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Effect of Peripheral Hydrophobic Alkoxy Substitution on the Organic Field Effect Transistor Performance of Amphiphilic Tris(phthalocyaninato) Europium Triple-Decker Complexes

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A series of four amphiphilic heteroleptic tris(phthalocyaninato) europium complexes with different lengths of hydrophobic alkoxy substituents on one outer phthalocyanine ligand $[Pc(15C5)_4]Eu[Pc(15C5)_4]Eu[Pc(OC_nH_{2n+1})_8]$ ($n = 4, 6, 10, 12$) (**1**, **2**, **4**, and **5**) was designed and prepared. Their film forming and organic field effect transistor properties have been systematically studied in comparison with analogous $[Pc(15C5)_4]Eu[Pc(15C5)_4]Eu[Pc(OC_8H_{17})_8]$ (**3**). Experimental results showed that all these typical amphiphilic sandwich triple-decker molecules have been fabricated into highly ordered films by the Langmuir−Blodgett (LB) technique, which displays carrier mobility in the direction parallel to the aromatic phthalocyanine rings in the range of 0.0032−0.60 $cm^2\ V^{-1}\ s^{-1}$ depending on the length of the hydrophobic alkoxy substituents. This is rationalized on the basis of comparative morphology analysis results of the LB films by the atomic force microscopy technique.

Introduction

Tremendous efforts have been paid to search for novel organic semiconductors for organic field effect transistors (OFET), and great progress has been made concerning the high carrier mobility and modulation ratio.[1] In addition to the intrinsic molecular chemical−physical properties of organic compounds, the performance of OFETs has also been found to closely relate to the packing model of organic molecules in the solid state.[2] As a result, the development of novel OFET material includes not only discovering new compounds with good chemical−physical properties but also exploring the relationship between the packing model of semiconductor molecules in the solid state and the device performance.

Phthalocyanine (Pc), as one of the most promising active materials for OFETs, has attracted much attention for a long time.[3] The vacuum deposited Pc thin films of CuPc and CoPc show *p*-type properties with carrier mobilities around 10^{-5} to $10^{-3}\ cm^2\ V^{-1}\ s^{-1}$.[4] Yan and co-workers have promoted the carrier mobility of a vacuum deposited Pc thin film to 0.11 $cm^2\ V^{-1}\ s^{-1}$ by using a composite of two kinds of phthalocyaninato metal complexes as active layers.[5] Recently, single-crystal CuPc-based OFET was reported to show a carrier mobility as high as 1.0 $cm^2\ V^{-1}\ s^{-1}$,[6] representing the highest mobility reported so far for Pc-based OFETs.[7] The Langmuir−Blodgett (LB) films of phthalocyanines have also been employed in the OFET device but display poor semiconducting properties because of the poor amphiphilic nature of the corresponding Pc compounds employed.[8] Very recently, our preliminary studies over amphiphilic heteroleptic tris(phthalocyaninato) rare earth triple-decker complex-based OFETs revealed that their LB films, in which the triple-decker molecules take a face-on conformation on the substrate and pack in an edge-to-edge way, show good OFET characteristics with a high carrier mobility, 0.24−0.60 $cm^2\ V^{-1}\ s^{-1}$, and an on/off current ratio of 10^5.[9] For the purpose of understanding the relationship between film structure and OFET performance and further confirming our previous results on this kind of triple-decker complex, we have devised and prepared a series of amphiphilic heteroleptic tris(phthalocyaninato) rare earth triple-decker complexes with different hydrophobic alkoxy side chains that we believe will affect the assembling properties of the molecules in the LB film and in turn the OFET performance of the device fabricated from the corresponding LB films.

Results and Discussion

Molecular Design and Synthesis. The heteroleptic tris(phthalcyaninato) rare earth triple-decker complexes involved in the present research were designed with the amphiphilic properties as the foremost characteristic. As shown in Figure 1, crown ethers were attached onto the middle and one of the two

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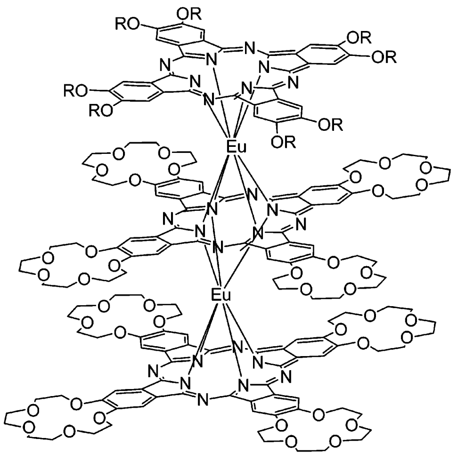

1: R = C_4H_9; **2**: R = C_6H_{13}; **3**: R = C_8H_{17}; **4**: R = $C_{10}H_{21}$; **5**: R = $C_{12}H_{25}$

Figure 1. Schematic molecular structures of amphiphilic heteroleptic tris(phthalocyaninato) rare earth triple-decker complexes [Pc(15C5)$_4$]Eu[Pc(15C5)$_4$]Eu[Pc(OC$_n$H$_{2n+1}$)$_8$] (n = 4, 6, 8, 10, 12) (**1**−**5**).

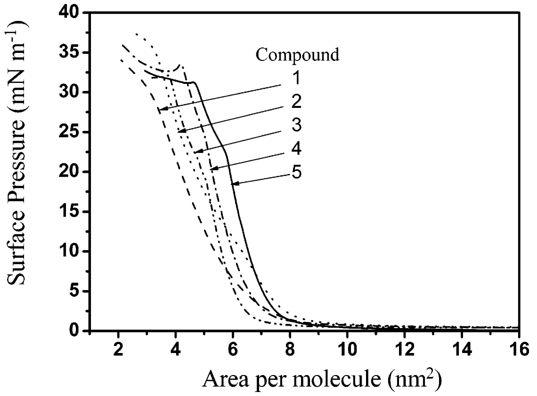

Figure 2. π−A isotherms of **1**−**5** on a water surface at room temperature.

outer phthalocyanines, forming the hydrophilic heads, while the long alkoxy chains were introduced onto the remaining outer phthalocyanine ligand of the triple-decker molecule as the hydrophobic tails. These compounds were prepared following published methods and were characterized by ^{1}H NMR and MALDI-TOF mass spectroscopy; for details, see the Supporting Information.[10] The typical amphiphilic properties of these molecules ensure the high quality of the monolayer and/or multilayer films fabricated by the LB technique.

Monolayer Properties. Reproducible pressure−surface area (π−A) isotherms of **1**−**5** indicate that all the compounds can form a stable monolayer on a pure water surface (Figure 2). The limiting molecular areas (A_{limit}) are obtained from the π−A isotherms by extrapolation of the liquid condensed phase to surface pressure zero and are summarized in Table 1. The A_{limit} of **1**−**5** is in the range of 6.07−7.31 nm^2, which is larger than that of a bisphthalocyanine molecule without substitution, 1.6 nm,[2,11] and smaller than that of a face-on arranged phthalocyanine with four benzo-18-crown-6 voids, 13.6 nm^2.[12] To calculate the molecular dimensions, a molecular model based on the minimized structure of these series of compounds has been built, and the diagonal distance and thickness of the molecule without alkoxyl chains were 2.8 and 1.4 nm, respectively (Figure S1, Supporting Information).[13] The projection of these triple-decker molecules on a water surface with a face-on configuration show an area of 6.25 nm^2, while that of an edge-on arranged triple-decker molecule gives an area of 3.92 nm^2 on the assumption that all the alkoxyl chains extended upward and do not contribute to the molecular area. The A_{limit} deduced from the π−A isotherms is close to the projection of a face-on arranged molecule and much larger than that of the edge-on arranged molecule, suggesting a face-on configuration for these molecules on a water surface. It is noteworthy that a similar face-on configuration has been suggested by Nolte for a tetra-benzo-18-crown-6 substituted phthalocyanine on a water surface.[12] The A_{limit} of the compounds with long side alkoxy chains (**4** and **5**) is much larger than that of the compounds with short side chains (**1** and **2**), suggesting significant contributions from the side groups to the mean molecular area. This fact implies that the side alkoxy chains did not extent upward strictly but with bending or inclining on the water surface.

Multilayer LB Films. The monolayers of these compounds on a water surface have been transferred to hydrophobic substrates by the vertical dipping method, and Z-type LB films were formed for all the compounds. The fact that the transfer ratio was maintained at an ideal value, 1, during the whole transfer process clearly indicates the formation of uniform thin films with a very good layered structure (Figures S2−S5, Supporting Information). This has been further proven by the peaks in the diffraction patterns in the low angle region of the multilayer LB films (Figure 3). The d spacing corresponding to monolayer thicknesses of the multilayer LB films was calculated from the 2θ values of the diffraction peaks following the Bragg equation, and the results are listed in Table 1. With the increase in the length of the side groups from -OC$_4$H$_9$ to -OC$_{12}$H$_{25}$, the layer spacing of the LB film increases from 2.45 to 3.28 nm, suggesting that the side alkoxy chains extend upward on the water surface or substrate and contribute significantly to the layer thickness of the LB film.

The orientation angles (dihedral angle between phthalocyanine rings and surface of substrate) of the phthalocyanine ring in these films were determined by a polarized absorption spectroscopic method.[14] Figure 4 shows the polarized absorption spectra of the LB films, and the experimental and calculated results are summarized in Table 2. The orientation angles calculated by the Yoneyama equation are in the range of 11−19°, which is much smaller than that of the edge-on arranged triple-decker phthalocyanines as reported in the literature,[15] confirming the face-on configuration for the molecules in the film deduced from the π−A isotherms. As a fact of the relatively larger error in measuring the orientation angle by polarized UV−vis absorption spectroscopy, ±5°,[16] the present results can therefore lead to such a conclusion that all the series of five compounds take a similar orientation in the LB film. In other words, the effect of the alkoxy side chains on the orientation of the triple-decker molecules is not significant.

The calculated monolayer thickness (d') based on the orientation angle, the chain length of the side groups, and the dimension of

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Table 1. Film Characterization Data and OFET Characteristics of 1−5

compound	**1**	**2**	**3**[a]	**4**	**5**
A_{limit} (nm^2)	6.07	6.28	6.51	6.66	7.31
solution ($\lambda_{\max}$, nm)	647	647	647	647	647
LB films ($\lambda_{\max}$, nm)	660	661	674	658	654
$\Delta\lambda_{\max}$ (red shift)	13	14	27	11	7
α (°)[b]	10.9	11.2	12.0	13.5	18.9
d spacing (nm)[c]	2.45	2.48	2.93	3.12	3.28
calcd layer spacing *d′* (nm)[d]	2.45	2.76	3.09	3.44	3.93
mobility (cm^2 V^{-1} s^{-1})	0.0032	0.014	0.60	0.21	0.053
on/off ratio	9.3 × 10	8.2 × 10^3	1.4 × 10^5	9.7 × 10^4	3.9 × 10

[a] Cited from ref 9. [b] Dihedral angle between phthalocyanine ring and surface of substrate determined by polarized UV−vis spectroscopy. [c] Layer spacing determined by low angle X-ray diffraction experiments. [d] Calculated layer spacing by molecular model and orientation angles of phthalocyanine ring determined from polarized UV−vis absorbance. $d' = (2.5 \times \sin \alpha° + 1.4 \times \cos \alpha° +$ the length of alkane chain) assuming -OC_4H_9 = 0.6 nm; -OC_6H_{13} = 0.9 nm; -OC_8H_{17} = 1.2 nm; -$OC_{10}H_{21}$ = 1.5 nm; and -$C_{12}H_{25}$ = 1.8 nm.

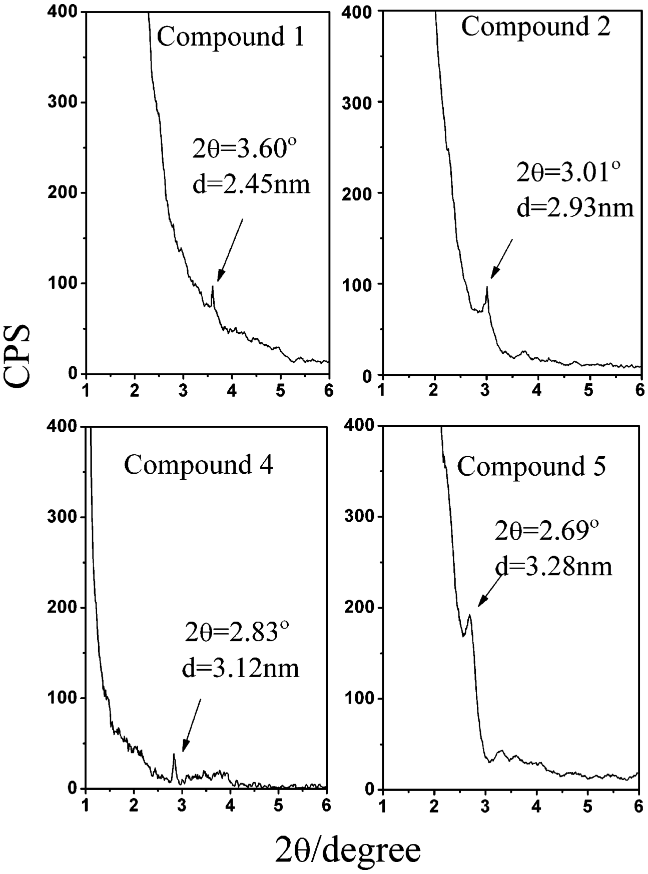

Figure 3. Low angle X-ray diffraction patterns of LB films of **1**, **2**, **4**, and **5**.

the molecule are listed in Table 1. The calculated value (*d′*) for **1**, with the shortest alkoxy chains, agrees well with the layer spacing (*d*) resulting from the low angle X-ray diffraction (LAXRD) experiments. However, along with increasing the length of the alkoxy side chains, the calculated value (*d′*) for **2**−**5** is much larger than that resulting from LAXRD experiments. This difference could be ascribed to the bending or inclining of the long alkoxyl chains as suggested by the π−A isotherms.

Device Fabrication. The devices fabricated from the LB films with a top contact configuration show typical *p*-channel characteristics as exemplified in Figure 5 and Figures S6−S8 (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] where I_{DS} is the source-drain current, V_G is the gate voltage, C_0 is the capacitance per unit area of the dielectric layer, and V_T is the threshold voltage.[17] The calculated results indicate that all the compounds show a good carrier mobility with a reasonable on/off ratio. In addition, the OFET performance was found to be affected by the length of the alkoxy side chains (Table 1 and Figure 5). Compounds **3** and **4**, respectively, with eight octyloxy and decyloxy groups at peripheral positions present the largest carrier mobility, while the compounds with longer or shorter alkoxy side chains, **1**, **2**, and **5**, show distinct smaller carrier mobilities (Figure 6).

To obtain information about the film structure of these compounds, UV−vis absorption spectra of **1**, **2**, **4**, and **5** in solution and in LB films were recorded as shown in Figure 7. Triple-decker **1**−**5** show an intense Q-band at about 647 nm in solution (Table 1). As compared to those for monomeric phthalocyaninato metal complexes and double-decker bisphthalocyaninato rare earth counterparts with the same side groups, a significant blue shift occurs on the Q-band of the triple-decker complexes in solution. In LB films, the Q-band of these triple-decker complexes red shifts from 647 nm to about 660 nm as compared to that in solution (Table 1). The blue and red shifts on the Q-bands of phthalocyanines can be explained in terms of the exciton coupling following Kasha's theory.[18] The blue shifts on the Q-band of phthalocyanine in the triple-decker compounds as compared to that in bisphthalocyanine and monomeric phthalocyanine are due to the formation of a face-to-face (*H* aggregates) stacked molecular structure and strong intramolecular interactions between phthalocyanine rings.[19] On the other hand, the red shift for the triple-decker compounds in the LB film as compared to that in solution can be ascribed to the formation of edge-to-edge-type aggregates (*J* aggregates),[20] suggesting effective interactions between the neighboring triple-decker molecules in each layer.[21] The effective intermolecular edge-to-edge interaction in the *J* aggregates together with the intense intramolecular π−π stacking in the triple-decker molecules provides the π electrons (as well as holes) with an extensive area for delocalization. This forms the most basic necessary characteristic for an organic semiconductor with good carrier mobility.[22]

Among the whole series of five triple-decker compounds, the one substituted with octyloxy groups, **3**, was found to show the

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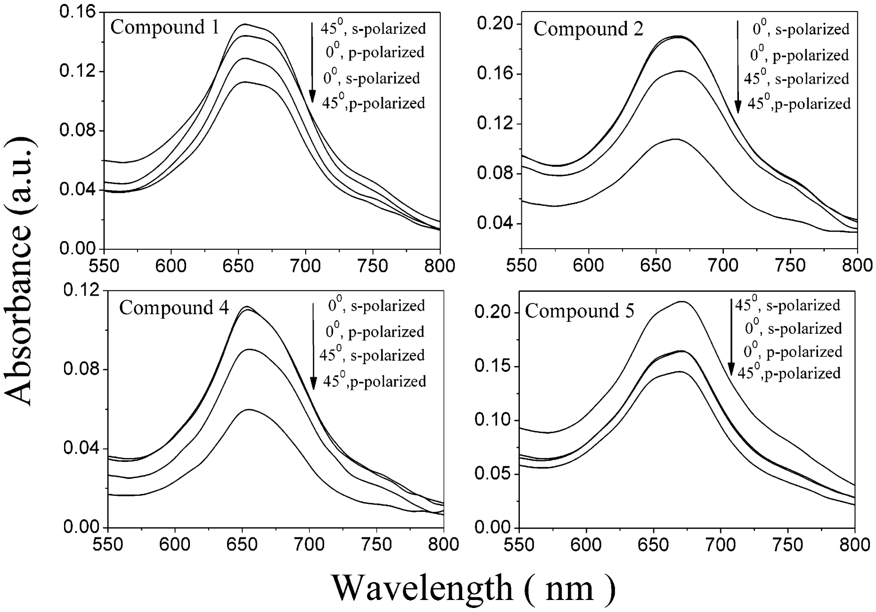

Figure 4. Polarized absorption spectra of LB films of **1**, **2**, **4**, and **5**. 0 and 45° represent the angles between the light and the normal of the substrate.

Table 2. Experimental Data and Calculated Results for Polarized Electron Absorption Spectroscopy of LB Films of 1, 2, 4, and 5

	0°			45°			
compound	$A_{\parallel}$	$A_{\perp}$	$D_{0°}$	$A_{\parallel}$	$A_{\perp}$	$D_{45°}$	α (deg)
1 (12 layers)	0.1285	0.1438	0.8935	0.1513	0.1126	1.344	10.9
2 (18 layers)	0.1905	0.1894	1.006	0.1625	0.1076	1.510	11.2
4 (10 layers)	0.1118	0.1100	1.016	0.08988	0.0595	1.511	13.5
5 (20 layers)	0.1646	0.1641	1.003	0.2105	0.1451	1.451	18.9

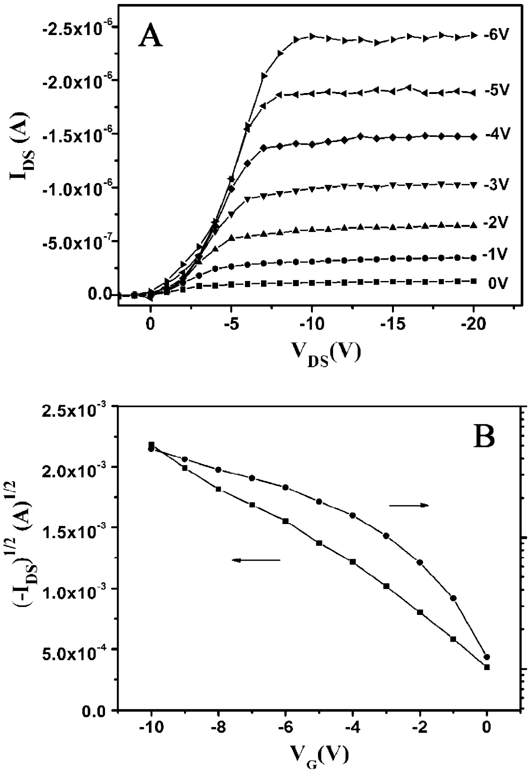

Figure 5. (A) Drain-source current (I_{DS}) vs drain-source voltage (V_{DS}) characteristic at different gate voltages for the 10 layer LB film of **5**. (B) Transfer characteristic at $V_{DS} = -20$ V for the 10 layer LB film of **5**.

largest red shift, indicating the strongest intermolecular interaction in the film. According to Kasha's theory, the red shift caused by the edge-to-edge interaction between neighboring transition dipole moments depends on the center-to-center distance, the angle between center-to-center vector and transition dipole moment, and the aggregation number.[18] As revealed by the polarized UV−vis absorption spectroscopic and $\pi-A$ isotherm results, all these compounds take a similar orientation on a water surface or substrate in a LB film. In other words, the center-to-center distance between neighboring molecules and angle is similar. The significant large red shift for the octyloxy substituted **3** in the LB film therefore must result from an extra large aggregation number in the film, which then results in the largest carrier mobility among the series of five compounds.

However, as tabulated in Table 1 and Figure 6, **4** shows a slightly smaller carrier mobility than **3**, while the red shift in the absorption band is not as significant as that for **3**. Moreover, **1** and **2** appear to have a large intermolecular interaction in the LB films in comparison to **5** according to UV−vis spectroscopic results; however, the OFET carrier mobility for the former two complexes is smaller than that for the latter one (Figure 6). These results can be rationalized in terms of morphology analysis of the multilayer LB films by atomic force microscopy (AFM). Figure 8 compares the morphologies of the multilayer LB films for all five triple-decker complexes. As can be found in Figure 8, the alkoxy side chains have a great influence on the molecular packing in LB films. From **1** to **5**, along with an increase in the length of the alkoxy side chains, the diameter of the aggregate domains increases from ca. 50 nm for **1** to 150 nm for **5** as shown in the images. This increase can be ascribed to the adhesive effect of the long alkoxy side chains, which provides an additional driving force for the aggregation and directs aggregate formation in the LB film into an increasing large nanoassembly in the order of **1** to **5**.[23] The increase in the domain size for **3** and **4** as compared to that of **1** and **2** significantly reduces the boundaries and carrier traps in the film and thus improves the carrier mobility. This has also been observed in many vacuum deposited solid film-based OFETs[24] and was theoretically rationalized according to Horowitz

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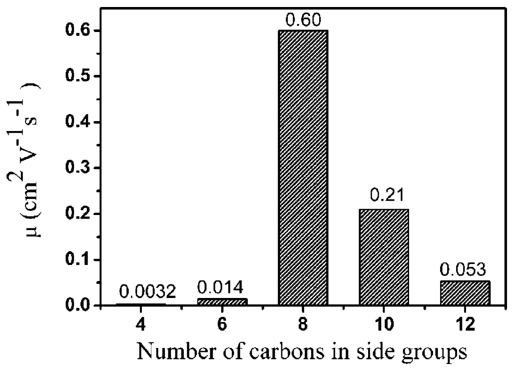

Figure 6. Plot of carrier mobility vs carbon number in alkoxy side chains of triple-decker **1**−**5**.

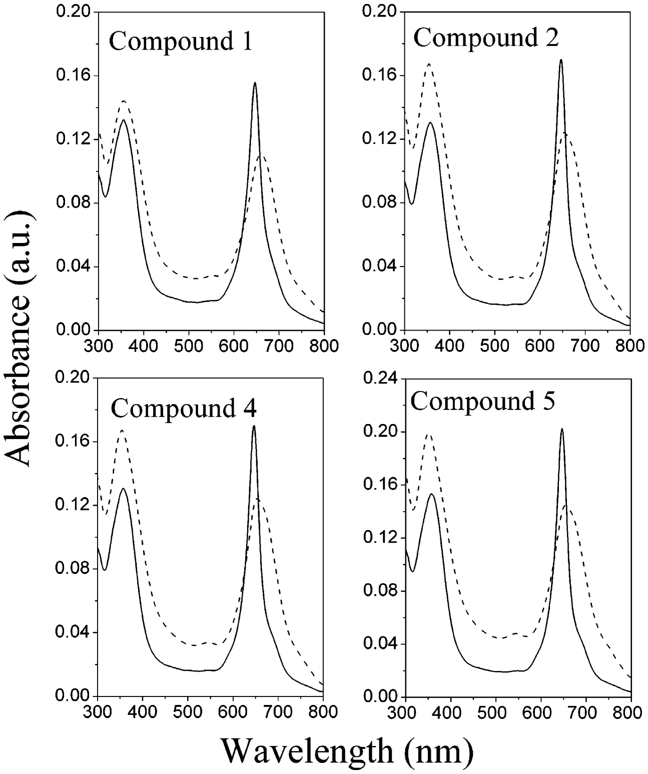

Figure 7. Electronic absorption spectra of **1**, **2**, **4**, and **5** in solution (solid line) and in LB films (dashed line).

and Hajlaoui.[25] However, it is worth noting that the further increase in the length of alkoxy side groups makes the LB film more orderless and leads to the formation of large gaps and cracks between aggregate domains for the compounds with long alkoxy side chains as exemplified by **5** (Figure 8E). These severe film discontinuities will affect the carrier mobility negatively for the corresponding OFET device.[26]

As discussed previously, both the film structure and the interaction between neighboring molecules are crucial for the OFET performance of the LB films. Longer alkoxy side chains in the triple-decker compounds diminish the interaction between neighboring molecules but improve the film structure. A delicate balance between the interaction and the film structure seems to be satisfied when the alkoxy side chains are octyloxy as well as decyloxy groups and therefore results in the maximum carrier mobility for **3** and **4**.

It is noteworthy again that the thus far reported results elucidate that π−π stacking is a favored packing mode for OFETs, which affords an intense interaction between neighboring molecules and makes the π electrons able to move freely along the long axis of the aggregates (normal to the aromatic rings), thus leading to high carrier mobilities.[27] However, our work on the amphiphilic tris(phthalocyaninato) rare earth complexes $[Pc(OC_8H_{17})_8]M[Pc(15C5)_4]M[Pc(15C5)_4]$ (M = Eu, Ho, Lu) indicates that the tightly packing triple-decker molecules can also form an effective channel for the current in the direction parallel to the aromatic phthalocyanine rings.[9] This seems to be contradictory with the generally accepted point in the OFETs field but can be rationalized by many studies that reveal that the edge-to-edge linked molecules can act as effective molecular wires in various circumstances.[28] The present systematic research results on the OFET characteristics of a series of five amiphiphilic heteroleptic tris(phthalocyaninato) rare earth analogues not only support our previous result but more importantly give information about the relationship between molecular structure and OFET properties of semiconducting organic materials via tuning the film structure and the interaction between neighboring molecules. This will lead to new substantial research to enhance the performance and theoretical understanding of OFETs.

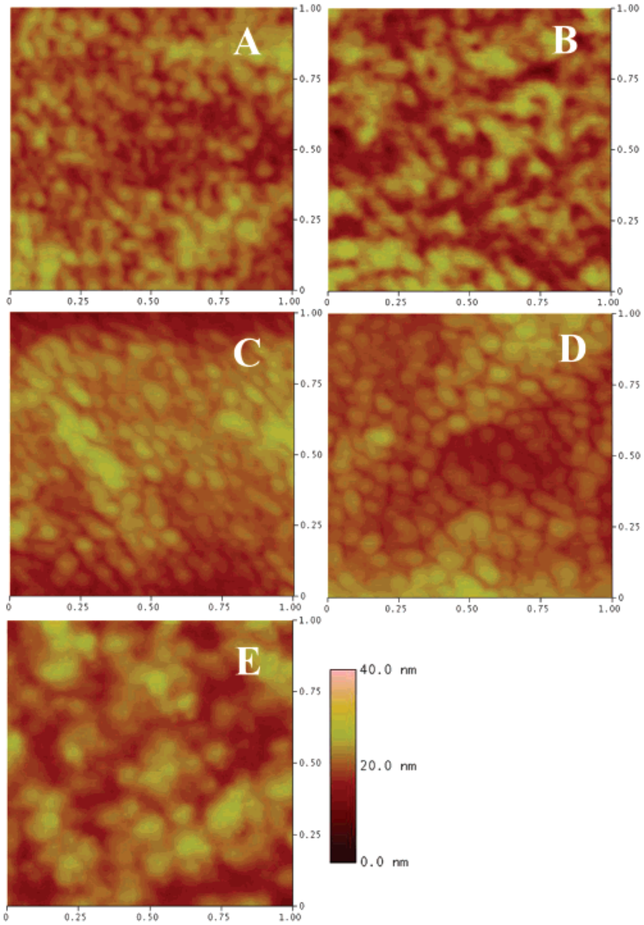

Figure 8. AFM images of LB films of **1**−**5** (A−E) deposited on SiO_2/Si substrates (scan range: 1 μm × 1 μm; height: 0−40 nm; tapping mode).

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[28] See, for example: Kim, D.; Osuka, A. *J. Phys. Chem. A* **2003**, *107*, 8791 and references therein.

Conclusion

We have demonstrated a high OFET performance of a series of heteroleptic tris(phthalocyaninato) rare earth triple-decker complexes, which has further confirmed our previous results that crown ether appended heteroleptic tris(phthalocyaninato) rare earth triple-decker complexes are a good OFET material.[9] The OFET performance is closely related to the amphiphilic nature of the triple-decker molecules that enables fabrication into well-ordered thin films by the LB technique, the intense intramolecular $\pi-\pi$ stacking interaction of the triple-decker molecules, and the effective intermolecular *J* aggregation interaction in the LB films. Nevertheless, the high carrier mobility in the direction parallel to the aromatic phthalocyanine ring was found to be affected by the length of the side alkoxy chains due to their effect on changing the molecular packing model in the LB film and tuning the interaction between neighboring molecules in each layer.

Experimental Procedures

Thin Film Deposition and Characterization. All compounds were prepared following a literature method.[10] Synthesis and characterization of **3** have been described in ref 9. The solution of $[Pc(15C5)_4]Eu[Pc(15C5)_4]Eu[Pc(OC_nH_{2n+1})_8]$ ($n = 4, 6, 10, 12$) (**1**, **2**, **4**, and **5**) dissolved in CH_2Cl_2 (1.46×10^{-5} to $\sim 1.59 \times 10^{-5}$ mol L^{-1}) was spread onto an ultrapure water (resistivity: 18 MΩ cm^{-1}, pH 6.4) subphase surface. The monolayer properties were studied by measuring pressure−area isotherms on a NIMA SYSTEM 622 LB trough. All LB films were deposited onto hydrophobic quartz plates by a vertical dipping method with a dipping speed of 7 mm min^{-1}, while the surface pressure was kept at 28 mN m^{-1}. UV−vis spectra and polarized UV−vis spectra for the films were recorded on a Hitachi U-4100 spectrophotometer. The LAXD experiment was carried out on a Rigaku D/max-γB X-ray diffractometer. Morphology examination was carried out on a Veeco Nanoscope Multimode III SPM with tapping mode.

OFETs Device Fabrication. The heavily doped silicon layer functioning as the gate electrode and the source-drain electrodes was thermally evaporated onto the LB films by use of a shadow mask. These electrodes had a width (*W*) of 28.6 mm and a channel length (*L*) of 0.24 mm. The ratio of the width to the length (*W*/*L*) of the channel was 119. The 4000 Å oxide layer was the gate dielectric, having a capacitance per unit area of 10 nF cm^{-2}. The electric characteristics of these devices were measured under air. The current−voltage characteristics were obtained with a Hewlett-Packard (HP) 4140B parameter analyzer at room temperature.

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Supporting Information Available: Details for synthesis, ^1H NMR, MALDI-TOF mass spectroscopy, and elemental analysis results of **1**, **2**, **4**, and **5**; area−time curves during film deposition and plot of I_{DS} vs V_{DS} together with transfer characteristics for **1**, **2**, **4**, and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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