Synthetic, Structural, Spectroscopic, and Electrochemical Studies of Heteroleptic Tris(phthalocyaninato) Rare Earth Complexes

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Three heteroleptic tris(phthalocyaninato) rare-earth triple-decker complexes [(Pc)M(Pc)M{Pc(α-$OC_5H_{11})_4$}] [M = Sm, Gd, Lu; Pc = phthalocyaninate; Pc(α-$OC_5H_{11})_4$ = 1,8,15,22-tetrakis(3-pentyloxy)phthalocyaninate] have been prepared as racemic mixtures by treating [M{Pc(α-$OC_5H_{11})_4$}(acac)], generated in situ, with the bis(phthalocyaninato) rare-earth double-decker complex [M$(Pc)_2$] in refluxing *n*-octanol. The molecular structures of the gadolinium and lutetium complexes have been determined by single-crystal X-ray diffraction analysis, both of which adopt the asymmetrical structure [(Pc)M(Pc)M{Pc(α-$OC_5H_{11})_4$}]. The outer Pc and Pc(α-$OC_5H_{11})_4$ rings are significantly domed, while the inner Pc ring is essentially planar. The ring-to-ring separation between the two adjacent Pc rings, as defined by the two N_4 mean planes, diminishes from [(Pc)Gd(Pc)Gd{Pc(α-$OC_5H_{11})_4$}] to [(Pc)Lu(Pc)Lu{Pc(α-$OC_5H_{11})_4$}] as a result of the smaller Lu^{III} ion. The decreased molecular symmetry for these complexes has also been revealed by the NMR spectra of the samarium and lutetium analogs, in which four sets of signals appear for the inner Pc ring protons due to the special disposition of the neighboring Pc(α-$OC_5H_{11})_4$ ring. Electrochemical studies have revealed four one-electron oxidations and up to five one-electron reductions for these complexes. The dependence of the phthalocyanine Q band as well as the first and second oxidation potentials on the size of the metal center indicates that substantial π-π interactions are present in these compounds.

Introduction

While monomeric chiral porphyrin and phthalocyanine derivatives have received increasing research interest in the past years,[1] chiral, sandwich-type tetrapyrrole metal complexes, however, still remain extremely rare.[2–4] Recently, we have reported a series of heteroleptic bis(phthalocyaninato) rare-earth complexes [M(Pc){Pc(α-$OC_5H_{11})_4$}] (M = Y, Sm–Lu) with a C_4 molecular symmetry.[5] As part of our continuing efforts in this regard, we have devised and prepared a new series of heteroleptic tris(phthalocyaninato) rare-earth triple-decker complexes [(Pc)M(Pc)M{Pc(α-$OC_5H_{11})_4$}] (M = Sm, Gd, Lu; Figure 1). In this paper, we report in detail the synthesis, structures, spectroscopic properties, and electrochemistry of these novel complexes. Due to the introduction of four 3-pentyloxy groups at the α-position of the outer Pc(α-$OC_5H_{11})_4$ ring, and the sandwich triple-decker molecular structure, these compounds are also intrinsically chiral in nature. However, due to the very small difference between the two enantiomers, they could not be separated and these triple-decker complexes have been found to exist as a pair of enantiomers co-crystallizing in the monoclinic *C*2/*c* system.

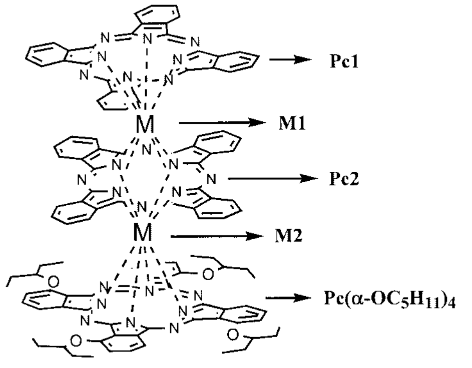

Figure 1. A schematic structure of the heteroleptic rare-earth triple-decker complexes [(Pc)M(Pc)M{Pc(α-$OC_5H_{11})_4$}] (**1**–**3**).

It is also worth pointing out that tris(phthalocyaninato) rare-earth triple-deckers were first briefly characterized by

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mass spectroscopy in the 1980s.[6] Since then, both homoleptic and especially the heteroleptic complexes developed very recently have attracted increasing research interest as good systems to study the interactions between two 4f electronic systems in an isolated environment and as a new category of single molecular magnets.[7a,7b,8] To the best of our knowledge, only a very few tris(phthalocyaninato) triple-deckers have been structurally characterized, including the homoleptic tris[tetra(15-crown-5)phthalocyaninato]lutetium compound $[Lu_2\{Pc(15\text{-}C\text{-}5)_4\}_3]$ reported by Troyanov et al.[9] and the heteroleptic $[(Pc)M\{Pc(OC_8H_{17})_8\}M'(Pc)]$ (M = Er, M′ = Lu; M = M′ = Er or Lu) reported by us.[7c] The present work adds the structural data of the intrinsically chiral $[(Pc)M(Pc)M\{Pc(\alpha\text{-}OC_5H_{11})_4\}]$ [M = Gd (**2**), Lu (**3**)]. These novel systems will also be of interest for further studies.

Results and Discussion

Synthesis of $[(Pc)M(Pc)M\{Pc(\alpha\text{-}OC_5H_{11})_4\}]$ [M = Sm (1), Gd (2), Lu (3)]

Two synthetic pathways have been reported to prepare heteroleptic rare earth(III) triple-decker complexes with two different kinds of phthalocyaninato ligands [(Pc′)M(Pc′)M(Pc′′)] or [(Pc′)M(Pc′′)M(Pc′)] (Pc′ ≠ Pc′′ = general phthalocyaninate). The first method involves the reaction between the monomeric [M(Pc′)X] and the metal-free H_2Pc'' in a suitable ratio. This method has only been applied to prepare the lutetium triple-decker $[(Pc)Lu\{Pc(15\text{-}C\text{-}5)_4\}Lu(Pc)]$.[10] The second pathway involves treatment of the monomeric [M(Pc′)X] with the double-decker $[M(Pc'')_2]$. This method has been generally utilized to prepare a series of different kinds of tris(phthalocyaninato) rare-earth compounds recently,[7,8] and is also a convenient and efficient methodology to prepare mixed (porphyrinato)(phthalocyaninato) rare-earth triple-deckers, including $[M_2(Pc')_2(Por)]$ and $[M_2(Pc')(Por)_2]$ (Por = general porphyrinate).[11] In the present work, we employed the second methodology, using $[M\{Pc(\alpha\text{-}OC_5H_{11})_4\}(acac)]$ (M = Sm, Gd, Lu), generated in situ from the corresponding $[M(acac)_3]\cdot nH_2O$ (M = Sm, Gd, Lu) and metal-free $H_2Pc(\alpha\text{-}OC_5H_{11})_4$, and $[M(Pc)_2]$ as starting materials. Reaction of $[M\{Pc(\alpha\text{-}OC_5H_{11})_4\}(acac)]$ with the corresponding $[M(Pc)_2]$ in refluxing *n*-octanol led to the heteroleptic triple-deckers $[(Pc)M(Pc)M\{Pc(\alpha\text{-}OC_5H_{11})_4\}]$ (M = Sm, Gd, Lu) in relatively good yields (24–42%). The reaction yield of these compounds is dependent on the size of the metal center: the yield is higher for lanthanides with a moderate size such as Sm and Gd, while the late lanthanide Lu analog gave a lower yield (Table 1). This result is in good accord with the trend observed for the mixed (porphyrinato)(phthalocyaninato) rare-earth triple-deckers $[M_2(Pc)_2(TClPP)]$ and $[M_2(Pc)(TClPP)_2]$ [TClPP = 5,10,15,20-tetrakis(4-chlorophenyl)porphyrinate].[12]

Spectroscopic Characterization

All the three new heteroleptic triple-deckers **1**–**3** were characterized by elemental analysis and various spectroscopic methods. Table 1 summarizes the analytical and mass spectroscopic data. The MALDI-TOF mass spectra of these compounds clearly show intense signals for the molecular ion $[M]^+$ or protonated molecular ion $[MH]^+$.

The diamagnetic lutetium(III) triple-decker $[(Pc)Lu(Pc)Lu\{Pc(\alpha\text{-}OC_5H_{11})_4\}]$ (**3**) gives a well-resolved ^1H NMR spectrum in $CDCl_3$. As shown in the ^1H-^1H COSY spectrum (Figure 2), the four most downfield signals (the doublets at $\delta = 9.07$ and 8.86 ppm, and the triplets at $\delta = 8.71$ and 8.64 ppm) are inter-correlated and can be attributed to one of the Pc rings. The other Pc rings' protons resonate as two typical AA′BB′ multiplets at $\delta = 8.48$–8.50 and 8.00–8.03 ppm. The appearance of two sets of signals for the Pc rings confirms that the compound adopts an unsymmetrical structure, i.e. $[(Pc)Lu(Pc)Lu\{Pc(\alpha\text{-}OC_5H_{11})_4\}]$. The former set of signals is tentatively assigned to the inner Pc ring as it is expected that the C_{4h} symmetry of the $Pc(\alpha\text{-}OC_5H_{11})_4$ ring may impose a different environment to its neighboring ring protons, leading to four different signals. The remaining three aromatic signals from $\delta = 7.3$ to 7.9 ppm are clearly due to the ring protons of $Pc(\alpha\text{-}OC_5H_{11})_4$.

The aliphatic protons' signals can also be assigned unambiguously with the help of the ^1H-^1H COSY spectrum (Figure 2). The virtual quintet at $\delta = 4.46$ ppm is due to the OCH proton, and the two multiplets at $\delta = 2.12$–2.22 and 2.33–2.42 ppm can be ascribed to one set of the two diastereotopic methylene protons, which are correlated with the methyl protons resonating as a virtual triplet at $\delta = 1.50$ ppm. The other set of methylene protons resonates as a quintet at $\delta = 1.68$ ppm and its neighboring methyl protons resonate as a triplet at $\delta = 0.53$ ppm. These results clearly show that a lowering of the symmetry of triple-decker complexes gives rise to more NMR signals.

Table 1. Analytical and mass spectroscopic data for the heteroleptic triple-deckers **1**–**3**.[a]

Compound	Yield [%]	$[M^+]$ or $[MH^+]$ [*m*/*z*]	Analysis [%][b]		
			C	H	N
$[(Pc)Sm(Pc)Sm\{Pc(\alpha\text{-}OC_5H_{11})_4\}]$ (**1**)	40	2182.8 (2182.9)[b]	62.55 (62.39)[d]	4.04 (3.98)[d]	14.91 (14.99)[d]
$[(Pc)Gd(Pc)Gd\{Pc(\alpha\text{-}OC_5H_{11})_4\}]$ (**2**)	42	2197.6 (2197.7)[c]	60.75 (60.35)[e]	3.97 (3.99)[e]	13.67 (14.32)[e]
$[(Pc)Lu(Pc)Lu\{Pc(\alpha\text{-}OC_5H_{11})_4\}]$ (**3**)	24	2233.3 (2233.1)[c]	59.95 (59.39)[f]	4.21 (4.18)[f]	12.39 (13.46)[f]

[a] Calculated values given in parentheses. [b] Mass corresponding to the most abundant isotopic peak of the molecular ion $[M^+]$. [c] Mass corresponding to the most abundant isotopic peak of the protonated molecular ion $[MH^+]$. [d] Contains 0.5 equiv. of $CHCl_3$. [e] Contains 1.0 equiv. of $CHCl_3$ and 1.0 equiv. of CH_3OH. [f] Contains 1.5 equiv. of $CHCl_3$ and 1.0 equiv. of $n\text{-}C_6H_{14}$.

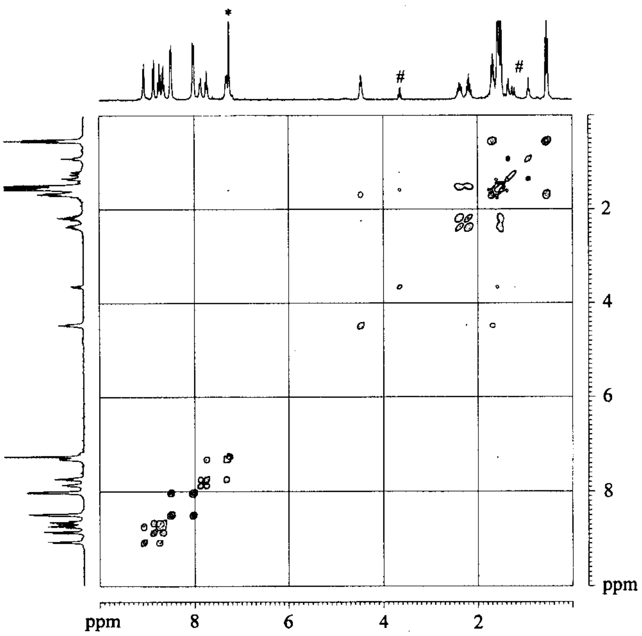

Figure 2. ^1H-^1H COSY spectrum of [(Pc)Lu(Pc)Lu{Pc(α-O-C_5H_{11})$_4$}] (**3**) in $CDCl_3$. The signals due to residual $CHCl_3$ and some impurities are denoted as * and #, respectively.

The ^1H NMR spectrum of the samarium(III) analog **1** shows similar spectral features, but some of the aromatic signals are overlapped and assignment could only be made by 2D NMR techniques. The total correlation spectroscopy (TOCSY)[13] spectrum (Figure S1a; see Supporting Information), in which the cross peaks indicate correlations between protons that belong to a common spin-system, is particularly useful. The spectrum clearly reveals that the two multiplets at δ = 7.92–7.97 and 7.62–7.69 ppm are correlated and can be assigned to the H_α and H_β protons of the outer Pc ring, respectively. The triplet at δ = 7.80 ppm, multiplet at δ = 7.62–7.69 ppm (overlapped with the outer Pc-H_β protons' signals), and the two doublets at δ = 7.52 and 7.11 ppm belong to a common spin system and can be attributed to the inner Pc ring. The multiplet at δ = 7.24–7.34 ppm contains overlapping signals for residual $CHCl_3$ and two sets of aromatic signals for Pc(α-OC_5H_{11})$_4$, which are correlated with the doublet at δ = 6.99 ppm. These correlations and the assignments are in agreement with the ^1H-^1H COSY spectrum (see Figure S1b in the Supporting Information).

The electronic absorption and MCD data of this series of compounds were measured in $CHCl_3$ and are shown in Figure 3. In general, the metal-dependent spectral features are analogous to those reported for related compounds [(Pc)M{Pc(OC_8H_{17})$_8$}M{Pc(OC_8H_{17})$_8$}],[7a] and thus could be assigned in the same manner. All the spectra of **1**–**3** show a typical Soret band at about 335 nm with a shoulder at the higher energy side at around 295 nm. The phthalocyanine Q bands appear around 643–652 nm as a very strong absorption with a weak satellite around 695–723 nm. Along with the decrease in the rare-earth ionic size from Sm to Lu, the Soret band for the three triple-deckers remains almost unchanged. In contrast, the main Q absorption band undergoes a blue shift and the satellite Q band is shifted to the red.

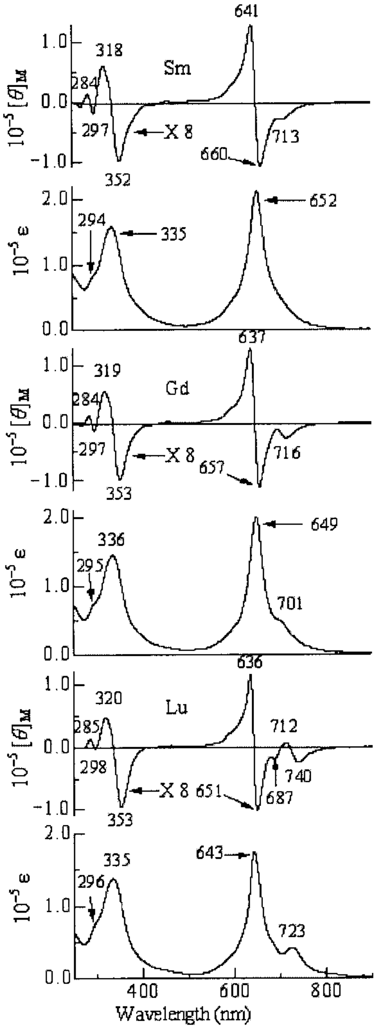

Figure 3. Electronic absorption and MCD spectra of [(Pc)M-(Pc)M{Pc(α-OC_5H_{11})$_4$}] (**1**–**3**) in $CHCl_3$.

The MCD spectra of **1**–**3** are different from those of the symmetrical mono(phthalocyaninato) metal and bis(phthalocyaninato) rare-earth complexes in that splitting of the absorption bands appears in the Q-band region. It is also different from that of H_2Pc in that the MCD spectra clearly show the presence of pseudo Faraday-*A* terms. A symmetrical and intense pseudo *A* term is observed for **1**–**3** at 643–652 nm. Another unsymmetrical and weaker *A* term is also observed corresponding to the second Q band at 695–723 nm, which is well resolved for the Lu compound. In the Soret region, two symmetrical and weak pseudo *A* terms appear in the MCD spectra of **1**–**3**, corresponding to the Soret band at about 335 nm and its shoulder at around 295 nm. In the case of a cofacial eclipsed Pc dimer of low symmetry,[14] it has previously been found that both the electronic absorption and MCD spectra do not reflect the symmetry of the constituent Pc units. As shown by the X-ray structures (to be discussed in the following section), compounds **1**–**3** have C_s symmetry so that Faraday *A* terms are not expected theoretically. However, since pseudo Faraday *A* terms are observed in Figure 3, we can further conclude that the absorption and MCD spectra of cofacial trimers do not reflect the molecular symmetry.

Structural Studies

Single crystals of [(Pc)M(Pc)M{Pc(α-OC_5H_{11})$_4$}] [M = Gd (**2**), Lu (**3**)] suitable for X-ray diffraction analysis were obtained by slow diffusion of MeOH into the corresponding $CHCl_3$ solutions. These compounds crystallize in the monoclinic system with a *C*2/*c* space group, but unfortunately two pairs of enantiomeric triple-decker molecules are contained in each unit cell,. Attempts to resolve the two enantiomers of the these triple-deckers by HPLC using a silica gel column coated with cellulose 2,3,6-tris(3,5-dimethylphenylcarbamate) were not successful due to the very small differences between the two enantiomers. The crystal structure of these compounds also contained solvated chloroform molecules, which come from the solvents used for recrystallization. The gadolinium and lutetium compounds have similar crystal structures.

The molecular structure of [(Pc)Gd(Pc)Gd{Pc(α-OC_5H_{11})$_4$}] (**2**) is shown in Figure 4. Each gadolinium ion is sandwiched between an outer phthalocyanine ligand, Pc or Pc(α-OC_5H_{11})$_4$, and the inner Pc ring. However, the two gadolinium ions in this compound are not exactly identical

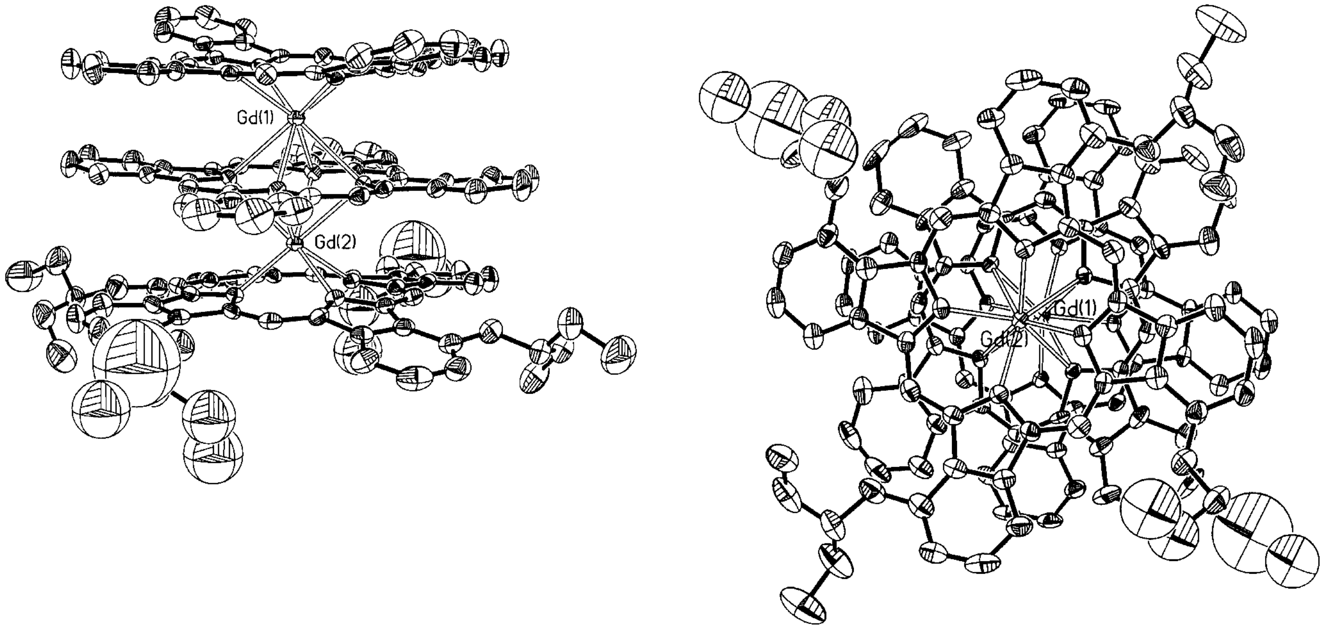

Figure 4. Molecular structure of [(Pc)Gd(Pc)Gd{Pc(α-OC_5H_{11})$_4$}] (**2**) in two different perspective views showing the 30% probability thermal ellipsoids for all non-hydrogen atoms.

Table 2. Comparison of the structural data for **2** and **3**.

	2	**3**
Average M1–N(Pc1) bond length [Å]	2.386	2.297
Average M1–N(Pc2) bond length [Å]	2.634	2.588
Average M2–N(Pc2) bond length [Å]	2.654	2.588
Average M2–N[Pc(α-OC_5H_{11})$_4$] bond length [Å]	2.364	2.307
M1–N_4(Pc1) plane distance [Å]	1.301	1.198
M1–N_4(Pc2) plane distance [Å]	1.765	1.721
M2–N_4(Pc2) plane distance [Å]	1.795	1.722
M2–N_4[Pc(α-OC_5H_{11})$_4$] plane distance [Å]	1.243	1.174
Interplanar distance N_4(Pc1)–N_4(Pc2)(Å)	3.067	2.920
Interplanar distance N_4(Pc2)–N_4 [Pc(α-OC_5H_{11})$_4$] [Å]	3.034	2.896
Dihedral angle between N_4(Pc1)–N_4(Pc2) [°]	0	0
Dihedral angle between N_4(Pc2)–N_4[Pc(α-OC_5H_{11})$_4$]	0	0
Average dihedral angle φ for the Pc1 ring [°][a]	9.1	10.1
Average dihedral angle φ for the Pc2 ring [°][a]	1.2	1.35
Average dihedral angle φ for the Pc(α-OC_5H_{11})$_4$ ring [°][a]	9.2	10.45
Average twist angle between Pc1 ring and Pc2 ring [°][b]	46.4	44.35
Average twist angle between Pc2 ring and Pc(α-OC_5H_{11})$_4$ ring [°][b]	41.4	47.5

[a] The average dihedral angle of the individual isoindole rings with respect to the corresponding N_4 mean plane. [b] Defined as the rotation angle of one ring away from the eclipsed conformation of the two rings.

in terms of the distance from the inner and outer phthalocyanine ligands because of the difference in the ring-to-ring interaction between the inner and the two different outer phthalocyanine rings (Table 2). Both the outer Pc and Pc(α-OC_5H_{11})$_4$ rings adopt conformations that are domed toward the gadolinium cations (φ = 9.1 and 9.2°). The two unsubstituted Pc rings connected by Gd1 are rotated by an angle of 46.4°, and the central Pc and the outer Pc(α-OC_5H_{11})$_4$ ligands connected by Gd2 are rotated by 41.4°. The coordination polyhedra of both Gd1 and Gd2 are therefore a slightly distorted square antiprism. The displacements of the two gadolinium ions with respect to the three isoindole–nitrogen mean planes are Gd1–N_4(Pc1) = 1.295 Å, Gd1–N_4(Pc2) = 1.762 Å, Gd2–N_4(Pc2) = 1.800 Å, and Gd2–N_4[Pc(α-OC_5H_{11})$_4$] = 1.247 Å. The average Gd1–N(Pc1) bond length (2.376 Å) is significantly shorter than the average Gd1–N(Pc2) distance (2.634 Å), and the Gd2–N[Pc(α-OC_5H_{11})$_4$] (2.363 Å) bond length is shorter than Gd2–N(Pc2) (2.659 Å), as the central phthalocyanine ligand (Pc2) is shared by two gadolinium ions rather than one metal ion for the outer Pc1 or Pc(α-OC_5H_{11})$_4$ ligand. Similar data were obtained for the lutetium triple-decker **3**.

Electrochemical Properties

The redox behavior of the heteroleptic triple-deckers **1**–**3** was studied by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in CH_2Cl_2. All the compounds exhibit four quasi-reversible one-electron oxidations and up to five quasi-reversible one-electron reductions, which can be attributed to the successive removal of electrons from, and addition of electrons to, the ligand-based orbitals, respectively. Figure 5 shows the voltammograms for [(Pc)Lu(Pc)Lu{Pc(α-OC_5H_{11})$_4$}] (**3**), which are typical for the other rare-earth counterparts. Table 3 collects the half-wave potentials of all these processes for these triple-deckers. As can be seen, while the half-wave potentials of the third and fourth oxidations of [(Pc)M(Pc)M{Pc(α-OC_5H_{11})$_4$}] remain virtually unchanged, the half-wave potentials of the first and second oxidations correlate linearly with the ionic size of the rare-earth metal center and are slightly shifted in the cathodic direction with a decrease in the rare-earth ionic size. The half-wave potentials of all the reductions for **1**–**3** appear to reveal no systematic trends with ionic radius. The potential difference between Oxd_1 and Red_1 ($\Delta E_{1/2}$) for the three heteroleptic triple-deckers **1**–**3** is also dependent on the central rare-earth ionic size, diminishing from 1.02 V for the Sm compound to 0.84 V for the Lu analog, indicating an increase in the ring-to-ring π-π interaction in the same order.[15]

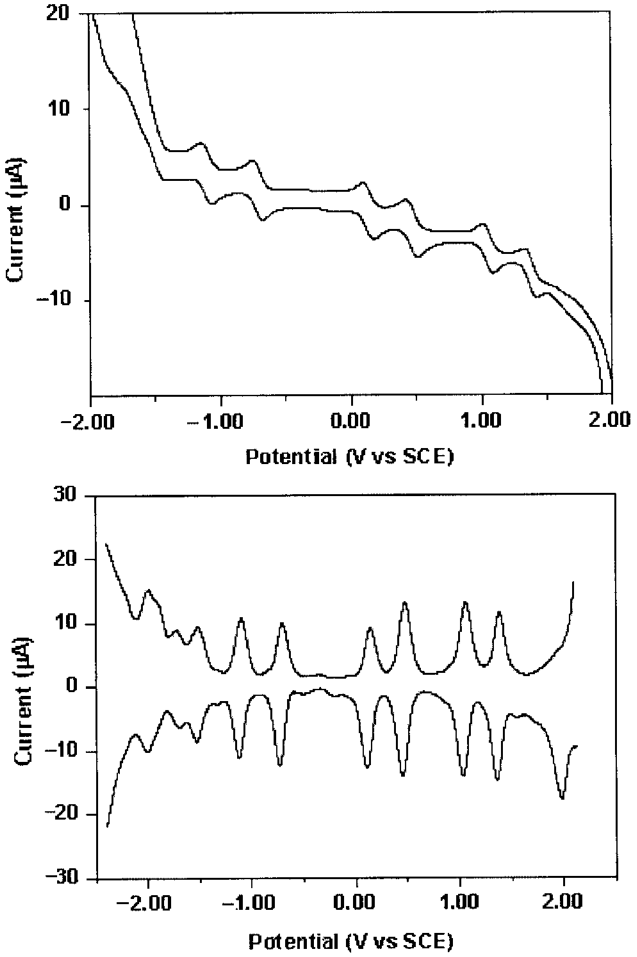

Figure 5. Cyclic voltammogram and differential pulse voltammogram of [(Pc)Lu(Pc)Lu{Pc(α-OC_5H_{11})$_4$}] (**3**) in CH_2Cl_2 containing 0.1 M [Bu_4N][ClO_4] at a scan rate of 20 and 10 mV s^{-1}, respectively.

Conclusions

In summary, we have prepared novel heteroleptic tris(phthalocyaninato) rare-earth complexes [(Pc)M(Pc)M{Pc(α-OC_5H_{11})$_4$}] (M = Sm, Gd, Lu) as racemic mixtures. The compounds have been fully characterized by vari-

Table 3. Half-wave redox potentials of **1**–**3** (mV vs. SCE) in CH_2Cl_2 containing 0.1 M TBAP.

	Oxd_4	Oxd_3	Oxd_2	Oxd_1	Red_1	Red_2	Red_3	Red_4	Red_5	$\Delta E^{o}_{1/2}$[a]
1	1.39 (74)[b]	1.10 (66)[b]	0.64 (66)[b]	0.32 (68)[b]	–0.70 (66)[b]	–1.09 (74)[b]	–1.42 (73)[c]	–1.62[c]	–1.84[c]	1.02
2	1.37 (78)[b]	1.06 (75)[b]	0.57 (64)[b]	0.25 (66)[b]	–0.72 (64)[b]	–1.11 (70)[b]	–1.45 (76)[c]	–1.61[c]		0.97
3	1.38 (81)[b]	1.06 (76)[b]	0.48 (62)[b]	0.13 (68)[b]	–0.71 (64)[b]	–1.11 (74)[b]	–1.52 (75)[c]	–1.71[c]	–1.93[c]	0.84

[a] $\Delta E^{o}_{1/2}$ is the potential difference between the first oxidation and first reduction processes, i.e. the HOMO–LUMO gap of the corresponding molecules. [b] Cathodic to anodic peak separation given in parentheses [mV] relative to the value of 60 mV for Fe^+/Fe. [c] Recorded by DPV.

ous spectroscopic and electrochemical methods. The molecular structures of the Gd and Lu analogs with a lower molecular symmetry have also been determined by X-ray diffraction analysis and NMR spectroscopy. Introduction of four 3-pentyloxy groups onto the α-positions of one outer phthalocyanine ring in the tris(phthalocyaninato)-rare-earth compounds induces a chirality in the resulting triple-decker molecules. Trials on the separation of the two enantiomers have not yet been successful.

Experimental Section

General: *n*-Pentanol and *n*-octanol were distilled from over sodium. Hexane used for chromatography was distilled from anhydrous $CaCl_2$. Column chromatography was carried out on silica gel columns (Merck, Kieselgel 60, 70–230 mesh) with the indicated eluents. Dichloromethane for voltammetric studies was freshly distilled from CaH_2 under nitrogen. All other reagents and solvents were used as received. The compounds 3-(3-pentyloxy)phthalonitrile,[16] $H_2Pc(\alpha\text{-}OC_5H_{11})_4$,[17] $M(acac)_3{\cdot}nH_2O$,[18] and $Li_2(Pc)$[19] were prepared according to the literature procedures.

Electronic absorption spectra were recorded on a Hitachi U-4100 spectrophotometer. Magnetic circular dichroism (MCD) spectra were recorded on a Jasco J-725 spectrodichrometer, with a Jasco electromagnet that produces a magnetic field of up to 1.09 T. The magnitude of this was expressed in terms of molecular ellipticity per tesla, $[\theta]_M/\text{deg}\,\text{dm}^3\,\text{mol}^{-1}\,\text{cm}^{-1}\,\text{T}^{-1}$. MALDI-TOF mass spectra were recorded on a Bruker BIFLEX III ultra-high 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 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. It 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 M solution of $[Bu_4N][ClO_4]$ in CH_2Cl_2 containing 0.5 mM of sample was purged with nitrogen for 10 min, then the voltammograms were recorded at ambient temperature. The scan rate was 20 and 10 mV s^{-1} for CV and DPV, respectively.

General Procedure for the Preparation of Triple-Decker Complexes 1–3: In a typical procedure, a mixture of $M(acac)_3{\cdot}nH_2O$ (M = Sm, Gd, Lu) (25 mg, ca. 0.05 mmol) and phthalonitrile (39 mg, 0.30 mmol) in *n*-pentanol (4 cm^3) was heated at 140 °C under nitrogen for about 8 h. The solvent was then removed in vacuo and the residue was subjected to chromatography on a silica gel column using $CHCl_3$ as eluent. The double-decker complex $M(Pc)_2$ was isolated and further purified by recrystallization from a mixture of $CHCl_3$/MeOH. The complex $M(Pc)_2$ (60 mg, ca. 0.05 mmol) was then treated with $M(acac)_3{\cdot}nH_2O$ (M = Sm, Gd, Lu) (25 mg, ca. 0.05 mmol) and metal-free phthalocyanine $H_2Pc(\alpha\text{-}OC_5H_{11})_4$ (43 mg, 0.05 mmol) in refluxing *n*-octanol (5 cm^3) for 3 h. After cooling to room temperature, the mixture was evaporated under reduced pressure and the residue was chromatographed on a silica gel column using $CHCl_3$ as eluent. Following two green fractions containing a small amount of $H_2Pc(\alpha\text{-}OC_5H_{11})_4$ and $M(Pc)_2$, respectively, a blue band containing the target heteroleptic triple-deckers $[(Pc)M(Pc)M\{Pc(\alpha\text{-}OC_5H_{11})_4\}]$ was developed, which was collected and the solvents evaporated. The crude product was purified by repeated chromatography followed by recrystallization from $CHCl_3$/MeOH or hexane, giving black needles.

X-ray Crystallography: Crystal data and details of data collection and structure refinement are given in Table 4. Data were collected on a Bruker SMART CCD diffractometer with an Mo-K_α sealed tube (λ = 0.71073 Å) at 293 K, using a ω-scan mode with an increment of 0.3°. Preliminary unit-cell parameters were obtained from 45 frames. Final unit-cell parameters were derived by global refinements of reflections obtained from integration of all the frame data. The collected frames were integrated using 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,[20] SADABS for absorption correction,[21] and SHELXL for space group and structure determination, refinements, graphics, and structure reporting.[22] 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 values of 0.0726–0.0757 for these compounds.

Table 4. Crystallographic data for **2** and **3**.

	2·2CHCl$_3$	**3**·2CHCl$_3$
Formula	$C_{118}H_{90}Cl_6Gd_2N_{24}O_4$	$C_{118}H_{90}Cl_6Lu_2N_{24}O_4$
M_r	2435.34	2470.78
Crystal size [mm^3]	0.23 × 0.17 × 0.11	0.32 × 0.28 × 0.13
Crystal system	monoclinic	monoclinic
Space group	*C*2/*c*	*C*2/*c*
a [Å]	17.521(12)	17.366(14)
b [Å]	21.717(14)	21.293(19)
c [Å]	30.90(2)	30.58(3)
β [°]	106.472(13)	106.470(13)
V [Å]	11273(13)	10843(17)
Z	4	4
F(000)	4912	4968
$D_{calcd.}$ [Mg·m^{-3}]	1.435	1.514
μ [mm^{-1}]	1.373	2.025
Data collection range [°]	1.53 to 25.00	1.39 to 25.00
Reflections collected	28196	28229
Independent reflections	9919 [R_{int} = 0.0783]	9566 [R_{int} = 0.0935]
parameters	695	690
R_2 [$I > 2\sigma(I)$]	0.0757	0.0726
wR_2 [$I > 2\sigma(I)$]	0.2051	0.2014
Goodness of fit	1.088	1.030

CCDC-239882 (for **2**) and -239883 (for **3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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