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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 $\{Pc[(OC_2H_4)_2OCH_3]_8\}Eu\{Pc[(OC_2H_4)_2OCH_3]_8\}Eu[Pc(OC_nH_{2n+1})_8]$ ($n = 6$, 8, 10,12) (**1**–**4**) were designed and prepared from the reaction between homoleptic bis(phthalocyaninato) europium compound $\{Pc[(OC_2H_4)_2OCH_3]_8\}Eu\{Pc[(OC_2H_4)_2OCH_3]_8\}$ and metal-free 2,3,9,10,16,17,23,24-octakis(alkoxy)-phthalocyanine $H_2Pc(OC_nH_{2n+1})_8$ ($n = 6$, 8, 10,12) in the presence of $Eu(acac)_3 \cdot H_2O$ (Hacac = acetylacetone) 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 macromolecules 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 subtsituents on one or two of the benzene rings, and hydrophobic alkyl 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.[7] 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-tetrapyrrole rare-earth complexes including heteroleptic bis- and tris-(phthalocyaninato) rare-earth complexes in the past two decades.[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 phthalocyanine-containing heteroleptic bis(phthalocyaninato) rare-earth complexes $M(Pc)[Pc(15C5)_n]$ (M = Eu, Lu; $n = 1-4$),[11] the absence of soft hydrophobic tails in these 15-crown-5-substituted phthalocyanine-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 phthalocyanine ligand bears four hydrophobic dodecyloxy substituents randomly located at the peripheral positions and the other with four hydrophilic poly(oxyethylene) groups.[12] Very lately, we reported on the LB film fabrication and field-effect transistor (FET) properties of a series of amphiphilic tris(phthalocyaninato) rare-earth complexes with eight hydrophobic alkoxy groups at the peripheral positions of one outer phthalocyanine ligand and four hydrophilic 15-crown-5 moieties at the other two phthalocyanine ligands $[Pc(15C5)_4]M[Pc(15C5)_4]M[Pc(OC_nH_{2n+1})_8]$ (M = Eu, Tb, Lu; n = 4, 6, 8, 10,12),[13] but details of the isolation, spectroscopic charracterization, and electrochemistry were not given.

In the present article, we describe the synthesis, spectroscopic, and electrochemical properties of a new series of novel amphiphilic tris(phthalocyaninato) europium(III) complexes with hydrophilic poly(oxyethylene) heads and hydrophobic alkoxy tails $\{Pc[(OC_2H_4)_2OCH_3]_8\}Eu\{Pc[(OC_2H_4)_2OCH_3]_8\}Eu[Pc(OC_nH_{2n+1})_8]$ (n = 6, 8, 10,12) (**1−4**) (Figure 1). In particular, these typical amphiphilic-sandwich triple-decker molecules have been fabricated into OFET devices by the Langmuir−Blodgett (LB) technique, which show good carrier mobility in the direction parallel to the aromatic phthalocyanine rings as high as 0.014−0.46 $cm^2\ V^{-1}\ s^{-1}$ for holes. Note that toward future potential industrial applications, the OFET devices in this work were fabricated in the *bottom contact configuration*. It must be pointed out that despite the pioneering work of Simon and co-workers in the semiconductivity of unsubstituted bis(phthalocyaninato) rare-earth complexes $M(Pc)_2$ (M = Tm, Lu) in the early 1990s,[14] reports on the OFET properties of sandwich-phthalocyaninato rare-earth compounds still remain rare, limited to the heteroleptic double-decker $M(Pc)[Pc(OC_8H_{17})_8]$ (M = Tb, Lu)[15] and 15-crown-5-substituted phthalocyanine-containing triple-decker $[Pc(15C5)_4]M[Pc(15C5)_4]M[Pc(OC_nH_{2n+1})_8]$ (M = Eu, Tb, Lu; n = 4, 6, 8, 10,12).[13] The present work therefore represents a new series of sandwich-phthalocyaninato rare-earth complexes with good OFET performance.

It is also noteworthy that 15-crown-5-substituted phthalocyanine-containing sandwich rare-earth complexes, in particular $M(Pc)[Pc(15C5)_n]$ (M = Eu, Lu; $n = 1-4$), have

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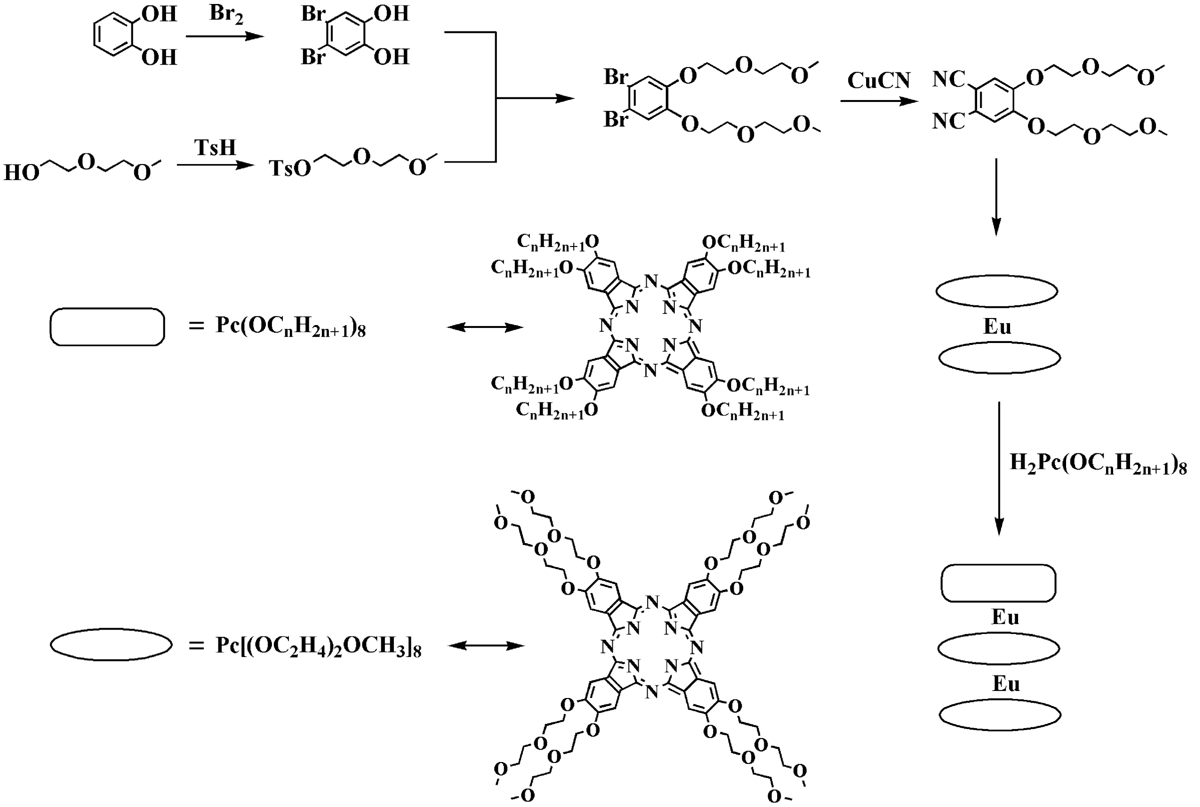

Figure 1. Synthesis of the amphiphilic heteroleptic tris(phthalocyaninato) rare-earth triple-decker complexes {Pc[$(OC_2H_4)_2OCH_3$]$_8$}Eu{Pc[$(OC_2H_4)_2OCH_3$]$_8$}Eu[Pc(OC_nH_{2n+1})$_8$] ($n = 6, 8, 10, 12$) (**1**−**4**).

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.[11] However, poly(oxyethylene)-substituted phthalocyanine-containing rare-earth complexes with a sandwich structure were relatively little studied, limited to the mixed sample of position isomers of double-decker {Pc[$(OC_2H_4)_{7.5}OCH_3$]$_4$}Lu[Pc($OC_{12}H_{25}$)$_4$],[12] {Pc[$(OC_2H_4)_3OCH_3$]$_8$}Lu[Pc(15C5)$_4$],[16] and {Pc[$(OC_2H_4)_n$OCH$_3$]$_8$}Lu{Pc[$(OC_2H_4)_n$OCH$_3$]$_8$} ($n = 1, 2, 3,4$).[16] There exists no report on poly(oxyethylene)-substituted phthalocyanine-containing rare-earth triple-decker complexes. The present compounds are therefore the first example of amphiphilic poly(oxyethylene)-substituted phthalocyanine-containing heteroleptic tris(phthalocyaninato) rare-earth triple-decker complexes.

Results and Discussion

Synthesis. Except for (Pc)Lu[Pc(15C5)$_4$]Lu(Pc), which was isolated by using monomeric compound Lu(Pc)(OAc) and metal-free H_2[Pc(15C5)$_4$] as starting materials,[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*), (Pc)M(Pc)M(Pc*), (Pc)M(Pc)M′(Pc*), and (Pc)M(Pc*)M(Pc) [H_2Pc = unsubstituted phthalocyanine; H_2Pc* = 2,3,9,10,16,17,23,24-octakis(octyloxy)phthalocyanine or 2,3,9,10,16,17,23,24-octakis(tetryloxy)phthalocyanine; M $\neq$ M′ = rare earth] reported were prepared by the condensation of monomeric (Pc′)M(X) [Pc′ = Pc, Pc(OC_4H_9)$_8$; X = acac, OAc] generated in situ from [M(acac)$_3$]·nH$_2$O/[M(OAc)$_3$]·nH$_2$O and Li$_2$Pc/H$_2$Pc′, and M(Pc′)$_2$ [Pc′ = Pc, Pc(OC_8H_{17})$_8$] in refluxing *n*-octanol or TCB.[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)$_4$]M[Pc(15C5)$_4$]M[Pc(OC_nH_{2n+1})$_8$] (M = Eu, Tb, Lu; $n = 4, 6, 8, 10,12$).[13] This is also true for {Pc[$(OC_2H_4)_2OCH_3$]$_8$}Eu{Pc[$(OC_2H_4)_2OCH_3$]$_8$}Eu[Pc(OC_nH_{2n+1})$_8$] ($n = 6, 8, 10,12$) (**1**−**4**) in the present case. The water-soluble homoleptic octakis[poly(oxyethylene)]-substituted bis(phthalocyaninato) europium compound {Pc[$(OC_2H_4)_2OCH_3$]$_8$}Eu{Pc[$(OC_2H_4)_2OCH_3$]$_8$} was synthesized via cyclic tetramerization of 4,5-di[poly(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_2Pc(OC_nH_{2n+1})$_8$ ($n = 6, 8, 10,12$) was prepared following the standard method.[18] Condensation of monomeric [Pc(OC_nH_{2n+1})$_8$]Eu(acac), generated in situ from [Eu(acac)$_3$]·H_2O and H_2Pc(OC_nH_{2n+1})$_8$, and {Pc[$(OC_2H_4)_2$OCH$_3$]$_8$}Eu{Pc[$(OC_2H_4)_2OCH_3$]$_8$} in refluxing TCB led to the isolation of typical amphiphilic heteroleptic tris(phtha-

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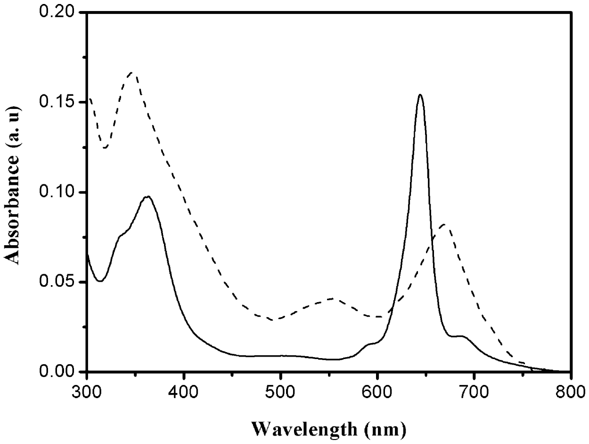

Figure 2. Electronic absorption spectra of **1** in solution (solid line) and in LB film (dashed line).

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

compound	λmax/nm (log ϵ)			
1	334 (4.89)	364 (5.00)	644 (5.19)	687 (4.34)
2	334 (4.84)	362 (4.94)	645 (5.17)	689 (4.30)
3	335 (4.83)	362 (4.93)	645 (5.14)	689 (4.26)
4	336 (4.80)	362 (4.89)	645 (5.14)	689 (4.23)

locyaninato) europium complexes $\{Pc[(OC_2H_4)_2OCH_3]_8\}Eu\{Pc[(OC_2H_4)_2OCH_3]_8\}Eu[Pc(OC_nH_{2n+1})_8]$ ($n = 6, 8, 10,12$) (**1**−**4**) in relatively good yield.

Satisfactory elemental analysis results have been obtained for all of these newly prepared heteroleptic amphiphilic europium triple-decker complexes **1**−**4**, which have good solubility in common organic solvents such as $CHCl_3$, CH_2Cl_2, and toluene after repeated column chromatography and recrystallization. They have also been characterized by MALDI-TOF mass and ^1H NMR spectroscopies. The MALDI-TOF mass spectra of these compounds clearly showed intense signals for the molecular ion $(M)^+$. The isotopic pattern closely resembles the simulated one, as exemplified by the spectrum of **2** given in Figure S1 (Supporting Information).

Spectroscopic Characteristics. The electronic absorption spectra of triple-decker complexes (**1**−**4**) were recorded in toluene, and the data are summarized in Table 1. Figures 2 and S2 (Supporting Information) display the UV−vis spectra of these heteroleptic triple-decker complexes in comparison with those in the LB film. They are analogous to those reported for related homoleptic and heteroleptic tris(phthalocyaninato) rare-earth compounds.[9,10] The absorption around 364 with a shoulder at the higher-energy side of ca. 334 nm can be attributed to the phthalocyaninato Soret band for **1**−**4**. The phthalocyaninato Q bands appear around 645 nm as a very strong absorption with a weak satellite around 689 nm.

The ^1H NMR spectra of all of the newly prepared triple-decker compounds **1**−**4** have been recorded in $CDCl_3$ at room temperature. The assignment of the spectra for these complexes 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 **1**−**4**. The aliphatic protons' signals are observed in the high field range of δ 6.56 to 0.87 (Figure S3, Supporting Information).

Table 2. Half-Wave Redox Potentials of Triple-Deckers **1**−**4** in CH_2Cl_2 Containing 0.1 M TBAP

compound	Oxd_4	Oxd_3	Oxd_2	Oxd_1	Red_1	Red_2	$\Delta E^o_{1/2}{}^a$
1	1.33	1.02	0.54	0.27	−0.81	−1.19	1.08
2	1.34	1.02	0.54	0.25	−0.82	−1.21	1.07
3	1.33	1.01	0.53	0.24	−0.82	−1.20	1.06
4	1.33	1.00	0.52	0.22	−0.84	−1.24	1.06

[a] $\Delta E^o_{1/2}$ is the potential difference between the first oxidation and first reduction processes, that is, the HOMO−LUMO gap of corresponding molecule.

For the series of heteroleptic tris(phthalocyaninato) europium compounds $\{Pc[(OC_2H_4)_2OCH_3]_8\}Eu\{Pc[(OC_2H_4)_2OCH_3]_8\}Eu[Pc(OC_nH_{2n+1})_8]$ ($n = 6, 8, 10,12$) (**1**−**4**), the characteristic phthalocyanine dianion IR bands for both $\{Pc[(OC_2H_4)_2OCH_3]_8\}^{2-}$ and $[Pc(OC_nH_{2n+1})_8]^{2-}$ 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 CH_2Cl_2. 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 CH_2Cl_2 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 triple-decker complexes does not change. The half-wave redox potential values versus SCE are summarized in Table 2. A typtical 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 alkoxy 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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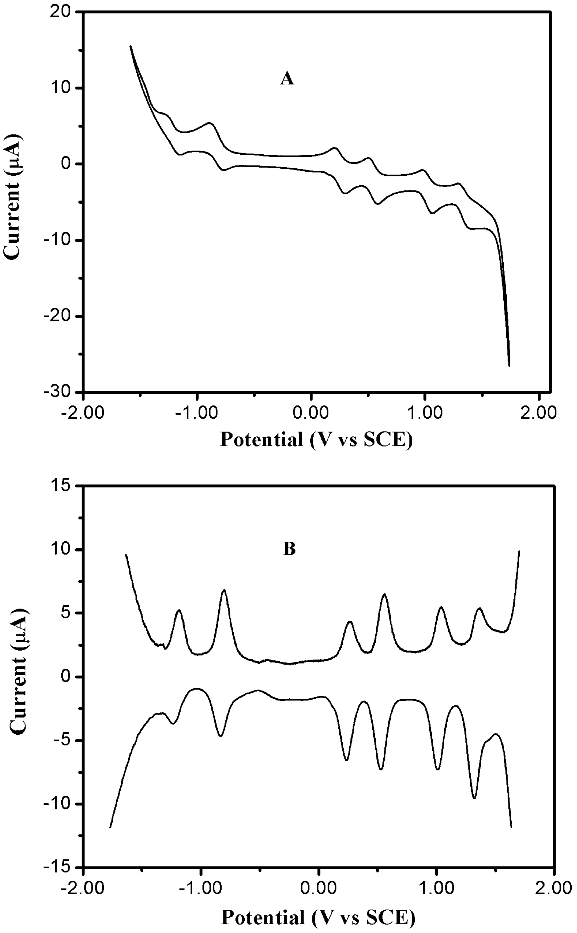

Figure 3. Cyclic voltammogram (A) and differential pulse voltammogram (B) of compound **2** in CH_2Cl_2 containing 0.1 M $[NBu_4][ClO_4]$ at a scan rate of 20 and 10 mV·S^{-1}, respectively.

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 nm^2, are close to the area of a phthalocyanine ring substituted with eight poly(oxyethylene) groups of $-(OC_2H_4)_2OCH_3$, 6.25 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 nm (Figure 4). Polarized absorption spectroscopic study results reveal that the orientation angles (dihedral angle between phthalocyanine rings and the surface of substrate) of the phthalocyanine ring in these films are in the range of 9.4−12.1°,[22] confirming the face-on configuration for the molecules in the film deduced from the π-A isotherms.

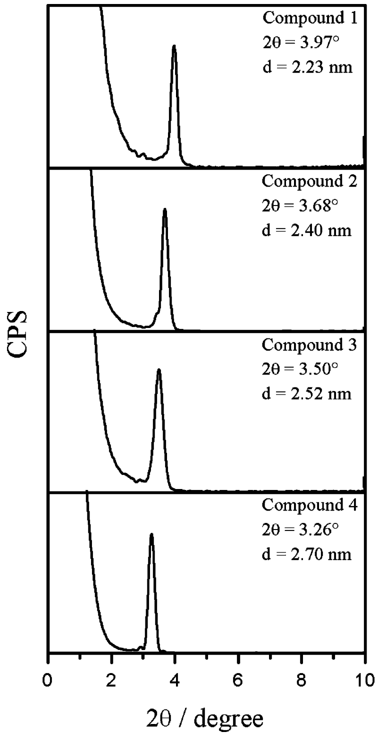

Figure 4. Low-angle X-ray diffraction patterns of the LB films of **1**−**4**.

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

compound	1	2	3	4
A_{limit} (nm^2)	7.20	7.15	7.28	7.02
Solution	644,334	645,334	645,335	645,356
LBfilms λ_{max} (nm)	673	665	661	658
$\Delta\lambda_{max}$ (red shift)	29	20	16	13
α (deg)[a]	9.4	11.8	6.8	12.1
d spacing (nm)[b]	2.23	2.40	2.52	2.70
mobility ($cm^2\ V^{-1}\ s^{-1}$)	0.46	0.17	0.096	0.014
on/off ratio	1.01×10^2	1.02×10^3	3.85×10^4	1.15×10^2

[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.

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 $\{Pc[(OC_2H_4)_2OCH_3]_8\}Eu\{Pc[(OC_2H_4)_2OCH_3]_8\}Eu[Pc(OC_6H_{13})_8]$ (**1**) LB film on the SiO_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

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

(21) (a) Chen, Y.; Zhang, Y.; Zhu, P.; Fan, Y.; Bian, Y.; Li, X.; Jiang, J. *J. Colloid Interface Sci.* **2006**, *303*, 256−263. (b) Wang, X.; Chen, Y.; Liu, H.; Jiang, J. *Thin Solid Films* **2006**, *496*, 619−625. (c) Chen, Y.; Liu, H.; Zhu, P.; Zhang, Y.; Wang, X.; Li, X.; Jiang, J. *Langmuir* **2005**, *21*, 11289−11295. (d) Chen, Y.; Liu, H.; Pan, N.; Jiang, J. *Thin Solid Films* **2004**, *460*, 279−285.

(22) (a) Yoneyama, M.; Sugi, M.; Saito, M.; Ikegama, K.; Kuroda, S.; Iizima, S. *Jpn. J. Appl. Phys.* **1986**, *25*, 961−965. (b) Kobayashi, N.; Lam, H.; Nevin, W. A.; Janda, P.; Leznoff, C. C.; Koyama, T.; Monden, A.; Shiral, H. *J. Am. Chem. Soc.* **1994**, *116*, 879−890.

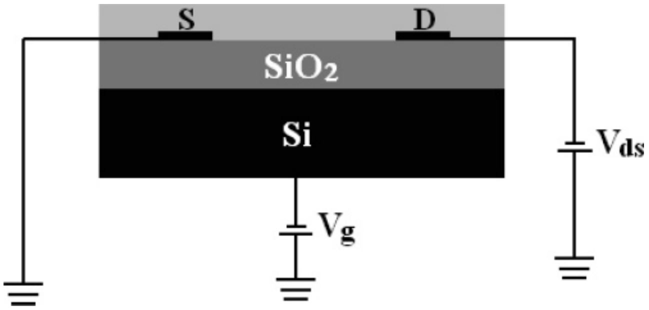

Figure 5. Schematic structure of the LB-film-based OFET device of the electrode.

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 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.

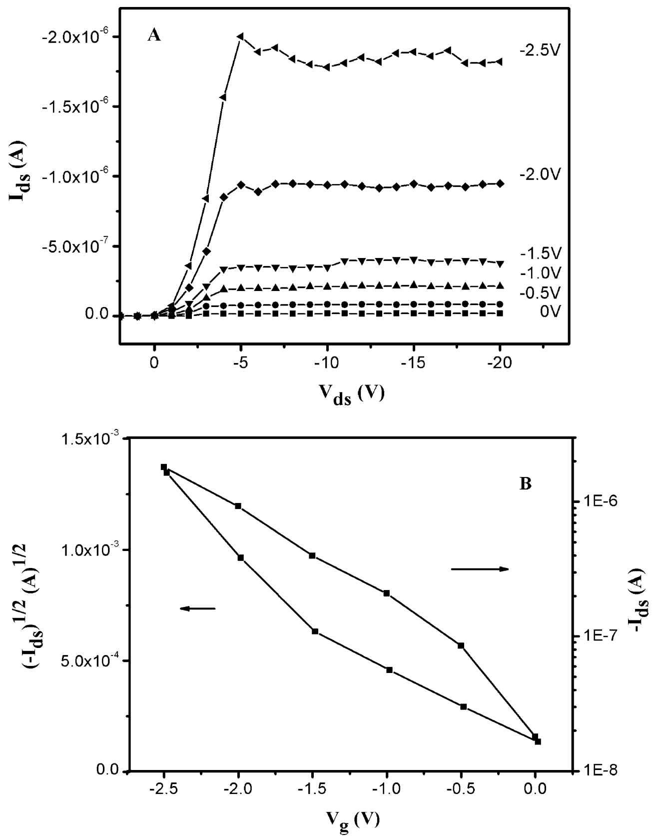

Figure 6. Drain-source current (I_{ds}) versus drain-source voltage (V_{ds}) characteristic at different gate voltage (A) and transfer characteristic at V_{ds} = −18 V (B) for the LB film of **1**.

The OFET devices show typical *p*-channel characteristics as exemplified in Figures 6 and S7−S9 (Supporting Information). The carrier mobility (μ) 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 $[Pc(15C5)_4]M[Pc(15C5)_4]M[Pc(OC_nH_{2n+1})_8]$ (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 $\{Pc[(OC_2H_4)_2OCH_3]_8\}Eu\{Pc[(OC_2H_4)_2OCH_3]_8\}Eu[Pc(OC_nH_{2n+1})_8]$ (**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 $\pi-\pi$ 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 $\pi-\pi$ stacking in the triple-decker molecules themselves

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(23) Zhang, J.; Wang, J.; Wang, H.; Yan, D. *Appl. Phys. Lett.* **2004**, *84*, 142−144.

(24) (a) Kymissis, I.; Dimitrakopoulos, C. D.; Purushothaman, S. *IEEE Trans. Electron Device Lett.* **2001**, *48*, 1060−1064. (b) Gundlach, D. J.; Jia, L. L.; Jackson, T. N. *IEEE Electron Device Lett.* **2001**, *22*, 571−573.

(25) Di, C.; Yu, G.; Liu, Y.; Xu, X.; Wei, D.; Song, Y.; Sun, Y.; Wang, Y.; Zhu, D.; Liu, J.; Liu, X. *J. Am. Chem. Soc.* **2006**, *128*, 16418−16419.

(26) Sze, S. M. *Physics of Semiconductor Devices*; John Wiley & Sons: New York, 1981.

provides the π electrons (as well as holes) with an extensive area 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 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 and preparing molecular materials for OFET devices and in particular 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 α-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 Ag/Ag^+ (0.01 mol dm^{-3}), 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 [$E_{1/2}$ (Fc^+/Fc) = 0.50 V vs SCE]. Typically, a 0.1 mol dm^{-3} solution of $[Bu_4N][ClO_4]$ in CH_2Cl_2 containing 0.5 mmol dm^{-3} of sample was purged with nitrogen for 10 min; then the voltammograms were recorded at ambient temperature. The scan rates were 20 and 10 mV s^{-1} for CV and DPV, respectively.

Chemicals. Anhydrous 1,2,4-trichlorobenzene (TCB) was purchased from Aldrich. Dichloromethane for voltammetric studies was freshly distilled from CaH_2 under nitrogen. Column chromatography was carried out on silica gel (Merck, Kieselgel 60, 70−230 mesh) with the indicated eluents. All of the other reagents and solvents were used as received. The compounds 4,5-dibromo-benzene-1,2-diol,[8a] $Eu(acac)_3{\cdot}H_2O$,[28] and $H_2[Pc(OC_nH_{2n+1})_8]$ (n = 6, 8, 10,12)[18] were prepared according to the published procedures.

Preparation of 2-(2-Methoxy-ethoxy)-ethyl-4-methylbenzosulfonate. To a mixture of 2-(2-methoxy-ethoxy)-ethanol (2.4 g, 0.02 mol) and triethylamine (4 mL, 0.03 mol) in dry CH_2Cl_2 (50 mL) at 0 °C, a suspension solution of 4-toluene sulfonyl chloride (3.8 g, 0.02 mol) in CH_2Cl_2 (20 mL) was added dropwise over 1 h. The mixture was stirred for 2 h at 0 °C and another 0.5 h at room temperature; then 70 mL ether was added. The mixture was filtered, and the filtrate was evaporated under reduced pressure. The residue was purified by silica gel column chromatography with ether as the eluent to give the target compound as a lucid oil (3.9 g, 93%). ^{1}H NMR (300 MHz): ($CDCl_3$) δ 7.90, 7.93 (d, 2 H, benzene ring), 7.45, 7.48 (d, 2 H, benzene ring), 4.27−4.30 (t, 2 H, OCH2), 3.79−3.83 (t, 2H, CH2), 3.67−3.73 (m, 2H, CH_2), 3.51−3.61 (m, 2H, CH_2), 3.22 (s, 3H, OCH_3), 2.35 (s, 3H, CH_3). MS (EI$^+$): M$^+$-45 (229), ($-CH_2OCH_3$); M$^+$-30 (199), ($-OCH_2$); M$^+$-44 (155), ($-OCH_2CH_2$); M$^+$-64 (91), ($-SO_2$). Anal. Calcd For $C_{12}H_{18}O_5S$: C, 52.54; H, 6.61; found: C, 52.46; H, 6.58.

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_2CO_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): ($CDCl_3$) δ 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, 4H, CH_2), 3.54−3.57 (m, 4H, CH_2), 3.38 (s, 6H, OCH_3). MALDI-TOF MS: an isotopic cluster peaking at m/z 494.6, Calcd for $C_{18}H_{24}N_2O_6Na$, [M]$^+$ 495.0. Anal. Calcd For $C_{16}H_{24}Br_2O_6$: C, 40.70; H, 5.12; found: C, 40.68; H, 5.30.

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 solvent was evaporated under reduced pressure, giving a white target compound 4,5-di[poly-(oxyethylene)]phthalonitrile (3.6 g, 28%). ^{1}H NMR (300 MHz): ($CDCl_3$) δ 7.28 (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, 4H, CH_2), 3.54−3.57 (m, 4H, CH_2), 3.39 (s, 6H, OCH_3). MALDI-TOF MS: an isotopic cluster peaking at m/z 387.1, Calcd for $C_{18}H_{24}N_2O_6Na$, [M]$^+$ 387.2. Anal. Calcd For $C_{18}H_{24}N_2O_6$: C, 59.33; H, 6.64; N, 7.69; found: C, 59.02; H, 6.72; N, 7.68.

Preparation of $Eu\{Pc[(OC_2H_4)_2OCH_3]_8\}_2$. A mixture 4,5-di-[poly(oxyethylene)]phthalonitrile (91 mg, 0.25 mmol) and $Eu(acac)_3{\cdot}H_2O$ (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_2H_4) δ 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

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(28) Sitites, J. G.; McCarty, C. N.; Quill, L. L. *J. Am. Chem. Soc.* **1948**, *70*, 3142−3143.

$EuC_{144}H_{192}N_{16}O_{48}$, $[M]^+$ 3067.1; an isotopic cluster peaking at *m/z* 3067.2. Anal. Calcd For $EuC_{144}H_{192}N_{16}O_{48}\cdot 0.5CHCl_3$: C, 55.51; H, 6.21; N, 7.17; found: C, 55.44; H, 6.20; N, 7.38.

General Procedure for the Preparation of {$Pc[(OC_2H_4)_2OCH_3]_8$}Eu{$Pc[(OC_2H_4)_2OCH_3]_8$}Eu[$Pc(OC_nH_{2n+1})_8$] ($n = 6, 8, 10, 12$) (1−4). These compounds were prepared by the raise-by-one-storey procedure. A mixture of $H_2Pc(OC_nH_{2n+1})_8$ (0.01 mmol), $Eu(acac)_3\cdot H_2O$ (5 mg, ca. 0.01 mmol), and $Eu\{Pc[(OC_2H_4)_2OCH_3]_8\}_2$ (30 mg, 0.01 mmol) in TCB was heated to reflux under nitrogen for 4 h. After being cooled to room temperature, the mixture was evaporated under reduced pressure and the residue was chromatographed on a silica gel column. A small amount of unreacted $H_2Pc(OC_nH_{2n+1})_8$ was eluted first with $CHCl_3$ as the eluent. Then, $CHCl_3$/MeOH (2%) was used to develop a blue fraction containing the target triple-deckers **1**−**4**. Repeated chromatography followed by recrystallization from $CHCl_3$ and MeOH/H_2O mixture (1:1) gave pure **1**−**4** as a dark powder in relatively good yield.

{$Pc[(OC_2H_4)_2OCH_3]_8$}Eu{$Pc[(OC_2H_4)_2OCH_3]_8$}Eu[$Pc(OC_6H_{13})_8$] (1). (23 mg, 48%). ^1H NMR (300 MHz): ($CDCl_3$) δ 12.15 (s, 8 H, Pc ring), 9.21 (br s, 8H, Pc ring), 9.15 (br s, 8H, Pc ring), 6.55 (br, 16H, CH_2 of poly(oxyethylene)), 5.80 (br, 8H, CH_2 of poly(oxyethylene)), 5.68 (br, 16H, CH_2 of poly(oxyethylene)), 5.06 (br, 8H, CH_2 of poly(oxyethylene)), 4.96−4.99 (br, 16H, CH_2 of poly(oxyethylene)), 4.70−4.80 (m, 16H, CH_2 of poly(oxyethylene)), 4.48−4.51 (m, 16H, CH_2 of poly(oxyethylene)), 4.24−4.28 (m, 16H, CH_2 of poly(oxyethylene)), 4.04 (s, 24H, CH_3 of poly(oxyethylene)), 3.83−3.95 (m, 16H, CH_2 of poly(oxyethylene)), 3.56 (s, 24H, CH_3 of poly(oxyethylene)), 2.58−2.67 (m, 16H, CH_2 of hexyloxy), 2.08−2.16 (m, 16H, CH_2 of hexyloxy), 1.68−1.80 (m, 48H, $CH_2CH_2CH_2$ of hexyloxy), 1.13−1.18 (m, 24H, CH_3 of hexyloxy). MALDI-TOF MS: Calcd for $C_{224}H_{304}Eu_2N_{24}O_{56}$ (M^+) 4532.9; found *m/z* 4532.4. Anal. Calcd (%) for $C_{224}H_{304}Eu_2N_{24}O_{56}\cdot 0.5CHCl_3$: C, 58.71; H, 6.68; N, 7.32; found: C, 58.71; H, 6.62; N, 7.45.

{$Pc[(OC_2H_4)_2OCH_3]_8$}Eu{$Pc[(OC_2H_4)_2OCH_3]_8$}Eu[$Pc(OC_8H_{17})_8$] (2) (21 mg, 42%). ^1H NMR (300 MHz): ($CDCl_3$) δ 12.15 (s, 8 H, Pc ring), 9.21 (br s, 8H, Pc ring), 9.15 (br s, 8H, Pc ring), 6.55 (br, 16H, CH_2 of poly(oxyethylene)), 5.81 (br, 8H, CH_2 of poly(oxyethylene)), 5.68 (br, 16H, CH_2 of poly(oxyethylene)), 5.06 (br, 8H, CH_2 of poly(oxyethylene)), 4.96−4.99 (br, 16H, CH_2 of poly(oxyethylene)), 4.68−4.79 (m, 16H, CH_2 of poly(oxyethylene)), 4.48−4.51 (m, 16H, CH_2 of poly(oxyethylene)), 4.25−4.28 (m, 16H, CH_2 of poly(oxyethylene)), 4.04 (s, 24H, CH_3 of poly(oxyethylene)), 3.83−3.95 (m, 16H, CH_2 of poly(oxyethylene)), 3.57 (s, 24H, CH_3 of poly(oxyethylene)), 2.57−2.69 (m, 16H, CH_2 of octyloxy), 2.04−2.16 (m, 16H, CH_2 of octyloxy),1.48−1.80 (m, 80H, $CH_2CH_2CH_2$ CH_2CH_2 of octyloxy), 1.13−1.26 (m, 24H, CH_3 of octyloxy); MALDI-TOF MS: Calcd for $C_{240}H_{336}Eu_2N_{24}O_{56}$ (M^+) 4757.3; found *m/z* 4757.4. Anal. Calcd (%) for $C_{240}H_{336}Eu_2N_{24}O_{56}\cdot 0.5CHCl_3$: C, 59.97; H, 7.04; N, 6.98; found: C, 59.96; H, 7.11; N, 6.93.

{$Pc[(OC_2H_4)_2OCH_3]_8$}Eu{$Pc[(OC_2H_4)_2OCH_3]_8$}Eu[$Pc(OC_{10}H_{21})_8$] (3) (20 mg, 38%). ^1H NMR (300 MHz): ($CDCl_3$) δ 12.15 (s, 8 H, Pc ring), 9.21(br s, 8H, Pc ring), 9.15 (br s, 8H, Pc ring), 6.56 (br, 16H, CH_2 of poly(oxyethylene)), 5.81 (br, 8H, CH_2 of poly(oxyethylene)), 5.69 (br, 16H, CH_2 of poly(oxyethylene)), 5.06 (br, 8H, CH_2 of poly(oxyethylene)), 4.96−4.99 (br, 16H, CH_2 of poly(oxyethylene)), 4.68−4.79 (m, 16H, CH_2 of poly(oxyethylene)), 4.48−4.51 (m, 16H, CH_2 of poly(oxyethylene)), 4.25−4.28 (m, 16H, CH_2 of poly(oxyethylene)), 4.04 (s, 24H, CH_3 of poly(oxyethylene)), 3.83−3.95 (m, 16H, CH_2 of poly(oxyethylene)), 3.57 (s, 24H, CH_3 of poly(oxyethylene)), 2.57−2.69 (m, 16H, OCH_2 of decyloxy), 2.05−2.16 (m, 16H, CH_2 of decyloxy),1.36−1.80 (m, 80H, $CH_2CH_2CH_2$ $CH_2CH_2CH_2CH_2$ of decyloxy), 0.90−0.95 (m, 24H, CH_3 of decyloxy); MALDI-TOF MS: Calcd for $C_{256}H_{368}Eu_2N_{24}O_{56}$ (M^+) 4981.7; found *m/z* 4981.6. Anal. Calcd (%) for $C_{256}H_{368}Eu_2N_{24}O_{56}\cdot 0.5CHCl_3$: C, 61.11; H, 7.37; N, 6.67; found: C, 61.23; H, 7.46; N, 6.64.

{$Pc[(OC_2H_4)_2OCH_3]_8$}Eu{$Pc[(OC_2H_4)_2OCH_3]_8$}Eu[$Pc(OC_{12}H_{25})_8$] (4) (17 mg, 32%). ^1H NMR (300 MHz): ($CDCl_3$) δ 12.15 (s, 8 H, Pc ring), 9.21 (br s, 8H, Pc ring), 9.15 (br s, 8H, Pc ring), 6.56 (br, 16H, CH_2 of poly(oxyethylene)), 5.81 (br, 8H, CH_2 of poly(oxyethylene)), 5.69 (br, 16H, CH_2 of poly(oxyethylene)), 5.06 (br, 8H, OCH_2 of poly(oxyethylene)), 4.96−4.99 (br, 16H, CH_2 of poly(oxyethylene)), 4.71−4.79 (m, 16H, CH_2 of poly-(oxyethylene)), 4.48−4.51 (m, 16H, CH_2 in poly(oxyethylene)), 4.25−4.28 (m, 16H, CH_2 of poly(oxyethylene)), 4.04 (s, 24H, CH_3 of poly(oxyethylene)), 3.83−3.95 (m, 16H, CH_2 of poly(oxyethylene)), 3.57 (s, 24H, CH_3 of poly(oxyethylene)), 2.58−2.67 (m, 16H, OCH_2 of dodexyloxy), 2.10−2.13 (m, 16H, CH_2 of dodexyloxy),1.26−1.80 (m, 144H, $CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2$ of dodexyloxy), 0.87−0.91 (m, 24H, CH_3 of dodexyloxy); MALDI-TOF MS: Calcd for $C_{272}H_{400}Eu_2N_{24}O_{56}$ (M^+) 5206.1; found *m/z* 5206.6. Anal. Calcd (%) for $C_{272}H_{400}Eu_2N_{24}O_{56}\cdot 0.5CHCl_3$: C, 62.15; H, 7.67; N, 6.38; found: C, 62.03; H, 7.70; N, 6.47.

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Supporting Information Available: Graphs of experimental and simulated isotopic patterns and electronic absorption and ^1H NMR spectra for compounds in this study. This material is available free of charge via the Internet at http://pubs.acs.org.

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