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High Performance Organic Field-Effect Transistors Based on Amphiphilic Tris(phthalocyaninato) Rare Earth Triple-Decker Complexes

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Research on organic field-effect transistors (OFETs) has achieved remarkable progress in the past decade. The carrier mobilities have been promoted to the range of 0.1−15.4 cm^2 V^{-1} s^{-1}, which is good enough to compete with amorphous silicon [mobility (μ) > 0.1 cm^2 V^{-1} s^{-1}]. These breakthroughs are closely related with the development of novel OFET materials, such as oligomeric thiophenes, linear-fused acenes, conjugated polymers, phthalocyanines (Pcs), and perylenes.[1]

Phthalocyanines are promising active materials for OFETs and have been studied widely for a long time.[2] The most investigated members in this family are CuPc and CoPc.[3] The mobilities of the vacuum deposited Pc thin films are found in the range of 10^{-5}−10^{-3} cm^2 V^{-1} s^{-1}. The best achievement of vacuum deposited thin film was obtained from a sandwich-type device constructed by using two kinds of phthalocyaninato metal complexes, displaying a mobility of 0.11 cm^2 V^{-1} s^{-1}.[4] A single crystal CuPc-based OFET was reported most recently with mobility as high as 1.0 cm^2 V^{-1} s^{-1},[5] representing the highest reported so far for Pc-based OFETs.

The Langmuir−Blodgett (LB) technique allows fine control of both the structure and the thickness of the film at the molecular level and has been employed in building films for OFET studies.[6] However, the mobilities of LB film-based OFETs, usually in the range of 10^{-7}−10^{-3} cm^2 V^{-1} s^{-1}, are far behind those of either vacuum deposited or solvent processed films. This, together with the fact that the LB technique is a difficult method for rapid manufacturing, has suppressed interest in using the LB technique in OFET studies. However, our recent research on the OFET properties of amphiphilic tris(phthalocyaninato) rare earth triple-decker complexes revealed that the LB films of this material show unexpectedly good OFET performance, with carrier mobilities reaching 0.24−0.60 cm^2 V^{-1} s^{-1}, which is among the highest mobilities achieved so far for LB film-based OFETs.

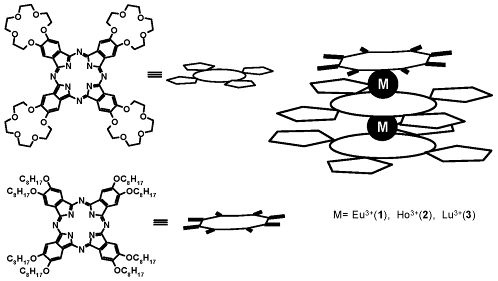

Figure 1. Schematic molecular structures of the triple-decker compounds.

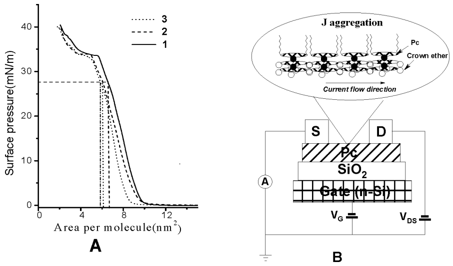

Figure 2. π−A isotherms (A) and schematic structure of the device (B, inset shows the schematic structure of *J* aggregates).

The structure of these amphiphilic tris(phthalocyaninato) rare earth complexes is shown in Figure 1. The sandwich triple-decker nature of these compounds was defined by MALDI-TOF mass spectra and ^{1}H NMR spectra (Supporting Information). In the molecules, three Pc rings are closely bonded in a "face-to-face" manner by two rare earth atoms through coordination bonds. These are the first examples of amphiphilic tris(phthalocyaninato) rare earth triple-decker complexes with crown-ether voids as hydrophilic heads and long alkyl chains as hydrophobic tails. The π−A isotherms are shown in Figure 2. These compounds are able to form very stable monolayers on the water surface. The limiting mean molecular areas are 5.88, 6.04, and 6.56 nm^2 for **1**, **2**, and **3**, respectively, when the surface pressure is kept at 28 mN m^{-1}. The multilayer films were deposited under these conditions. These values are very close to the area of a phthalocyanine ring plus four crown-ether voids,[7] revealing that the triple-decker compounds adopt a "face-on" arrangement on the water surface. The transmission electronic microscopy (TEM) image (Figure S1 of Supporting Information) of this monolayer on the surface of mica shows uniformly dispersed domains.

These monolayers have been transferred reproducibly to hydrophilic substrates by the vertical dipping method. *Z*-type LB films were formed for all three compounds. The fact that the transfer ratio was maintained at an ideal value, 1, during the whole transfer process indicates the formation of uniform thin films. This conclusion is further supported by the linear increase in the absorbance of the LB film along with the number of layers. Small-angle X-ray diffraction patterns (XRD) of the thin film of the three compounds show similar results, with one diffraction peak around 2.5 nm (Figure S2 of Supporting Information), which is the thickness of the molecule when the alkyl chains extend upward in the film. These results suggest a very regular layered structure for these LB films. Polarized absorption spectra were employed to detect the orientation (dihedral angle between Pc rings and the surface of substrate) of the Pc rings in the film.[8] All three compounds gave similar results, with orientation angles close to 0°. This further confirms the face-on ordering deduced from the π−A isotherms. The morphology of a 20 layer film of **2** was

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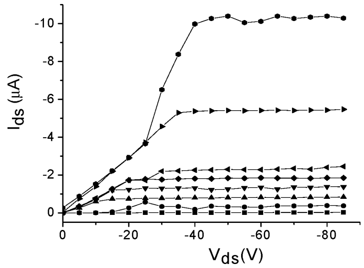

Figure 3. Drain−source current (I_{ds}) versus drain−source voltage (V_{ds}) characteristic for **2** at constant V_g (0, -5, -10, -15, -20, -25, -35, -40 V from bottom to top).

characterized by atomic force microscopy (AFM) (Figure S1 of Supporting Information). The image shows a very smooth surface decorated with some pinholes and defects.

The triple-decker compounds show a Q-band at 645 nm in solution, which blue-shifts dramatically compared with that of mononuclear phthalocyaninato metal complexes in solution (around 690 nm).[2] This significant blue-shift can be ascribed to strong intramolecular $\pi-\pi$ interaction among the three stacked Pc rings.[9] In LB films, the Q-band of these triple-decker complexes red-shifts to 674 nm (Figure S3 of Supporting Information), indicating the formation of *J* aggregates (edge-to-edge)[10] and a very strong interaction between the neighboring molecules in one layer. The strong intramolecular $\pi-\pi$ stacking in the triple-decker molecules together with strong intermolecular edge-to-edge interaction in the *J* aggregates provide the π electrons with an extensive area for delocalization.

The FET devices were fabricated with top contact configuration on a layer of SiO_2 dielectrics (500 nm). Gold electrodes with the dimension of 28.6 mm width × 0.24 mm length were applied after LB film deposition (20 layer) by using shadow mask.[6e] The devices were dried in vacuum at room temperature for 10 days before electronic testing, which was carried out at ambient temperature and open to air. X-ray photoelectron spectroscopic (XPS) measurement on the LB films confirmed the absence of any alkali ions.

The device shows typical *p*-channel characteristics, as exemplified in Figure 3 and Figures S4−S9 (Supporting Information). We calculated the carrier mobility (μ) by using the saturation region transistor equation, $I_{ds} = (W/2L)\mu C_0\ (V_g - V_t)^2$, for **2** and **3**, and linear region transistor equation, $I_{ds} = (W/L)C_0\mu(V_g - V_t)V_{ds}$ for **1**, 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.[11] The 20 layer LB films of **1**, **2**, and **3** showed good performance with carrier mobilities of 0.60 (V_{ds}, -55 V), 0.40 (V_{ds}, -75 V), and 0.24 (V_{ds}, -75 V) cm^2 V^{-1} s^{-1}, respectively.

The performance of OFETs is closely related to the packing mode of organic molecules in thin solid films. Several reports elucidated that $\pi-\pi$ stacking is a favored packing mode for OFETs.[12] The $\pi-\pi$ stacking affords strong interactions between neighboring molecules, and π electrons can thus move freely along the long axis of the aggregates (normal to the aromatic rings), thus leading to high mobilities. Single-crystal phthalocyanines (β form) also show high mobility along the long axis, which is perpendicular to the Pc ring.[5] However, the systems we present here are different, that is, the aromatic rings of Pc are parallel to the current flow direction as shown in Figure 2. Though the relationship between the mobility and film structure is not yet fully understood, we believe that, in addition to the contribution from Pc ring stacking, the contribution from *J* aggregation to the mobility might be significant. This is supported by many studies showing that edge-to-edge linked molecules can act as molecular wires in various circumstances.[13]

In conclusion, we have presented good OFET properties of three amphiphilic tris(phthalocyaninato) rare earth complexes. The high OFET performance can be ascribed to the intramolecular $\pi-\pi$ stacking and the intermolecular *J* aggregation in the LB films. This represents one of the best results so far obtained for all LB film-based OFETs. The good performance proves that these tris(phthalocyaninato) rare earth triple-decker compounds are very promising organic semiconductors. The design and synthesis of new sandwich compounds with good solubility in organic solvents and the optimization of the device fabrication are in progress.

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Supporting Information Available: Details of the structure characterization and device fabrication for **1**−**3**: XRD, TEM, and AFM of LB films for **1**−**3**, plot of I_{ds} versus V_{ds} for **1** and **3**. This material is available free of charge via Internet at http://pubs.acs.org.

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