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Lanthanide(III) Double-Decker Complexes with Octaphenoxy- or Octathiophenoxyphthalocyaninato Ligands – Revealing the Electron-Withdrawing Nature of the Phenoxy and Thiophenoxy Groups in the Double-Decker Complexes

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A series of heteroleptic and homoleptic bis(phthalocyaninato) lanthanide(III) complexes, namely M(Pc)[Pc(OPh)$_8$], M[Pc(OPh)$_8$]$_2$, Eu(Pc)[Pc(SPh)$_8$], and Eu[Pc(SPh)$_8$]$_2$ [M = Eu, Ho, Lu; Pc = unsubstituted phthalocyaninate; Pc(OPh)$_8$ = 2,3,9,10,16,17,23,24-octaphenoxyphthalocyaninate; Pc(SPh)$_8$ = 2,3,9,10,16,17,23,24-octathiophenoxyphthalocyaninate] (**1**–**8**) have been prepared. The molecular structure of Eu[Pc(OPh)$_8$]$_2$ (**4**) has been determined by single-crystal X-ray diffraction analysis. All of the new sandwich compounds have been characterized with various spectroscopic methods. Their electrochemical characteristics show that the introduction of phenoxy or thiophenoxy groups onto the peripheral positions of the phthalocyaninato ligand makes the double-decker harder to oxidize and easier to reduce than the analogous compounds without the (thio)phenoxy group. Theoretical calculations, with the semi-empirical PM3 method, indicate that the change in the energy level of the frontier orbitals of these ligands induced by the electron-withdrawing substituents is responsible for these unusual electrochemical properties.

Introduction

It is well established that bis(phthalocyaninato) metal complexes can serve as molecular materials for electronic devices such as semiconductors, visual displays, and field-effect transistors because of their intriguing electrical and optical properties.[1–3] As the bulk characteristics of molecular materials are closely related to the properties of individual molecules, various modifications have been made on these sandwich compounds with the goal to improve their performance as advanced materials. To facilitate the solution processing fabrication and formation of various mesophases and supramolecular structures, long alkyl chains, oxyethylene chains, or crown-ether units are usually added onto the peripheral or non-peripheral positions of the macrocyclic ligands.[1–3] However, to the best of our knowledge, there has been no report on double-decker complexes that contain phthalocyanine ligands substituted with eight bulky phenoxy groups at either the peripheral or non-peripheral positions. In this paper, we describe the synthesis, structure, spectroscopic, and electrochemical properties of a new series of eight homoleptic and heteroleptic lanthanide(III) complexes with octa-β-phenoxy or thiophenoxy phthalocyaninato ligands. Schematic structures of these compounds are shown in Figure 1.

It is worth noting that the electronic nature of the phenoxy and thiophenoxy groups has been a point of debate. They are usually regarded as an electron-donating group because of their similarity to the alkoxy or thioalkoxy groups,[4] but they can also act as an electron-withdrawing group depending on the nature of the group connected to these substituents.[5] In the present case, electrochemical studies showed that the introduction of eight phenoxy or thiophenoxy groups on the peripheral positions of the phthalocyaninato ligands slightly hinders the oxidation and facilitates the reduction of the resulting double-decker complexes. Similar results have also been previously observed for the metal-free 2(3),9(10),16(17),23(24)-tetraphenoxyphthalocyanine and 2,3,9,10,16,17,23,24-octaphenoxyphthalocyanine.[6] The results also revealed the electron-withdrawing nature of these substituents in the double-decker complexes. This was in agreement with the calculations on the frontier molecular orbitals of the metal-free phthalocyaninato ligands H$_2$Pc, H$_2$Pc(OPh)$_8$, and H$_2$Pc(SPh)$_8$.

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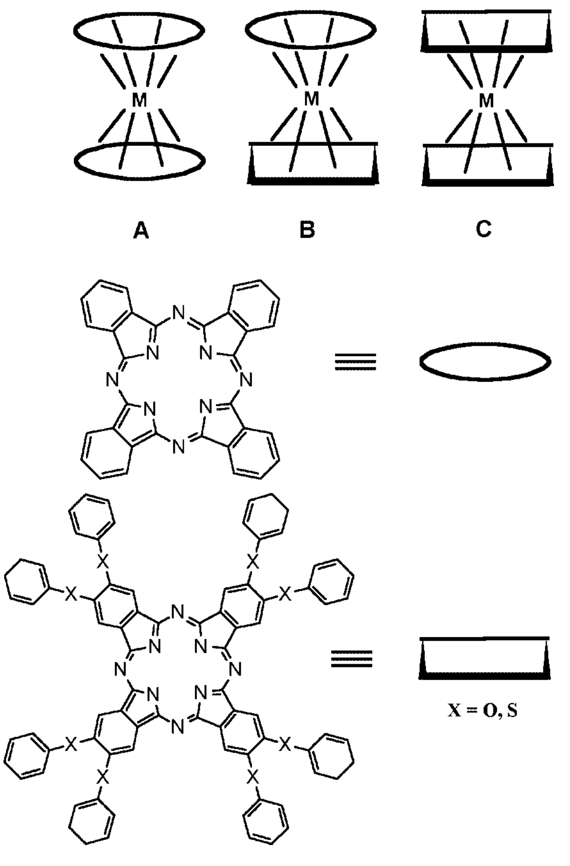

Figure 1. Schematic structures of bis(phthalocyaninato) lanthanide(III) complexes.

Results and Discussion

Synthesis

A substantial number of bis(phthalocyaninato)rare earth complexes have been synthesized and characterized.[1–3] A classical method for the preparation of homoleptic sandwich compounds involves the self-cyclic tetramerization of phthalonitriles in the presence of metal salts, whereas the heteroleptic analogues are usually prepared by the treatment of a rare earth acetate with two different lithium phthalocyaninates.[7–9] To facilitate the preparation and purification, in the present work, heteroleptic double-deckers M(Pc)[Pc(OPh)$_8$] (M = Eu, Ho, Lu) (**1**–**3**) and Eu(Pc)[Pc(SPh)$_8$] (**7**) were obtained by cyclic tetramerization of the corresponding disubstituted phthalonitriles with the half-sandwich compounds M(Pc)(acac) as the template in refluxing *n*-pentanol in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU).[10] It is worth mentioning that half-sandwich phthalocyaninato rare earth complexes M(Pc)(acac) were usually prepared by the reaction of M(acac)$_3$·nH$_2$O with Li$_2$Pc.[1b,1c] We found that M(Pc)(acac) could be easily synthesized and isolated by the treatment of M(acac)$_3$·nH$_2$O with phthalonitrile and DBU in *n*-pentanol at 100 °C for a short period of time (1.5 h). This method could also be applied to substituted phthalonitriles for the preparation of M[Pc(OPh)$_8$](acac) and Eu[Pc(SPh)$_8$](acac) complexes.

For the purpose of comparative studies, homoleptic analogues M[Pc(OPh)$_8$]$_2$ (M = Eu, Ho, Lu) (**4**–**6**) and Eu[Pc(SPh)$_8$]$_2$ (**8**) were also synthesized by the general cyclic tetramerization method.

Spectroscopic Characterization

Satisfactory elemental analyses (Table 1) were obtained for both the heteroleptic and homoleptic double-decker complexes **1**–**8**, which had been repeatedly purified by column chromatography and recrystallization. These new sandwich compounds were also characterized with a range of spectroscopic methods. The MALDI-TOF mass spectra of **1**–**8** showed an intense cluster corresponding to the molecular ion (M$^+$); these data are also given in Table 1.

The electronic absorption data of this series of compounds were measured in CHCl$_3$ and are compiled in Table 2. Typical electronic absorption spectra of heteroleptic and homoleptic bis(phthalocyaninato)rare earth(III) complexes were observed for these newly prepared compounds, and the bands could therefore be assigned in a similar manner. Figure 2 displays the electronic absorption spectra of Eu(Pc)[Pc(OPh)$_8$] (**1**) and Eu[Pc(OPh)$_8$]$_2$ (**4**) as typical examples of the heteroleptic and homoleptic series, together with that of the unsubstituted Eu(Pc)$_2$. Compared with the unsubstituted analogues, almost all of the absorptions of M(Pc)[Pc(OPh)$_8$] (**1**–**3**) and Eu(Pc)[Pc(SPh)$_8$] (**7**) were redshifted when one Pc ring was replaced by the substituted ligand Pc(OPh)$_8$ or Pc(SPh)$_8$. Further redshifts were observed in the electronic absorption spectra of

Table 1. Analytical and mass spectroscopic data for double-decker complexes **1**–**8**.[a]

Compound	M$^+$ [m/z][b]	Analysis [%]		
		C	H	N
Eu(Pc)[Pc(OPh)$_8$] (**1**)	1913.5 (1913.4)	69.79 (70.28)	3.32 (3.38)	11.72 (11.71)
Ho(Pc)[Pc(OPh)]$_8$ (**2**)	1927.9 (1926.8)	69.51 (69.29)	3.50 (3.50)	11.52 (11.44)[c]
Lu(Pc)[Pc(OPh)$_8$] (**3**)	1937.8 (1936.8)	67.45 (67.68)	3.46 (3.26)	11.25 (11.23)[c]
Eu[Pc(OPh)$_8$]$_2$ (**4**)	2651.7 (2651.6)	71.95 (72.49)	3.77 (3.66)	8.36 (8.47)
Ho[Pc(OPh)$_8$]$_2$ (**5**)	2664.2 (2663.5)	70.52 (70.79)	3.71 (3.57)	8.27 (8.23)[c]
Lu[Pc(OPh)$_8$]$_2$ (**6**)	2674.2 (2673.6)	71.87 (71.88)	3.76 (3.62)	8.48 (8.38)[c]
Eu(Pc)[Pc(SPh)$_8$] (**7**)	2042.3 (2042.3)	64.96 (65.06)	3.27 (3.13)	11.05(10.82)[c]
Eu[Pc(SPh)$_8$]$_2$ (**8**)	2907.4 (2907.6)	65.03 (64.97)	3.48 (3.28)	7.76 (7.55)

[a] Calculated values given in parentheses. [b] By MALDI-TOF mass spectrometry. The value corresponds to the most abundant isotopic peak of the molecular ion (M$^+$). [c] For **2**·CH$_3$OH, **3**·1/2CHCl$_3$, **5**·1/2CHCl$_3$, **7**·1/4CHCl$_3$, and **8**·1/2CHCl$_3$.

Table 2. Electronic absorption data for double-decker complexes **1**–**8** in $CHCl_3$.

Compound	λ_{max} [nm] (logε)							
Eu(Pc)[Pc(OPh)$_8$] (**1**)	326 (5.15)	350 (5.02)	485 (4.54)	609 (4.63)	676 (5.27)	909 (3.70)	1399 (3.94)	1612 (4.18)
Ho(Pc)[Pc(OPh)]$_8$ (**2**)	323(5.11)	349(4.99)	472(4.50)	604(4.59)	669(5.31)	917(3.76)	1410(4.18)	1609(3.93)
Lu(Pc)[Pc(OPh)$_8$] (**3**)	321(5.11)	347(5.02)	466(4.52)	600(4.57)	665(5.34)	913(3.85)	1410(4.19)	1526(3.82)
Eu[Pc(OPh)$_8$]$_2$ (**4**)	331 (5.20)	365 (5.17)	500 (4.58)	614 (4.76)	681 (5.34)	909 (3.79)	–	1654 (4.05)
Ho[Pc(OPh)$_8$]$_2$ (**5**)	328(5.13)	362(5.14)	492(4.53)	608(4.68)	674(5.33)	917(3.81)	1410(4.28)	1617(4.07)
Lu[Pc(OPh)$_8$]$_2$ (**6**)	326(5.15)	361(5.18)	484(4.58)	605(4.69)	670(5.39)	911(3.92)	1410(4.28)	1526(4.01)
Eu(Pc)[Pc(SPh)$_8$] (**7**)	327(5.08)	–	452(4.54)	624(4.68)	694(5.25)	924(3.62)	1658(4.11)	1858(3.87)
Eu[Pc(SPh)$_8$]$_2$ (**8**)	311(5.12)	341(5.09)	450(4.72)	646(4.88)	715(5.23)	949(3.71)	1847(5.00)	2030(4.12)

M[Pc(OPh)$_8$]$_2$ (**4**–**6**) and Eu[Pc(SPh)$_8$]$_2$ (**8**) as a result of the replacement of the second Pc ring by Pc(OPh)$_8$ or Pc(SPh)$_8$ (Table 2). It is worth noting that in comparison with those of the alkoxy-substituted bis(phthalocyaninato)europium counterparts, namely Eu(Pc)[Pc(OC_5H_{11})$_8$][10a] and Eu[Pc(OC_5H_{11})$_8$]$_2$,[10d] a significant redshift takes place in the main absorption band in the near IR range of the thiophenoxy-substituted double-decker compounds **7** and **8**. In contrast, an insignificant shift was observed for the same band of phenoxy-substituted double-decker compounds **2** and **3**.

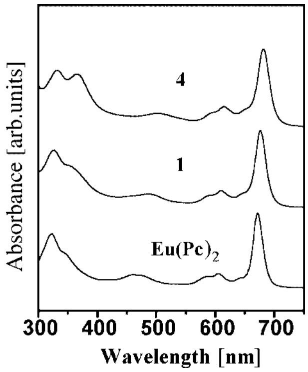

Figure 2. UV/Vis spectra of Eu(Pc)$_2$, Eu(Pc)[Pc(OPh)$_8$] (**1**), and Eu[Pc(OPh)$_8$]$_2$ (**4**) in $CHCl_3$.

IR spectroscopy is a very useful tool for the characterization of the phthalocyaninato ligand in sandwich tetrapyrrole complexes.[11] The IR spectra of **1**–**8** shows a medium-to-strong band in the range of 1317–1326 cm^{-1}, as observed for M(Pc)$_2$ (M = Eu, Ho, Lu), which is a diagnostic marker band for the phthalocyanine π-radical anions Pc$^{\cdot-}$, [Pc(OPh)$_8$]$^{\cdot-}$, and [Pc(SPh)$_8$]$^{\cdot-}$.

Upon the addition of hydrazine hydrate as a reducing agent,[12,13] well-resolved ^{1}H NMR spectra were obtained for the reduced form of bis(phthalocyaninato)lanthanide(III) complexes **1**–**8**, in which both the macrocyclic ligands become diamagnetic dianions. Figure 3 shows the ^{1}H NMR spectrum of the reduced form of **7**. For this heteroleptic compound, the non-peripheral and peripheral protons of the unsubstituted phthalocyaninato ligand resonate at δ = 11.08 and 9.09 ppm, respectively, as two relatively broad signals, whereas the non-peripheral protons of the substituted phthalocyanine ring resonate as a singlet at δ = 10.79 ppm. Three well-resolved signals at δ = 8.79–8.82 (doublet), 8.29–8.34 (triplet), and 8.07–8.12 (triplet) ppm in the ratio of 2:2:1 are shown for the thiophenoxy *ortho*, *meta*, and *para* protons, respectively. The observation of only one group of signals for the pairs of *ortho* and *meta* protons of the thiophenoxy group suggests that the thiophenoxy group is relatively free to rotate along the C_{ipso}–S bond in the double-decker complex under these conditions. Similar results were observed for phenoxy analogues **1**–**6**. This is in contrast to the restricted rotation of the aryl groups of *meso*-tetraarylporphyrinato ligands in double-decker complexes M(Por)(Ring) [Por = *meso*-tetrakis(4-chlorophenyl)porphyrinate (TClPP), *meso*-tetrakis(4-*tert*-butylphenyl)porphyrinate (TBPP); Ring = general phthalocyaninate (Pc′), general naphthalocyaninate (Nc′)].[12,14,15] This could be due to the lower steric hindrance of the additional *O*/*S* atom.

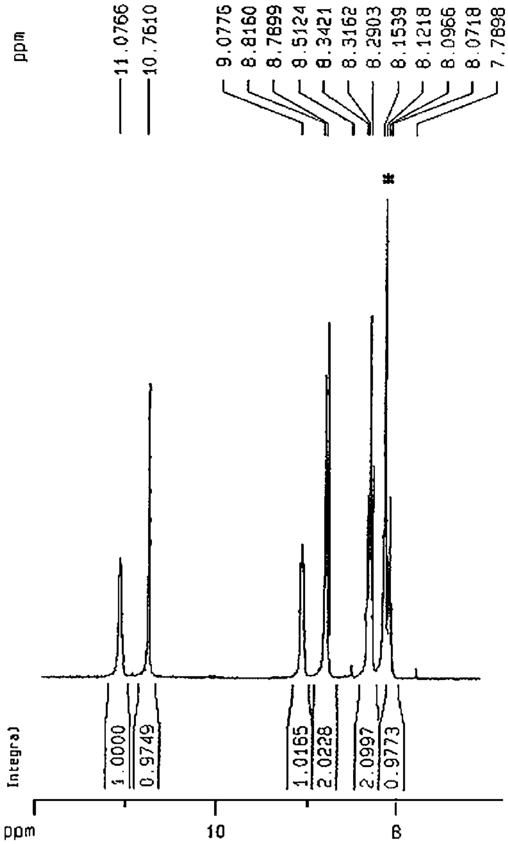

Figure 3. ^{1}H NMR spectrum of the reduced form of Eu(Pc)[Pc(SPh)$_8$] (**7**) in $CDCl_3$/[D$_6$]DMSO (1:1) which contains ca. 1% hydrazine hydrate; * indicates residual $CHCl_3$.

Structural Studies

Single crystals of Eu[Pc(OPh)$_8$]$_2$ (**4**) for X-ray diffraction analysis were obtained by the slow diffusion of MeOH into a THF solution of this compound. Unfortunately, the quality of the crystals was not high enough to obtain a suitable X-ray structure. Even when the data were collected at –150 °C, the R_1 value (0.1854) was still relatively high. This might be related to the disorder of the phenoxy groups. According to this set of data, the compound crystallizes in the orthorhombic system with eight double-decker molecules per unit cell. Figure S1 (Supporting Information) shows the molecular structure of **4** from two different perspectives. The europium center is octa-coordinated by the isoindole nitrogen atoms of the two octaphenoxyphthalocyaninato ligands with an average Eu–N bond length of 2.439 Å, and forms a square antiprism. The two N_4 mean planes are virtually parallel (dihedral angle = 0.4°) with a plane-to-plane separation of 2.851 Å with the europium atom lying in the center between the two ligands. In a similar structure to that of other bis(tetrapyrrole)rare earth double-decker complexes, such as Ce(Pc)(TPyP),[12] the two ligands are not planar and display a saucer shape. The extent of ligand deformation, as defined by the average dihedral angle φ of the individual isoindole rings with respect to the corresponding N_4 mean plane, is 7.2°. The twist angle, which is defined as the rotation angle of one ring away from the eclipsed conformation of the two rings, is close to 45° for this complex; this shows that the two ligands are almost fully staggered. This staggered orientation probably acts to minimize the nonbonding interactions between the two substituted phthalocyanines.

Electrochemical Properties

The electrochemical behavior of compounds **1**–**8** was examined by cyclic voltammetry (CV) and by differential pulse voltammetry (DPV), and the results are summarized in Table 3. For comparison, the data for the unsubstituted analogue Eu(Pc)$_2$ were also listed.[16] For all these complexes, one to two quasi reversible one-electron oxidation(s) and four to five quasi reversible one-electron reductions were revealed. The first oxidation and the first reduction processes involve the removal of an electron from and the addition of an electron to the singly occupied molecular orbital, respectively. Comparison of the first oxidation potentials and the first reduction potentials among the set M(Pc)$_2$, M(Pc)[Pc(OPh)$_8$], and M[Pc(OPh)$_8$]$_2$, and among the set Eu(Pc)$_2$, Eu(Pc)[Pc(SPh)$_8$], and Eu[Pc(SPh)$_8$]$_2$, reveals that the incorporation of the eight phenoxy or thiophenoxy groups on the phthalocyanine ring makes the compounds slightly harder to oxidize and easier to reduce than the analogous compounds without the (thio)phenoxy group. These results are in contrast to those found for alkoxy- or alkyl-substituted phthalocyanines, which clearly reveal the electron-withdrawing nature of these phenoxy and thiophenoxy substituents on the phthalocyaninato ligand.[16]

According to our calculations on the frontier molecular orbitals, with the semi-empirical PM3 method, the introduction of eight phenoxy or thiophenoxy groups on the peripheral positions of the phthalocyaninato ligand results in a decrease in the energy of the HOMO of the macrocycle ligand (Figure 4). As a result, these substituents at the peripheral positions of the phthalocyaninato ligand act mainly as electron-withdrawing groups and make this macrocyclic ligand harder to oxidize and easier to reduce.

On the basis of previous discussions, the interactions between the two rings of the monomer cause a splitting of their π-HOMO and π-LUMO, which results in a decrease in the energy of the HOMO and LUMO of the bis(phthalocyaninato)europium double-decker complexes.[16,17] This is supported by the experimental results. As shown in Table 3, the halfwave potentials for the first oxidation and reduction potentials (Oxd$_1$ and Red$_1$), which involve the HOMO of the double-decker complexes, are shifted in the more positive direction along with the increase in the number of Pc(OPh)$_8$ or Pc(SPh)$_8$ ligands from M(Pc)$_2$, M(Pc)[Pc(OPh)$_8$], to M[Pc(OPh)$_8$]$_2$ or from Eu(Pc)$_2$, Eu(Pc)[Pc(SPh)$_8$], to Eu[Pc(SPh)$_8$]$_2$, whereas the potentials for the second and third reductions, Red$_2$ and Red$_3$, which now involve the LUMO of these compounds, are also shifted in the positive direction in the same order.

The effect of the size of the rare earth metal is demonstrated, again, by the fact that the halfwave potentials for the first oxidation and for the first reduction of M(Pc)[Pc(OPh)$_8$] and M[Pc(OPh)$_8$]$_2$ are slightly shifted in the negative direction as the radius of the rare earth metal decreases in the order Eu, Ho, Lu (Table 3).[16]

Table 3. Halfwave redox potentials for double-decker complexes **1**–**8** in CH_2Cl_2 which contains 0.1 M [NBu$_4$][ClO$_4$].

	O_2	O_1	R_1	R_2	R_3	R_4	R_5	$\Delta E°_{1/2}$[b]
Eu(Pc)[Pc(OPh)$_8$] (**1**)	+1.61	+0.63	+0.20	–1.00	–1.31	–1.67	–	0.43
Ho(Pc)[Pc(OPh)]$_8$ (**2**)	–	+0.56	+0.12	–1.02	–1.32	–1.62	–1.83[c]	0.44
Lu(Pc)[Pc(OPh)$_8$] (**3**)	+1.69	+0.52	+0.07	–1.04	–1.36	–1.72	–	0.45
Eu[Pc(OPh)$_8$]$_2$ (**4**)	+1.59	+0.70	+0.26	–0.96	–1.24	–1.63	–	0.44
Ho[Pc(OPh)$_8$]$_2$ (**5**)	+1.60	+0.61	+0.16	–0.98	–1.28	–1.66	–	0.45
Lu[Pc(OPh)$_8$]$_2$ (**6**)	+1.62	+0.58	+0.13	–0.99	–1.29	–1.73	–	0.45
Eu(Pc)$_2$[a]	+1.59	+0.55	+0.12	–1.06	–1.29	–1.54[c]	–1.70[c]	0.43
Eu(Pc)[Pc(SPh)$_8$] (**7**)	+1.57	+0.64	+0.22	–0.90	–1.25	–1.57	–1.77[c]	0.42
Eu[Pc(SPh)$_8$]$_2$ (**8**)	+1.52	+0.67	+0.30	–0.84	–1.08	–1.48[c]	–1.79[c]	0.37

[a] Data taken from ref.[16]. [b] $\Delta E°_{1/2}$ is the potential difference between the first oxidation and the first reduction processes. [c] Recorded by DPV.

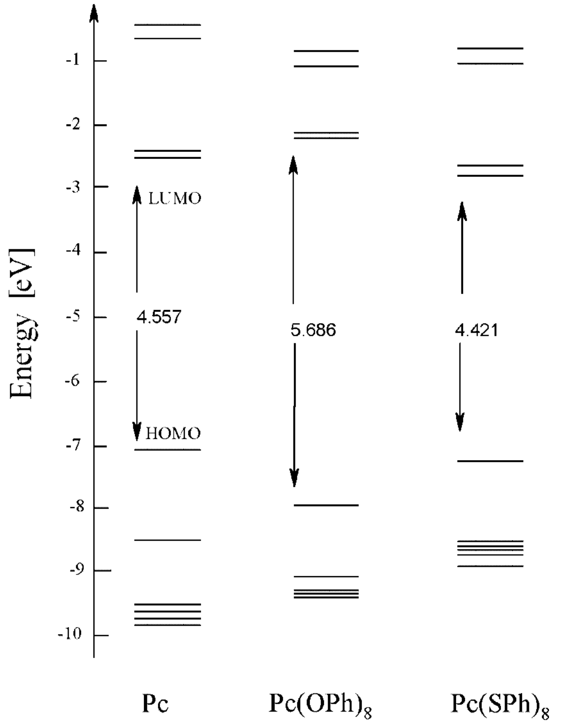

Figure 4. Partial energy diagram of H_2Pc, $H_2Pc(OPh)_8$, and $H_2Pc(SPh)_8$ obtained from theoretical calculations with the PM3 method.

Conclusions

A series of lanthanide(III) double-decker complexes with the octaphenoxy- or octathiophenoxyphthalocyaninato ligand were synthesized and characterized. Their solution structures were investigated by ^1H NMR spectroscopy, which indicated that the phenoxy and thiophenoxy substituents are relatively free to rotate along the C_{ipso}–O or C_{ipso}–S bonds. Their electrochemical characteristics revealed that these substituents are electron-withdrawing when connected to the peripheral positions of the phthalocyanine ring. This conclusion was supported by the theoretical calculations on the energy levels of the frontier molecular orbitals of the corresponding phthalocyaninato ligands.

Experimental Section

General: Hexanes and *n*-pentanol were distilled from anhydrous $CaCl_2$ and sodium, respectively. Phthalonitriles and the electrolyte $[Bu_4N][ClO_4]$ were recrystallized from toluene and acetone, respectively. Dichloromethane for voltammetric studies was freshly distilled from CaH_2 under a nitrogen atmosphere. Column chromatography was carried out on silica gel (Merck, Kieselgel 60, 70–230 mesh) with the indicated eluents. All other reagents and solvents were of reagent grade and used as received. The compounds $M(acac)_3 \cdot nH_2O$,[18] 4,5-bis(phenoxy)phthalonitrile,[19] and 4,5-bis(thiophenoxy)phthalonitrile[19] were prepared according to the literature methods.

The UV/Vis and near-IR spectra were obtained with a Hitachi U-4100 spectrophotometer. IR spectra (KBr pellets) were recorded with a BIORAD FTS-165 spectrometer. MALDI-TOF mass spectra were recorded with a Bruker APEX47e ultra-high resolution Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer with α-cyano-4-hydroxycinnamic acid as the matrix. Elemental analyses were performed by the Institute of Chemistry, Chinese Academy of Sciences. ^1H NMR spectra were measured with a Bruker DPX 300 spectrometer in $CDCl_3/[D_6]DMSO$ (1:1) in the presence of ca. 1% (by volume) hydrazine hydrate. Spectra were referenced internally with residual DMSO (δ = 2.49 ppm).

Electrochemical measurements were carried out with a BAS CV-50W voltammetric analyzer. The cell comprised inlets for a glassy carbon disk working electrode of 2.0 mm in diameter and a silver-wire counter electrode. The reference electrode was Ag/Ag^+, which was connected to the solution by a Luggin capillary whose tip was placed close to the working electrode. The electrode was corrected for junction potentials by being referenced internally to the ferrocenium/ferrocene (Fe^+/Fe) couple [$E_{1/2}$ (Fe^+/Fe) = 501 mV 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, the voltammograms were then recorded at ambient temperature. The scan rates were 20 and 10 $mV\,s^{-1}$ for CV and DPV, respectively.

The frontier molecular orbital energy calculations for unsubstituted and substituted phthalocyanines were carried out with the semi-empirical PM3 method.[20] The input structures of $H_2[Pc(OPh)_8]$ and $H_2[Pc(SPh)_8]$ were derived from the optimized geometry of metal free H_2Pc.[21] All calculations were carried out with the Gaussian98W program.[22]

X-ray Crystallography: Crystal data and details of data collection and structure refinement for **3** are given in Table S1 (Supporting Information). Data were collected with a Bruker SMART CCD diffractometer with an Mo-K_α sealed tube (λ = 0.71073 Å) at –150 °C, with a ω scan mode and an increment of 0.3°. Preliminary unit cell parameters were obtained from 300 frames. Final unit cell parameters were derived by global refinements of reflections obtained from the integration of all the frame data. The collected frames were integrated with the preliminary cell-orientation matrix. The SMART software was used for collecting frames of data, indexing reflections and determination of lattice constants; SAINT-PLUS for integration of intensity of reflections and scaling;[23] SADABS for absorption correction;[24] and SHELXL for space group and structure determination, refinements, graphics and structure reporting.[25] All the H atoms in these compounds were obtained geometrically. These H atoms were included in the subsequent least-squares refinement as fixed contributors. The final refinement with anisotropic temperature factors for non-H atoms led to R = 0.1854 for compound **4**.

General Procedure for the Preparation of Heteroleptic M(Pc)[Pc(OPh)$_8$] (1–3) and Eu(Pc)[Pc(SPh)$_8$] (7): A mixture of $M(acac)_3 \cdot nH_2O$ (93 mg, 0.20 mmol), phthalonitrile (102 mg, 0.80 mmol), and DBU (20 mg, 0.13 mmol) in *n*-pentanol (3 mL) was heated at 100 °C for 1.5 h under a slow stream of nitrogen to yield the half-sandwich compound M(Pc)(acac). The resulting blue solution was cooled to room temperature. The crude product was precipitated by the addition of hexanes into the solution and purified by chromatography with $CHCl_3$/MeOH (1:1) as the eluent (94 mg, 48%). The obtained product, M(Pc)(acac) (76 mg, 0.10 mmol), was mixed with DBU (20 mg, 0.13 mmol) and 4,5-bis(phenoxy)phthalonitrile (124 mg, 0.40 mmol) or 4,5-bis(thiophenoxy)phthalonitrile (137 mg, 0.40 mmol) in *n*-pentanol (3 mL), and the resulting mixture was heated at reflux for 8 h. The volatiles were removed under reduced pressure to afford a dark green residue which was chromatographed with $CHCl_3$/MeOH (9:1) as the eluent. A small amount of metal-free phthalocyanine $H_2Pc(OPh)_8$ or $H_2Pc(SPh)_8$ was collected first, and then the heteroleptic product $M(Pc)[Pc(OPh)_8]$ or $Eu(Pc)[Pc(SPh)_8]$ was developed. Repeated chromatography followed by recrystallization from $CHCl_3$ and MeOH afforded pure $M(Pc)[Pc(OPh)_8]$ (**1**–**3**) or $Eu(Pc)[Pc(SPh)_8]$ (**7**) as a darkish-blue powder with a yield of ca. 30%. It is noteworthy that these heteroleptic double-decker complexes could also be prepared from the reaction of $M[Pc(OPh)_8](acac)$ or $M[Pc(SPh)_8](acac)$ with phthalonitrile by the same procedure.

$Eu(Pc)[Pc(OPh)_8]$ (1): 56 mg, 28%. ^1H NMR (300 MHz, $CDCl_3$/[D$_6$]DMSO): δ = 11.22–11.28 (m, 8 H, Pc-H), 10.67 (s, 8 H, Pc*-H), 9.00–9.06 (m, 8 H, Pc-H), 8.46 (d, J = 7.8 Hz, 16 H, Ph-H$_o$), 8.22 (t, J = 7.8 Hz, 16 H, Ph-H$_m$), 7.80 (t, J = 7.8 Hz, 18 H, Ph-H$_p$) ppm.

$Ho(Pc)[Pc(OPh)_8]$ (2): 53 mg, 26%. ^1H NMR (300 MHz, $CDCl_3$/[D$_6$]DMSO): δ = 4.17 (s, 18 H, Ph-H$_p$), 3.85 (s, 16 H, Ph-H$_m$), 0.34 (s, 16 H, Ph-H$_o$), –1.71 (br. s, 8 H, Pc-H), –8.98 (br. s, 8 H, Pc-H or Pc*-H), –10.26 (br. s, 8 H, Pc-H or Pc*-H) ppm.

$Lu(Pc)[Pc(OPh)_8]$ (3): 61 mg, 29%. ^1H NMR (300 MHz, $CDCl_3$/[D$_6$]DMSO): δ = 9.02 (s, 8 H, Pc-H), 8.39 (s, 8 H, Pc*-H), 8.06 (s, 8 H, Pc-H), 7.74 (s, 16 H, Ph-H$_o$), 7.55 (s, 16 H, Ph-H$_m$), 7.43 (s, 18 H, Ph-H$_p$) ppm.

$Eu(Pc)[Pc(SPh)_8]$ (7): 64 mg, 30%. ^1H NMR (300 MHz, $CDCl_3$/[D$_6$]DMSO): δ = 11.08 (s, 8 H, Pc-H), 10.76 (s, 8 H, Pc*-H), 9.08 (s, 8 H, Pc-H), 8.82 (d, J = 7.8 Hz, 16 H, Ph-H$_o$), 8.29 (t, J = 7.6 Hz, 16 H, Ph-H$_m$), 8.12 (t, J = 7.5 Hz, 18 H, Ph-H$_p$) ppm.

General Procedure for the Preparation of Homoleptic $M[Pc(OPh)_8]_2$ (4–6) and $Eu[Pc(SPh)_8]_2$ (8): A mixture of $M(acac)_3 \cdot nH_2O$ (47 mg, 0.10 mmol), 4,5-bis(phenoxy)phthalonitrile (248 mg, 0.80 mmol) or 4,5-bis(thiophenoxy)phthalonitrile (274 mg, 0.80 mmol), and DBU (20 mg, 0.13 mmol) in *n*-pentanol (3 mL) was heated at reflux for 8 h under a slow stream of nitrogen. The volatiles were removed under reduced pressure to give a dark green residue, which was chromatographed with $CHCl_3$ as the eluent. Repeated chromatography followed by recrystallization from $CHCl_3$ and MeOH afforded $M[Pc(OPh)_8]_2$ (**4**–**6**) or $Eu[Pc(SPh)_8]_2$ (**8**) as darkish-blue crystals with the yield of ca. 40%.

$Eu[Pc(OPh)_8]_2$ (4): 127 mg,43%. ^1H NMR (300 MHz, $CDCl_3$/[D$_6$]-DMSO): δ = 10.79 (s, 16 H, Pc*-H), 8.00 (d, J = 7.8 Hz, 32 H, Ph-H$_o$), 7.75 (t, J = 7.8 Hz, 32 H, Ph-H$_m$), 7.43 (t, J = 7.8 Hz, 16 H, Ph-H$_p$) ppm.

$Ho[Pc(OPh)_8]_2$ (5): 119 mg, 40%. ^1H NMR (300 MHz, $CDCl_3$/[D$_6$]DMSO): δ = 4.65 (s, 16 H, Ph-H$_p$), 4.39 (s, 32 H, Ph-H$_m$), 1.04 (s, 32 H, Ph-H$_o$), –9.74 (s, 16 H, Pc*-H) ppm.

$Lu[Pc(OPh)_8]_2$ (6): 107 mg, 36%. ^1H NMR (300 MHz, $CDCl_3$/[D$_6$]DMSO): δ = 8.58 (s, 16 H, Pc*-H), 7.41 (t, J = 7.7 Hz, 32 H, Ph-H$_o$), 7.19 (t, J = 8.5 Hz, 32 H, Ph-H$_m$), 7.13 (s, 16 H, Ph-H$_p$) ppm.

$Eu[Pc(SPh)_8]_2$ (8): 135 mg, 42%. ^1H NMR (300 MHz, $CDCl_3$/[D$_6$]DMSO): δ = 10.47 (s, 16 H, Pc*-H), 8.24 (d, J = 7.8 Hz, 32 H, Ph-H$_o$), 7.83 (t, J = 7.6 Hz, 32 H, Ph-H$_m$), 7.68 (t, J = 7.3 Hz, 16 H, Ph-H$_p$) ppm.

Supporting Information (see footnote on the first page of this article): Molecular structure of $Eu[Pc(OPh)_8]_2$ (**4**) from two different perspectives for all non-hydrogen atoms and crystallographic data for $Eu[Pc(OPh)_8]_2$ (**4**).

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