed to provide the $\pi$ electrons (or holes) with an extensive area for delocalization.

As exemplified in **Figure 3**, the OFET device fabricated from $Eu_2[Pc(OPhF)_8]_3$ on the HMDS-treated $SiO_2$/Si substrate using the QLS technique with a bottom-gate top-contact configuration showed typically ambipolar (both p- and n-channel) characteristics in air. The carrier mobility $\mu$ was calculated by using the saturation region transistor equation, $I_{ds} = (W/2L)\mu C_0(V_G - V_T)^2$, where $I_{ds}$ is the source–drain current, $V_G$ the gate voltage, $C_0$ the capacitance per unit area of the dielectric layer, and $V_T$ the threshold voltage.[25] In air, the device fabricated had an average hole mobility of 0.24 cm$^2$ V$^{-1}$ s$^{-1}$ ($V_{ds} = -10$ V; Figure 3A). Nevertheless, under ambient conditions this device simultaneously displays an average electron mobility of 0.042 cm$^2$ V$^{-1}$ s$^{-1}$ ($V_{ds} = +40$ V; Figure 3B). It is worth noting that the devices fabricated from this triple-decker compound are found to be sensitive to the combined action of humidity and sunlight. Their performance, however, remains stable even after being kept in air for four weeks but with exclusion of light (Figure S8 in the Supporting Information).

In addition, relatively low threshold voltages ($V_T$) were obtained for these OFET devices, –1.1 and +13 V for holes and electrons, respectively (Figure 3). It is worth emphasizing that the threshold voltage of –1.1 V for the p-type devices represents the lowest threshold voltage for triple-decker-based p-type OFET devices reported thus far,[15a] showing a great application potential in low-power nanoelectronics. In fact, the threshold voltage of +13 V for the n-type devices in the present case appears to be also good enough for n-type OFET devices, usually in the range of +0.9 to +45 V.[8] Besides, the value of pinchoff voltage, which can be experimentally determined by the drain voltage intersection point of two extrapolated straight lines in the linear and saturation regions of the $I_{ds}$–$V_{ds}$ output characteristics, is relatively low, –7.6 V and +27.5 V for holes and electrons, respectively (Figure S9 in the Supporting Information). Obviously, for the present OFET device fabricated from $Eu_2[Pc(OPhF)_8]_3$, low threshold voltages and low pinchoff voltages ($V_{PO}$), as well as

the HMDS dielectric (providing a pristine interface between the QLS film and gate dielectric to decrease the interface defects), play important roles in the reduction of the operating voltage ($|V_G| \leq 20$ V) of the OFETs, which would contribute to cost savings by allowing the use of lower-cost driver electronics, making OFETs particularly suitable for the most rapidly growing portable applications, for example, in e-paper and radio frequency identification (RFID) tags.[26]

In conclusion, we have presented good OFET properties of a novel tris(phthalocyaninato) europium triple-decker complex bearing peripheral electron-withdrawing groups. The high carrier mobility and low threshold voltage for both holes and electrons can be ascribed to the suitable HOMO and LUMO energies, intense intramolecular $\pi$–$\pi$ stacking interaction, and the strong intermolecular face-to-face interaction in the H-aggregate in the QLS films. This is the first example of an air-stable, single-component ambipolar OFET device of phthalocyanine derivatives fabricated by solution processing. The good OFET performance proves the very promising and great application potential of tris(phthalocyaninato) rare earth triple-decker compounds of this kind in organic nanoelectronics. Further efforts towards the design and synthesis of new sandwich compounds and the optimization of the device fabrication are in progress.

## Experimental Section

$Eu_2[Pc(OPhF)_8]_3$ was prepared from the reaction between $Eu(acac)_3 \cdot H_2O$ and $H_2Pc(OPhF)_8$ (Supporting Information). Electrochemical measurements were carried out with a BAS CV-50W voltammetric analyzer. Electronic absorption spectra were recorded with a Hitachi U-4100 spectrophotometer. OFET devices were fabricated on heavily doped silicon wafers with a thermally grown 500 nm thick $SiO_2$

layer by evaporating gold electrodes onto the $Eu_2[Pc(OPhF)_8]_3$ QLS film using a shadow mask. Electrodes with two sets of dimensions ($W = 8.16$ mm, $L = 145.7$ μm, $W/L = 56.0$ and $W = 28.6$ mm, $L = 240$ μm, $W/L = 119$) were used for OFET measurements. QLS films were prepared following a previously published method.[17] Before the QLS film was deposited, the surface of the $SiO_2/Si$ substrate was treated according to a literature method using HMDS.[27] The electric characteristics of the devices were measured in air. The current–voltage characteristic was obtained with a Hewlett-Packard (HP) 4140B parameter analyzer at room temperature.

## Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

## Acknowledgements

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