Synthesis, Characterization, and OFET Properties of Amphiphilic Heteroleptic Tris(phthalocyaninato) Europium(III) Complexes with Hydrophilic Poly(oxyethylene) Substituents

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A series of amphiphilic heteroleptic tris(phthalocyaninato) europium complexes with hydrophilic poly(oxyethylene) heads and hydrophobic alkoxy tails \( \text{Pc}[(\text{OC}_2\text{H}_4)_2\text{OCH}_3]_n\text{Eu}[\text{Pc}((\text{OC}_2\text{H}_4)_2\text{OCH}_3)_n]_6 \) (\( n = 6, 8, 10, 12 \)) were designed and prepared from the reaction between homoleptic bis(phthalocyaninato) europium compound \( \text{Pc}[(\text{OC}_2\text{H}_4)_2\text{OCH}_3]_n\text{Eu}[\text{Pc}((\text{OC}_2\text{H}_4)_2\text{OCH}_3)_n]_6 \) and metal-free \( 2,3,9,10,16,17,23,24\)-octakis(alkoxy)-phthalocyanine \( \text{H}_2\text{Pc}[(\text{OC}_2\text{H}_2n_+1)_6] \) in boiling 1,2,4-trichlorobenzene (TCB). These novel sandwich triple-decker complexes have been characterized by a wide range of spectroscopic methods and have been electrochemically studied. With the help of the Langmuir–Blodgett (LB) technique, these typical amphiphilic triple-decker complexes have been fabricated into organic field effect transistors (OFET) with an unusual bottom contact configuration. The devices display good OFET performance with the carrier mobility for holes in the direction parallel to the aromatic phthalocyanine rings, which shows dependence on the length of the hydrophobic alkoxy side chains, decreasing from 0.46 for 1 to 0.014 cm\(^2\) V\(^{-1}\) s\(^{-1}\) for 4 along with the increase in the carbon number in the hydrophobic alkoxy side chains.

Introduction

The non-naturally occurring phthalocyanines have been an important industrial commodity used as inks, dyestuffs, and catalysts for sulfur effluent removal since their first synthesis early last century.\(^1\) Quite recently, these macro-molecules have found applications as the photoconducting agent in photocopiers, laser printers, and optical read/write disks.\(^2\) They are expected to play important role in material chemistry due to their potential applications in sensors and biosensors.\(^3\) For this purpose, various methods, in particular the Langmuir–Blodgett technique, developed for the amphiphilic molecules have been employed to fabricate them into highly ordered film.\(^4\) As a consequence, amphiphilic monomeric phthalocyanines with hydrophilic substituents on one or two of the benzene rings, and hydrophobic alky or alkoxy groups on the remaining benzene rings of the phthalocyanine ligand have been prepared and reported.\(^5\)

It is well-known that phthalocyanines can form sandwich-type complexes with a range of large metal ions including rare-earth metals.\(^6\) The resulting phthalocyaninato rare-earth double- and triple-decker complexes possess intriguing and

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unique electronic and optical properties, which render them useful in material science because of their possible applications in molecular electronics, nonlinear optics, and molecular information storage materials. It is worth noting that for the purpose of knowing more about the nature of the ring-to-ring interactions in the bis- and tris-(tetrapyrrole) metal complexes, effective pathways have been developed for preparing various series of sandwich-tetrpyrrole rare-earth complexes including heteroleptic bis- and tris-(phthalocyaninato) rare-earth complexes in the past two decades. As a result, the synthesis of amphiphilic-sandwich bis- or tris(phthalocyaninato) rare-earth complexes bearing hydrophobic heads on one phthalocyanine ligand and hydrophilic tails on the remaining phthalocyanine ring(s) of the double- or triple-decker molecules appears to be much easier in comparison with the monomeric phthalocyanine counterparts with the help of these well-established methods. However, real amphiphilic-sandwich-phthalocyaninato rare-earth double- and triple-decker complexes with hydrophilic and hydrophobic tails on different phthalocyanine rings concomitantly still remain extremely rare so far. Despite reports on the synthesis and structure of a series of 15-crown-5-substituted phthalocyaninato-containing heteroleptic bis(phthalocyaninato) rare-earth complexes $M(\text{Pc})_2 (M = \text{Eu, Tb})$, $n = 1-4$), the absence of soft hydrophobic tails in these 15-crown-5-substituted phthalocyaninato-containing double-decker molecules induces them not as real amphiphilic-sandwich-phthalocyaninato rare-earth complexes and makes it hard to fabricate them into highly ordered films by Langmuir–Blodgett technique. Recently, L’Her et al. reported the preparation and spectroscopic characterization of an amphiphilic bis(phthalocyaninato) lutetium compound, which is a mixed sample containing more than one isomer in which one phthalocyaninato ligand bears four hydrophobic dodecyl chains, and this is a mixed sample containing more than one isomer in which one phthalocyaninato ligand bears four hydrophobic dodecyl chains.8–10 As a result, the synthesis of amphiphilic-sandwich bis- or tris(phthalocyaninato) rare-earth complexes bearing hydrophobic heads on one phthalocyanine ligand and hydrophilic tails on the remaining phthalocyanine ring(s) of the double- or triple-decker molecules appears to be much easier in comparison with the monomeric phthalocyanine counterparts with the help of these well-established methods. However, real amphiphilic-sandwich-phthalocyaninato rare-earth double- and triple-decker complexes with hydrophilic and hydrophobic tails on different phthalocyanine rings concomitantly still remain extremely rare so far. Despite reports on the synthesis and structure of a series of 15-crown-5-substituted phthalocyaninato-containing heteroleptic bis(phthalocyaninato) rare-earth complexes $M(\text{Pc})_2 (M = \text{Eu, Tb})$, $n = 1-4$), the absence of soft hydrophobic tails in these
been intensively studied as the bridge to link the gap between the electronic structures of bis(phthalocyaninato) rare-earth double-deckers and infinite supramolecular phthalocyanine 1D stacks or polymers.\textsuperscript{11} However, poly(oxyethylene)-substituted phthalocyanine-containing rare-earth complexes 

**Results and Discussion**

**Synthesis.** Except for (Pc)Lu[Pc(15C5)\textsubscript{4}]Lu(Pc), which was isolated by using monomeric compound Lu(Pc)(OAc)\textsubscript{3} as starting materials,\textsuperscript{17} all of the remaining well-characterized heteroleptic tris(phthalocyaninato) rare-earth complexes in which two different phthalocyanine ligands are contained in one molecule including (Pc)M(Pc*)M(Pc*)\textsuperscript{4}, (Pc)M(Pc)M(Pc*)\textsuperscript{4}, (Pc)M(Pc)M(Pc*)\textsuperscript{4}, and (Pc)M(Pc*)M(Pc)\textsuperscript{4} (Pc*), and (Pc)M(Pc*)M(Pc)\textsuperscript{4} [H\textsubscript{2}Pc = unsubstituted phthalocyanine; H\textsubscript{2}Pc* = 2,3,9,10,16,17,23,24-octakis(orthoxy)-phthalocyaninato or 2,3,9,10,16,17,23,24-octakis(tetraoxy)-phthalocyaninato; M = M* = rare earth] reported were prepared via the condensation of monomeric (Pc*)M(X) [Pc* = Pc, Pc(OH\textsubscript{2}C\textsubscript{2}H\textsubscript{4})\textsubscript{8}; X = acac, OAc] generated in situ from [M(acac)\textsubscript{3}]\textsubscript{4}nH\textsubscript{2}O/[M(OAc)\textsubscript{3}]\textsubscript{4}nH\textsubscript{2}O and Li\textsubscript{2}Pc/H\textsubscript{2}Pc’, and M(Pc’)\textsubscript{2} [Pc’ = Pc, Pc(OH\textsubscript{2}C\textsubscript{2}H\textsubscript{4})\textsubscript{8}] in refluxing n-octanol or TCB.\textsuperscript{9,10} Actually, similar methodology was employed for preparing the 15-crown-5-substituted phthalocyanine-containing amphiphilic heteroleptic tris(phthalocyaninato) rare-earth compounds [Pc(15C5)\textsubscript{4}]M[Pc(15C5)\textsubscript{4}]M[Pc(OH\textsubscript{2}C\textsubscript{2}H\textsubscript{4})\textsubscript{8}] (M = Eu, Tb, Lu; n = 4, 6, 8, 10, 12).\textsuperscript{13} This is also true for [Pc[[Pc(OH\textsubscript{2}C\textsubscript{2}H\textsubscript{4})\textsubscript{8}]]\textsubscript{4}]Eu[Pc[[Pc(OH\textsubscript{2}C\textsubscript{2}H\textsubscript{4})\textsubscript{8}]]\textsubscript{4}]Eu[Pc[[Pc(OH\textsubscript{2}C\textsubscript{2}H\textsubscript{4})\textsubscript{8}]]\textsubscript{4}] (n = 6, 8, 10, 12) (1–4) in the present case. The water-soluble homoleptic octakis(poly(oxyethylene))-substituted bis(phthalocyaninato) europium compound Pc[[Pc(OH\textsubscript{2}C\textsubscript{2}H\textsubscript{4})\textsubscript{8}]]\textsubscript{4} was synthesized via cyclic tetramerization of 4,5-dipoly(oxyethylene)phthalonitrile, which was obtained using the chemical pathway shown in Figure 1 with catechol as a starting material. Metal-free phthalocyanine with eight alkoxy groups onto the peripheral positions H\textsubscript{2}Pc(Pc\textsubscript{2}H\textsubscript{2}n+1)\textsubscript{8} (n = 6, 8, 10, 12) was prepared following the standard method.\textsuperscript{18} Condensation of monomeric [Pc(OH\textsubscript{2}C\textsubscript{2}H\textsubscript{4})\textsubscript{8}]Eu(acac)\textsubscript{3}, generated in situ from [Eu(acac)\textsubscript{3}]H\textsubscript{2}O and H\textsubscript{2}Pc(Pc\textsubscript{2}H\textsubscript{2}n+1)\textsubscript{8}, and {Pc[(OC\textsubscript{2}H\textsubscript{4})\textsubscript{2}OCH\textsubscript{3}]\textsubscript{8}} in refluxing TCB led to the isolation of typical amphiphilic heteroleptic tris(phtha-
The phthalocyaninato Q bands appear around 645 nm as a singlet signal appearing in the low-field region at 12.15, 12.19, and 12.21. This result is well supported by the optical properties of 1–4. Electronic absorption studies have been carried out in CDCl3 at room temperature. The assignment of the spectra for these compounds is straightforward because of the resolved multiplicity in the signals for the alkyl chain protons. Three singlet signals appearing in the low-field region at δ 12.15, 9.21, and 9.15 are obviously due to the α protons of the three Pc rings, respectively, of these triple-decker compounds.

For the series of heteroleptic tris(phthalocyaninato) europium compounds \{Pc[(OC2H4)nOCH3]8}Eu\{Pc[(OC2H4)nOCH3]8\}Eu[Pc(O2C)H2n+1]8 (n = 6, 8, 10,12) (1–4), the characteristic phthalocyanine dianion IR bands for both \{Pc[(OC2H4)nOCH3]8\}2– and \{Pc(O2C)H2n+1\}2– at ca. 1380 cm\(^{-1}\) attributed to the symmetric C–H bendings of the –CH\(_3\) groups in side chains of phthalocyanine rings together with the isoindole stretching vibrations are observed in these spectra.\(^{19}\) The intense absorption bands observed respectively at ca. 1047 and 1275 cm\(^{-1}\) are attributed to the symmetric and asymmetric C–O–C stretching. The intense absorption bands at ca. 2853 (symmetric), 2872 (antisymmetric), and 2925 cm\(^{-1}\) (symmetric) in the IR spectra are attributed to the C–H stretching vibrations of the –CH\(_2\)– and –CH\(_3\) groups of the side chains, respectively.

**Electrochemical Properties.** The electrochemical behavior of all of the triple-decker complexes was investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in CH2Cl2. These triple-decker compounds display four one-electron oxidations labeled as Oxd\(_1\)–Oxd\(_4\) and two one-electron reductions (Red\(_1\)–Red\(_2\)) within the electrochemical window of CH2Cl2 under the present conditions. The separation between the reduction and oxidation peak potentials for each process is 65–90 mV. All of these processes are attributed to the successive removal from, or addition of one electron to, the ligand-based orbitals because the oxidation state of the central tervalent europium ions in addition of one electron to, the ligand-based orbitals because the oxidation state of the central tervalent europium ions in triple-decker complexes does not change. The half-wave redox potential values versus SCE are summarized in Table 2. A typical representative CV and DPV for 2 are displayed in Figure 3.

It is worth noting that the difference of the redox potentials of the first oxidation and first reduction for 1–4, lying between 1.06 and 1.08 V, remains almost unchanged along with the change of alkyl groups of one of the two outer phthalocyanine ligands. This result is well supported by the optical properties of 1–4. Electronic absorption studies have revealed that the lowest-energy electronic absorption band remains unchanged at ca. 689 nm in the electronic spectra of 1–4, which involves the electronic transition from the HOMO to the degenerate LUMO.

**Film Characterization and OFET Properties.** Reproducible pressure-surface area (π-A) isotherms of 1–4

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**Table 1.** Electronic Absorption Spectral Data for the Triple-Deckers 1–4 in Toluene

<table>
<thead>
<tr>
<th>compound</th>
<th>λ(_{\text{max}})/nm (log ε)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>334 (4.89) 364 (5.00) 644 (5.19) 687 (4.34)</td>
</tr>
<tr>
<td>2</td>
<td>334 (4.84) 362 (4.94) 645 (5.17) 689 (4.30)</td>
</tr>
<tr>
<td>3</td>
<td>335 (4.85) 362 (4.95) 645 (5.14) 689 (4.26)</td>
</tr>
<tr>
<td>4</td>
<td>336 (4.80) 362 (4.89) 645 (5.14) 689 (4.23)</td>
</tr>
</tbody>
</table>

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**Table 2.** Half-Wave Redox Potentials of Triple-Deckers 1–4 in CH2Cl2 Containing 0.1 M TBAP

<table>
<thead>
<tr>
<th>compound</th>
<th>Oxd(_1)</th>
<th>Oxd(_2)</th>
<th>Oxd(_3)</th>
<th>Oxd(_4)</th>
<th>Red(_1)</th>
<th>Red(_2)</th>
<th>ΔE(_{1/2}) a</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.33</td>
<td>1.02</td>
<td>0.54</td>
<td>0.27</td>
<td>−0.81</td>
<td>−1.19</td>
<td>1.08</td>
</tr>
<tr>
<td>2</td>
<td>1.34</td>
<td>1.02</td>
<td>0.54</td>
<td>0.25</td>
<td>−0.82</td>
<td>−1.21</td>
<td>1.07</td>
</tr>
<tr>
<td>3</td>
<td>1.33</td>
<td>1.01</td>
<td>0.53</td>
<td>0.24</td>
<td>−0.82</td>
<td>−1.20</td>
<td>1.06</td>
</tr>
<tr>
<td>4</td>
<td>1.33</td>
<td>1.00</td>
<td>0.52</td>
<td>0.22</td>
<td>−0.84</td>
<td>−1.24</td>
<td>1.06</td>
</tr>
</tbody>
</table>

\(\ast\) ΔE\(_{1/2}\) is the potential difference between the first oxidation and first reduction processes, that is, the HOMO–LUMO gap of corresponding molecule.

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indicate that all of the compounds can form a stable monolayer on a pure water surface because of their typical amphiphilic properties (Figure S4, Supporting Information).

The limiting molecular areas of $1-4$ obtained by extrapolation of the liquid-condensed phase to surface pressure zero, $7.02-7.28 \text{ nm}^2$, are close to the area of a phthalocyanine ring substituted with eight poly(oxyethylene) groups of $-(\text{OC}_2\text{H}_4)_2\text{OCH}_3$, $6.25 \text{ nm}^2$, calculated according to the PCMODEL program (Table 3). 20 This suggests that triple-decker molecules are lying with a face-on orientation on the water surface. The monolayers have been transferred to hydrophobic substrates by the vertical dipping method, and Z-type LB films were revealed to form for all of the compounds. 21 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 very good layered structure (Figure S5, Supporting Information). This was further proved by the low-angle X-ray diffraction experiments, which show one diffraction peak corresponding to the $d$ spacing in the range of $2.23-2.70 \text{ nm}$ (Figure 4). Polarized absorption spectroscopic study results reveal that the orientation angles (dihedral angle between phthalocyanine ring and the surface of substrate) of the phthalocyanine ring in these films are in the range of $9.4-12.1^\circ$, 22 confirming the face-on configuration for the molecules in the film deduced from the $\pi$-$\pi$ isotherms.

The LB films were also characterized by the AFM technique. Figure S6 (Supporting Information) shows the 3D height image, phase image, and phase shift of the 10-layers \{Pc[(OC_2H_4)_2OCH_3]_8\}Eu{Pc[(OC_2H_4)_2OCH_3]_8}\} 1 LB film on the SiO\textsubscript{2} surface as a typical representative. The profiles adjacent to the individual phase images show the phase shift corresponding to the line across the phase images. The 3D topographic image in part a of Figure S6 (Supporting Information) shows that the tris(phthalocyaninato) europium molecules in the films are in

Table 3. Film Characterization Data and OFET Characteristics of Compounds 1–4

<table>
<thead>
<tr>
<th>compound</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{\text{lim}}$ (nm$^2$)</td>
<td>7.20</td>
<td>7.15</td>
<td>7.28</td>
<td>7.02</td>
</tr>
<tr>
<td>Solution</td>
<td>644,334</td>
<td>645,334</td>
<td>645,335</td>
<td>645,356</td>
</tr>
<tr>
<td>LBfilms</td>
<td>$\lambda_{\text{max}}$ (nm)</td>
<td>673</td>
<td>665</td>
<td>661</td>
</tr>
<tr>
<td>$\Delta\lambda_{\text{max}}$ (red shift)</td>
<td>29</td>
<td>20</td>
<td>16</td>
<td>13</td>
</tr>
<tr>
<td>$\alpha$ (deg)</td>
<td>9.4</td>
<td>11.8</td>
<td>6.8</td>
<td>12.1</td>
</tr>
<tr>
<td>d spacing (nm)</td>
<td>2.23</td>
<td>2.40</td>
<td>2.52</td>
<td>2.70</td>
</tr>
<tr>
<td>mobility (cm$^2$ V$^{-1}$ s$^{-1}$)</td>
<td>0.46</td>
<td>0.17</td>
<td>0.096</td>
<td>0.014</td>
</tr>
<tr>
<td>on/off ratio</td>
<td>$1.01 \times 10^2$</td>
<td>$1.02 \times 10^3$</td>
<td>$3.85 \times 10^4$</td>
<td>$1.15 \times 10^5$</td>
</tr>
</tbody>
</table>

$^a$ The dihedral angle between the phthalocyanine ring and the surface of substrate determined by polarized UV–vis spectroscopy. $^b$ Layer spacing determined by low-angle X-ray diffraction experiments.

(20) PCMODEL for Windows, version 6.0; Serena Software: Bloomington, IN, U.S.A.


the form of a nummular aggregate. The corresponding phase-shift profile in part c of Figure S6 (Supporting Information) also shows that the roughness (ca. 3 nm) of the surface is very flat. The aggregate domains are smooth and ordered in a parallel arrangement, which is favorable for the operation of FET.

It has been demonstrated that the OFET devices fabricated with a top contact configuration usually display better performance over those with a bottom contact configuration because of the better electrode metal–organic contact,\(^{23}\) which however also exhibits a significant obstacle to large-scale manufacturing due to its incompatibility with the photolithographic processes.\(^{24}\) Looking toward future potential industrial applications, OFET devices with a bottom contact configuration were fabricated in the present case. The heavily doped silicon layer functioning as the gate electrode and the source/drain gold electrodes with dimensions of 28.6 mm width and 0.24 mm length were thermally evaporated onto a 500-nm-thick SiO\(_2\) dielectric layer by the use of a shadow mask. The semiconductor layer of amphiphilic heteroleptic tris(phthalocyaninato) europium complexes was deposited by the LB technique (Figure 5).\(^{25}\) The phosphilic heteroleptic tris(phthalocyaninato) europium compounds was deposited by the LB technique (Figure 5).\(^{25}\) 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.

The OFET devices show typical p-channel characteristics as exemplified in Figures 6 and S7–S9 (Supporting Information). The carrier mobility (\(\mu\)) was calculated 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.\(^{26}\) The results indicate that all of the compounds show good carrier mobility in the same order of 0.014–0.46 cm\(^2\) V\(^{-1}\) s\(^{-1}\). In line with the results on the 15-crown-5-substituted triple-decker analogues [Pc(15C\(_5\))\(_n\)]M[Pc(15C\(_5\))\(_n\)]M[Pc(OCH\(_2\)\(_2\)\(_2\)OCH\(_3\))]\(_8\) (M = Eu, Tb, Lu; \(n = 6, 8, 10, 12\)),\(^{13}\) the OFET performance for the present series of poly(oxyethylene)-substituted phthalocyanine-containing amphiphilic heteroleptic tris(phthalocyaninato) europium complexes \{Pc[(OC\(_2\)H\(_4\)]\(_2\)OCH\(_3\)]\(_8\)Eu{Pc[(OC\(_2\)H\(_4\))]\(_2\)OCH\(_3\)]\(_8\)}Eu[Pc(OCH\(_2\)\(_2\)\(_2\)OCH\(_3\))]\(_8\)} (1–4) also shows dependence on the length of the hydrophobic alkoxy side chains. Along with the increase in carbon number in the hydrophobic alkoxy groups from 6 in 1 to 12 in 4, the carrier mobility decreases in the same order, indicating a significant effect of the molecular structure on the OFET device functional properties of corresponding molecular materials. The decrease in the OFET performance of triple-decker complexes 1–4 along with the increase in the length of the hydrophobic alkoxy side chains is attributed to the decrease in the effective π–π interaction between neighboring triple-decker molecules in the same layer and in particular between different layers in the LB films in the same order. This is actually in accordance with the result deduced from low-angle X-ray diffraction experiments that the d spacing of each layer of triple-decker molecules in the LB films increases from 2.23 for 1 to 2.70 nm for 4 (Table 3).

As can be seen from Figure 2, all four triple-decker compounds 1–4 show an intense Q band at about 645 nm in solution. In the LB films, the Q band of these triple-decker complexes red-shifts to 658–673 nm compared with that in solution. (Table S1, Supporting Information), indicating the formation of edge-to-edge J aggregates\(^{27}\) and effective interaction between the neighboring triple-decker molecules in each layer. This together with the intense intramolecular π–π stacking in the triple-decker molecules themselves

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provides the π electrons (as well as holes) with an extensive character for delocalization. This forms the basic necessary characteristic for an organic semiconductor with good carrier mobility.\(^{13}\)

**Conclusion**

In summary, a new series of four amphiphilic heteroleptic tris(phthalocyaninato) europium(III) complexes with hydrophilic poly(oxyethylene) heads and hydrophobic alkoxy tails have been carefully designed and prepared. The OFET devices with a bottom contact configuration fabricated from these typical amphiphilic heteroleptic tris(phthalocyaninato) europium complexes by the LB technique show good carrier mobility for holes in the direction parallel to the aromatic phthalocyanine rings. The present work, representing a new series of sandwich-phthalocyaninato rare-earth complexes with good OFET performance, sheds further light on devising a series of sandwich-phthalocyaninato rare-earth complexes for understanding the relationship between molecular structure and OFET functional properties.

**Experimental Section**

**Measurements.** \(^1\)H NMR spectra were recorded on a Bruker DPX 300 spectrometer (300 MHz) in CDCl\(_3\) using the residual solvent resonance of CHCl\(_3\) at 7.26 ppm relative to SiMe\(_4\) as an internal reference. Electronic absorption spectra were recorded on a Hitachi U-4100 spectrophotometer. MALDI-TOF mass spectra were taken on a Bruker BIFLEX III ultrahigh-resolution Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer with \(\alpha\)-cyano-4-hydroxycinnamic acid as matrix. Elemental analyses were performed by the Institute of Chemistry, Chinese Academy of Sciences. Electrochemical measurements were carried out with a BAS CV-50W 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 a Luggin capillary whose tip was placed close to the working electrode. It was corrected for junction potentials by being dried over anhydrous MgSO\(_4\), and evaporated. The crude product was purified by silica gel column chromatography with petroleum ether/ethyl acetate (1:2) as the eluent as the yellow oil (7.1 g, 75%). \(^1\)H NMR (300 MHz): (CDCl\(_3\)) \(\delta\) 7.14 (s, 2 H, benzene ring), 4.12–4.15 (t, 4 H, OCH\(_2\)), 3.83–3.86 (t, 4 H, CH\(_2\)), 3.69–3.71 (m, 4 H, CH\(_2\)), 3.54–3.57 (m, 4 H, CH\(_2\)), 3.38 (s, 6 H, OCH\(_3\)). MALDI-TOF MS: an isotopic cluster peaking at \(m/z\) 494.6. Anal. Calcd for C\(_{13}\)H\(_{24}\)N\(_2\)O\(_6\)Na: C, 54.28; H, 5.81; N, 4.92. Found: C, 54.15; H, 5.70; N, 4.87.

**Preparation of 4,5-Dibromo-benzene-1,2-poly(oxyethylene).** To a mixture of 4,5-dibromo-benzene-1,2-diol (5.4 g, 0.02 mol) and dry fine-powdered K\(_2\)CO\(_3\) (6.9 g, 0.05 mol) in DMF (50 mL), a solution of 1-[2-(2-methoxy-ethoxy)-ethoxy]-4-toluene (10.5 g, 0.05 mol) in DMF (10 mL) was added dropwise over 1 h. The mixture was stirred overnight at 40 °C and then poured into 300 mL water, stirring for another 0.5 h. The mixture was then extracted with ether (3 × 50 mL). The combined extracts were washed with water, dried over anhydrous MgSO\(_4\), and evaporated. The residue was purified by silica gel column chromatography with petroleum ether/ethyl acetate (2:1) as the eluent to give the target compound as a yellow oil (7.1 g, 75%). \(^1\)H NMR (300 MHz): (CDCl\(_3\)) \(\delta\) 7.14 (s, 2 H, benzene ring), 4.12–4.15 (t, 4 H, OCH\(_2\)), 3.83–3.86 (t, 4 H, CH\(_2\)), 3.69–3.71 (m, 4 H, CH\(_2\)), 3.54–3.57 (m, 4 H, CH\(_2\)), 3.38 (s, 6 H, OCH\(_3\)). MALDI-TOF MS: an isotopic cluster peaking at \(m/z\) 494.6. Anal. Calcd for C\(_{13}\)H\(_{24}\)N\(_2\)O\(_6\)Na: C, 54.28; H, 5.81; N, 4.92. Found: C, 54.15; H, 5.70; N, 4.87.

**Preparation of 4,5-Di[poly(oxyethylene)]phthalonitrile.** A mixture of 4,5-dibromo-benzene-1,2-poly(oxyethylene) (9.4 g, 0.02 mol) and CuCN (4.5 g, 0.05 mol) in DMF (100 mL) was heated to reflux for 8 h under nitrogen. After being cooled to room temperature, the mixture was poured to ammonia (500 mL) and blown with fresh air. Then, the solution was extracted with ether (3 × 100 mL). The combined extracts were washed with water, dried over anhydrous MgSO\(_4\), and evaporated. The crude product was chromatographed over a silica gel column with petroleum ether/ethyl acetate (1:2) as the eluent. The solution was evaporated to give a yellow oil (7.1 g, 75%). \(^1\)H NMR (300 MHz): (CDCl\(_3\)) \(\delta\) 7.26 (s, 2 H, benzene ring), 4.24–4.27 (t, 4 H, OCH\(_2\)), 3.88–3.91 (t, 4 H, CH\(_2\)), 3.69–3.72 (m, 4 H, CH\(_2\)), 3.54–3.57 (m, 4 H, CH\(_2\)), 3.39 (s, 6 H, OCH\(_3\)). MALDI-TOF MS: an isotopic cluster peaking at \(m/z\) 387.1. Calcd for C\(_{13}\)H\(_{24}\)N\(_2\)O\(_6\)Na: [M\(^+\)] \(m/z\) 387.2. Anal. Calcd for C\(_{13}\)H\(_{24}\)N\(_2\)O\(_6\)Na: C, 59.33; H, 6.64; N, 7.69; found: C, 59.02; H, 6.72; N, 7.68.

**Preparation of Eu[PC(OCl\(_2\)H\(_2\))O\(_2\)CH\(_3\)]\(_2\).** A mixture 4,5-di[poly(oxyethylene)]phthalonitrile (91 mg, 0.25 mmol) and Eu(acac)_\(_2\)_2H\(_2\)O (27 mg, 0.06 mmol) in n-pentanol (6 mL) was heated to reflux under nitrogen for 8 h. After being cooled to room temperature, the mixture was evaporated under reduced pressure, and the residue was chromatographed on a silica gel column with CHCl\(_3\) as the eluent. A green band containing the target double-decker complex was developed. Repeated chromatography followed by recrystallization from CHCl\(_3\) and petroleum ether gave a pure target compound as a dark powder (37 mg, 31%). \(^1\)H NMR (300 MHz): (CDCl\(_3\)/DMSO with 1% N\(_2\)H\(_4\)) \(\delta\) 10.64 (s, 16 H, Pc rings), 6.01–6.03 (br, 16 H, OCH\(_2\)), 5.47–5.50 (br, 16 H, OCH\(_2\)), 4.79–4.88 (br, 32 H, CH\(_2\)), 4.34–4.38 (m, 32 H, CH\(_2\)), 4.00–4.04 (m, 32 H, CH\(_2\)), 3.68(s, 48 H, OCH\(_3\)). MALDI-TOF MS: Calcd for \(\text{C}_{18}\text{H}_{24}\text{N}_{2}\text{O}_{6}\text{Eu}_{2}\): [M\(^+\)] \(m/z\) 1140.2. Calcd for C\(_{18}\)H\(_{24}\)N\(_2\)O\(_6\)Eu\(_2\): C, 59.33; H, 6.64; N, 7.69; found: C, 59.02; H, 6.72; N, 7.68.


General Procedure for the Preparation of \( \text{[Pc}(\text{OC}_2\text{H}_4\text{O})_5\text{CH}_3]_8 \) Eu\( \text{[Pc}(\text{OC}_2\text{H}_4\text{O})_5\text{CH}_3]_8 \) Eu\( \text{[Pc}(\text{OC}_2\text{H}_4\text{O})_5\text{CH}_3]_8 \) (1) (2.16 mg, 42%). \( ^1\)H NMR (300 MHz): (CDCl\(_3\)) \( \delta \) 12.15 (s, 8 H, Pc ring), 9.21 (br s, 8 H, Pc ring), 9.15 (br s, 8 H, Pc ring), 6.55 (br, 16 H, CH\(_2\) of poly(oxyethylene)), 5.68 (br, 16 H, CH\(_2\) of poly(oxyethylene)), 5.06 (br, 8 H, CH\(_2\) of poly(oxyethylene)), 4.96-4.99 (br, 16 H, CH\(_2\) of poly(oxyethylene)), 4.70-4.80 (m, 16 H, CH\(_2\) of poly(oxyethylene)), 4.48-4.51 (m, 16 H, CH\(_2\) of poly(oxyethylene)), 4.24-4.28 (m, 16 H, CH\(_2\) of poly(oxyethylene)), 4.04 (s, 24 H, CH\(_3\) of poly(oxyethylene)), 3.83-3.95 (m, 16 H, CH\(_2\) of poly(oxyethylene)), 3.56 (s, 24 H, CH\(_3\) of poly(oxyethylene)), 2.67 (m, 16 H, CH\(_2\) of hexyloxy), 2.08-2.16 (m, 16 H, CH\(_2\) of hexyloxy), 1.68-1.80 (m, 48 H, CH\(_2\)CH\(_2\)CH\(_2\) of hexyloxy), 1.13-1.18 (m, 24 H, CH\(_3\) of hexyloxy). MALDI-TOF MS: Calcd for C\(_{256}\)H\(_{368}\)Eu\(_2\)N\(_{24}\)O\(_{56}\) (M\(^+\)) 4532.9; found m/z 4532.4. Anal. Calcd (%) for C\(_{256}\)H\(_{368}\)Eu\(_2\)N\(_{24}\)O\(_{56}\) 0.5CH\(_3\)Cl: C, 58.71; H, 6.68; N, 7.32; found: C, 58.71; H, 6.62; N, 7.45.

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