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Mixed (Phthalocyaninato)(Porphyrinato) Rare Earth Double-Decker Complexes with C_4 Chirality: Synthesis, Resolution, and Absolute Configuration Assignment

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Mixed (phthalocyaninato)(porphyrinato) rare earth double-decker complexes [HM^{III}{$Pc(\alpha$-3-$OC_5H_{11})_4$}{TOAPP}] [$Pc(\alpha$-3-$OC_5H_{11})_4$ = 1,8,15,22-tetrakis(3-pentyloxy)-phthalocyaninate; TOAPP = meso-tetrakis(4-octylamino-phenyl)porphyrinate; M = Y (**1**), Ho (**2**)] were prepared as a racemic mixture by treating metal-free phthalocyanine $H_2Pc(\alpha$-3-$OC_5H_{11})_4$ with half-sandwich complexes [M^{III}(acac)(TOAPP)], generated in situ from $M(acac)_3 \cdot nH_2O$ and H_2TAPP [TAPP = meso-tetrakis(4-amino-phenyl)porphyrinate], in refluxing 1-octanol. The obtained double-deckers were characterized by elemental analysis and various spectroscopic methods. The molecular structures of **1** and **2** were determined by single-crystal X-ray diffraction analysis. The compounds crystallize in the triclinic system with a pair of enantiomeric double-deckers per unit cell. Resolution of **1** and **2** was achieved using a chiral HPLC technique combined with the formation of their diastereomeric mixture using L-Boc-Phe-OH as the chiral resolving agent, yielding for the first time the pure diastereoisomers of chiral mixed (phthalocyaninato)(porphyrinato) rare earth double-decker complexes with C_4 symmetry. The absolute configuration of these chiral complexes was assigned by comparing the experimental circular dichroism spectrum with a simulated one on the basis of time-dependent density functional theory calculations.

Introduction

Chiral porphyrinic compounds are abundant in living systems as photoreaction centers (chlorophyll),[1] redox and rearrangement catalysts (cytochrome and vitamin B_{12}),[2] and oxygen carriers (hemoglobin).[3] Due to their fundamental importance in many biological processes, chiral porphyrins (Pors) have been extensively studied in view of biomimetic synthetic models,[4−6] in which the Por units play essential roles as light-harvesting antennae,[4] electron and energy donors and acceptors,[4,5] and selective coordination and recognition sites.[4h,5d,5g,5k,5n,6] In addition, as the most important artificial analogues of Pors, chiral phthalocyanines (Pcs) have also attracted increasing attention over the past two decades.[7−9] Chiral Pcs with chiral carbons in the side chains,[8] optically active aromatic units,[9] and planar asymmetry[7b] have been synthesized and reported.

On the other hand, considerable effort has been focused on the investigation of sandwich-type phthalocyaninato and porphyrinato metal complexes due to their intriguing

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structures, properties, and potential applications in material science.[10−12] However, to the best of our knowledge, chiral sandwich tetrapyrrole metal complexes still remain extremely rare. Aida and co-workers synthesized and realized the resolution for D_2-chiral bis(porphyrinato) cerium and zirconium double-decker complexes.[13] The ligand rotation for the reduced and oxidized forms of these compounds was studied using optical activity as a probe.[13c] Shinkai et al. induced optical activity in bis(porphyrinato) cerium double-decker complexes through positive homotropic allosterism by hydrogen bonding between chiral dicarboxylic acids or saccharides and the pyridyl nitrogen atoms of bis[tetrakis(4-pyridyl)porphyrinato] cerium.[14] Simon reported the synthesis and characterization of the first chiral heteroleptic (phthalocyaninato)(naphthalocyaninato) lutetium(III) double-decker complex [Lu^{III}(Pc)(Nc*)] (Nc* = the Cs isomer of 1,2-naphthalocyaninate) as a racemic mixture.[15]

We are motivated to design and prepare new chiral sandwich-type phthalocyaninato and porphyrinato rare earth complexes with a view to creating novel applications in material science and catalysis. Very recently, the first optically active mixed (phthalocyaninato)(porphyrinato) rare earth complexes [HM^{III}{Pc-$(OBNP)_2$}(TClPP)] [M = Y and Eu; Pc-$(OBNP)_2$ = binaphthylphthalocyaninate, TClPP = meso-tetrakis(4-chlorophenyl)porphyrinate] were prepared by this group.[16] The chirality was induced in the

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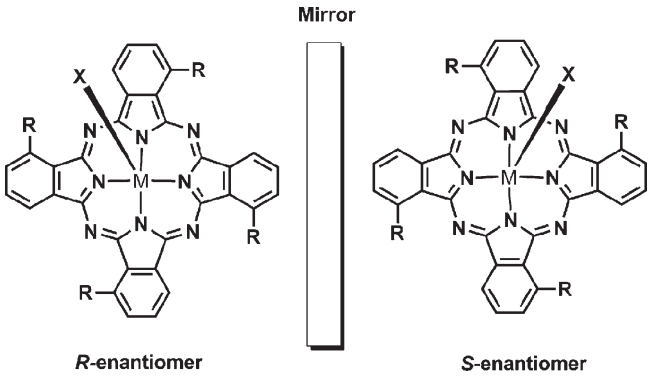
Chart 1. Schematic Structures of the Two Enantiomers of 1,8,15,22-Tetra-Substituted Phthalocyaninato Metal Complex with C_4 Chirality



sandwich double-decker compounds by nonperipheral linked (*R*)- and (*S*)-binaphthol substituents at the Pc ligand. Another strategy toward chiral sandwich-type tetrapyrrole rare earth complexes involves utilization of the 1,8,15,22-tetrakis-(alkoxy)-substituted phthalocyanine ligand with C_{4h} symmetry.[8b,17] As shown in Chart 1, this tetrapyrrole ligand possesses a single-handed rotational arrangement of the substituted pattern, actually two enantiotopic faces. As a result, attachment of the entity on either side of the Pc ring will eliminate the mirror plane of C_{4h} symmetry and lead to chiral molecules with a C_4[7b] or even further decreased symmetry, C_2 or C_1. With this in mind, a series of novel chiral complexes containing this Pc ligand, such as monomeric phthalocyaninato lead(II) complexes [Pb{Pc(α-OR)$_4$}] (R = 3-pentyloxy, 2,4-dimethyl-3-pentyloxy, 2-naphthyloxy),[18] heteroleptic bis(phthalocyaninato) rare earth double-deckers [M(Pc){Pc(α-3-OC_5H_{11})$_4$}] (M = Y, Sm−Lu),[19] heteroleptic tris(phthalocyaninato) rare earth triple-deckers [(Pc)M(Pc)M{Pc(α-3-OC_5H_{11})$_4$}] (M = Sm, Gd, and Lu),[20] and mixed (phthalocyaninato)(porphyrinato) rare earth double-deckers [HM^{III}{Pc(α-3-OC_5H_{11})$_4$}{TClPP}] and [M^{III}{Pc(α-3-OC_5H_{11})$_4$}{TClPP}] (M = Sm, Eu, Y),[12d] have been prepared. The molecular chirality with C_4 symmetry of these molecules was clearly revealed by single-crystal X-ray diffraction analysis. However, attempts to resolve these compounds by chiral high-performance liquid chromatography (HPLC) were unsuccessful due to their limited solubility in hexane-containing solvent systems and the limited scope of chiral HPLC columns available. In the present paper, we describe the synthesis and first resolution of mixed (phthalocyaninato)(porphyrinato) rare earth double-decker complexes [HM^{III}{Pc(α-3-OC_5H_{11})$_4$}{TOAPP}] [M = Y (**1**), Ho (**2**)] with C_4 symmetry, by using a chiral HPLC technique combined with the formation of their diastereomeric mixture, utilizing L-Boc-Phe-OH as the chiral resolving agent. The absolute configurations of these C_4-chiral complexes were assigned by comparing experimental circular dichroism (CD) spectra with the simulated one on the basis of time-dependent density functional theory (TD-DFT).

Results and Discussion

Synthesis and Characterization of [HM^{III}{Pc(α-3-OC_5H_{11})$_4$}{TOAPP}] [M = Y (1), Ho (2)]. The synthesis of mixed (phthalocyaninato)(porphyrinato) rare earth double-decker complexes [HM^{III}{Pc(α-3-OC_5H_{11})$_4$}{TOAPP}] (M = Y (**1**), Ho (**2**)) involves the prior generation of the half-sandwich complexes [M^{III}(acac)(TOAPP)] from [M(acac)$_3$·nH$_2$O] and [H$_2$TAPP],[21] followed by treatment with metal-free phthalocyanine [H$_2$Pc(α-3-OC_5H_{11})$_4$], Scheme 1. It is worth noting that the reaction produces a mixture of the neutral form [M^{III}{Pc(α-3-OC_5H_{11})$_4$}{TOAPP}] and protonated form [HM^{III}{Pc(α-3-OC_5H_{11})$_4$}{TOAPP}] of the target compounds.[12d,16] The neutral form of this type of double-decker is less stable than the protonated species. For easy processing, the reaction mixture was treated with hydrazine hydrate prior to isolation and purification to convert the neutral form into the corresponding protonated one. The isolation yields for **1** and **2** were 45% and 40%, respectively. Double-deckers **1** and **2** are soluble in common organic solvents such as CH_2Cl_2, $CHCl_3$, and toluene, which allows characterization of these compounds by various spectroscopic methods, including matrix-assisted laser desorption ionization−time of flight mass spectrometry (MALDI-TOF MS), ^{1}H NMR, and UV−vis and near IR spectroscopy. Both double-deckers **1** and **2** gave satisfactory elemental analysis data. MALDI-TOF MS spectra of **1** and **2** show intense signals of protonated molecular ions [MH^+], providing evidence for the identity of these sandwich double-decker compounds. Due to the paramagnetic nature of Ho(III), little or no NMR data of **2** could be obtained. However, upon the addition of 1% hydrazine hydrate into a mixed solvent of $CDCl_3$ and DMSO-d_8 (1:1 v/v), a well-resolved ^{1}H NMR spectrum of **1** with virtually all of the expected signals was obtained, Figure S1 (Supporting Information).

The electronic absorption spectra of **1** and **2** are displayed in Figures 1 and S2 (Supporting Information), resembling those of double-deckers containing two dianionic ligands such as [HM^{III}{Pc(α-3-OC_5H_{11})$_4$}(TClPP)] (M = Sm, Eu, Y),[12d] [HY^{III}{Pc(α-3-OC_4H_9)$_8$}(TClPP)],[12d] [HM^{III}{Pc-(OBNP)$_2$}(TClPP)] (M = Y, Eu),[16] [Ce^{IV}(Pc)(TPP)] [TPP = meso-tetraphenylporphyrinate],[22] [M^{IV}(Pc)(Por)] (M = Zr, Hf, Th, U),[23] and

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(21) In this step, upon refluxing in 1-octanol for a prolonged time (> 24 h), the *p*-amino groups of H$_2$TAPP reacted with 1-octanol producing *p*-octylamino groups efficiently. Thus, half-sandwich complexes [M^{III}(acac)(TOAPP)] were formed instead of [M^{III}(acac)(TAPP)]. The reported examples of direct N-alkylation of anilines with alkyl alcohols can be seen: (a) Watanabe, Y.; Morisaki, Y.; Kondo, T.; Mitsudo, T. *J. Org. Chem.* **1996**, *61*, 4214–4218. (b) Fujita, K.; Li, Z.; Ozeki, N.; Yamaguchi, R. *Tetrahedron Lett.* **2003**, *44*, 2687–2690. (c) Fujita, K.; Enoki, Y.; Yamaguchi, R. *Tetrahedron* **2008**, *64*, 1943–1954. (d) Balcells, D.; Nova, A.; Clot, E.; Gnanamgari, D.; Crabtree, R. H.; Eisenstein, O. *Organometallics* **2008**, *27*, 2529–2535. (e) Blank, B.; Madalska, M.; Kempe, R. *Adv. Synth. Catal.* **2008**, *350*, 749–758.
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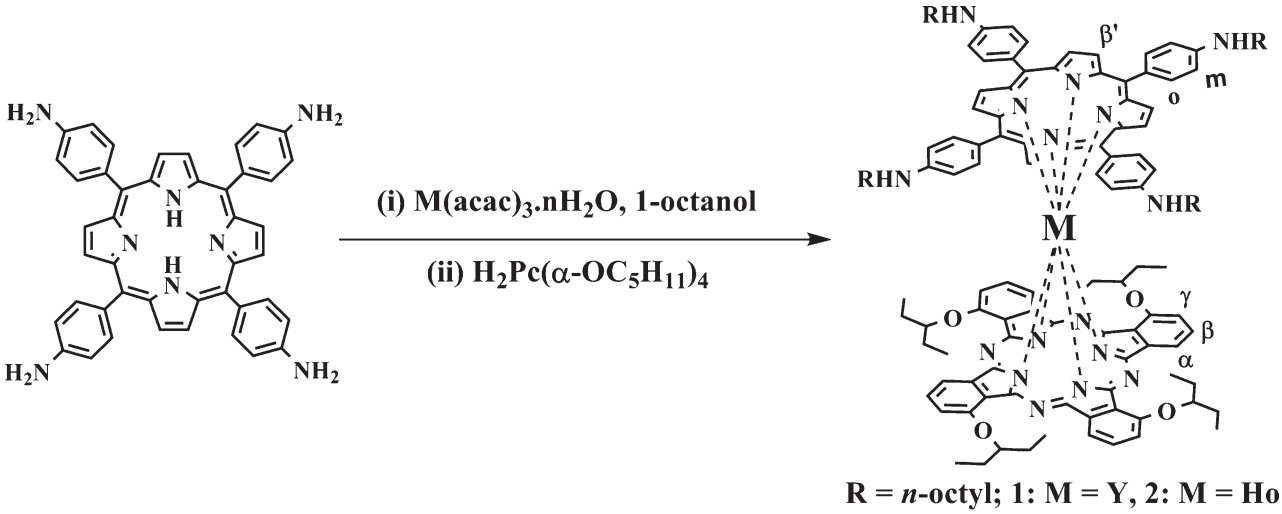
Scheme 1. Synthesis of Mixed (Phthalocyaninato)(Porphyrinato) Rare Earth Double-Decker Complexes **1** and **2**



$Li[M^{III}(Pc)(TPyP)]$ [M = Eu, Gd; TPyP = meso-tetrakis-(4-pyridyl)porphyrinate].[24] The spectra show medium-to-strong Pc and Por Soret bands at 311 and 414 nm, respectively, and several Q bands in the region of 450−1000 nm in addition to a charge transfer band at ca. 620 nm (for details, see Figure 4).[23,25] A near IR absorption band at approximately 1200 nm, characteristic of the nonprotonated neutral mixed (phthalocyaninato)(porphyrinato) rare earth double-decker complexes, was not detected for **1** and **2**, confirming the "reduced" protonated nature of these double-deckers.

The molecular structures of compounds **1** and **2** were determined by X-ray diffraction analyses. Single crystals of the compounds were obtained by the slow diffusion of MeOH into a corresponding solution of the complexes in $CHCl_3$. Compounds **1** and **2** crystallize in the triclinic system, $P\bar{1}$ space group with one pair of enantiomeric double-decker molecules per unit cell, Figure S3 (Supporting Information). Figure 2 shows the molecular structure of the yttrium compound **1** in two different perspective views. The Y center is octa-coordinated by the isoindole and pyrrole N-atoms of phthalocyaninato and porphyrinato ligands, respectively, forming a slightly distorted square antiprism. The two N_4 mean planes are virtually parallel (dihedral angle = 0.60 °) with a plane-to-plane separation of 2.786 Å. Similar to the structures of many double-decker complexes,[11] the two ligands are not planar and display a saucer shape domed toward the metal center. As shown in Table 1, the mean M−N[Pc(α-3-$OC_5H_{11})_4$] bond distance is longer than the mean M−N(Por) bond distance for the two complexes due to the smaller cavity size and the larger steric hindrance of Pc(α-3-$OC_5H_{11})_4$ compared with those of TOAPP. Similar results have also been found for other heteroleptic (phthalocyaninato)(porphyrinato)lanthanide complexes,[12a,d,22a,26] in which the metal atom lies closer to the N_4 mean plane of Por than that of Pc. As expected, the average M−N bond distance and the interplanar distance decrease with the ionic radius [1.019 and 1.015 Å for octa-coordinated Y(III) and Ho(III), respectively)] of the rare earth center. The extent of ligand deformation, as defined by the average dihedral angle φ of the individual isoindole or pyrrole rings with respect to the corresponding N_4 mean plane, also decreases monotonically with the size of the metal center. For the two complexes, the value of φ is larger for Pc(α-3-$OC_5H_{11})_4$ than for TOAPP, showing that the former macrocycle is more deformed than the latter, probably due to the four bulky 3-pentyloxy substituents. The average twist angle θ, which is defined as the rotation angle of one macrocycle away from the eclipsed conformation of the two macrocycles, deviates from 45°, which corresponds to the fully staggered conformation, by about 6° in the molecular structures of **1** and **2**. This is consistent with the previous results of protonated mixed ring rare earth double-decker complexes [HM^{III}{Pc(α-3-$OC_5H_{11})_4$}(TClPP)] (M = Sm, Eu, Y).[12d]

Resolution. As mentioned earlier, despite the preparation of a series of 1,8,15,22-tetrakis(alkoxy)-substituted phthlocyanine-containing complexes with C_4 chirality,[12d,18−20] attempts to resolve these compounds have so far failed. In the present work, a meso-tetrakis(4-octylamino-phenyl)porphyrin ligand (TOAPP) was incorporated into the chiral mixed (phthalocyaninato)(porphyrinato) rare earth double-decker complexes **1** and **2**. However, attempts to achieve resolution for both complexes failed again, even with the aid of a chiral HPLC column (ChiralPak IA). For the purpose of increasing the difference in chirality between the two enantiomers of **1** and **2**, the octylamino groups in the two double-deckers were functionalized by *tert*-butyloxycarbonyl (Boc) anhydride-protected L-phenylalanine (Boc-L-Phe-OH) via an N,N′-dicyclohexylcarbodiimide (DCC)-assisted coupling reaction.[27] As a result, diastereomeric mixtures of homochiral amino acid modified **1** and **2**, denoted as **1**·L-Phe-Boc and **2**·L-Phe-Boc, respectively, were obtained and unambiguously characterized by MALDI-TOF MS and elemental analysis. When subjected to normal phase HPLC with a HiQ SIL column, no

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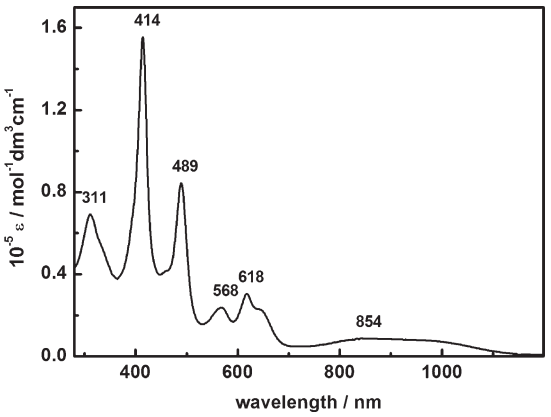

Figure 1. Electronic absorption spectrum of [Y^{III}H{Pc(α-$OC_5H_{11})_4$}-{TOAPP}] (**1**) in $CHCl_3$.

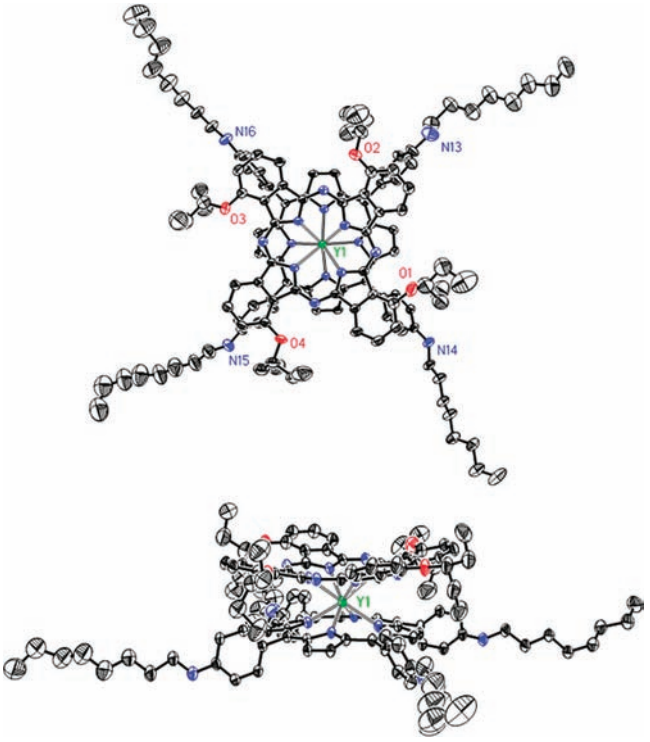

Figure 2. Molecular structure of [HY^{III}Pc(α-$OC_5H_{11})_4$}{TOAPP}] (**1**) from two perspectives. Hydrogen atoms are omitted for clarity, and the ellipsoids are drawn at the 30% probability level.

indication of separation was observed for either **1**·L-Phe-Boc or **2**·L-Phe-Boc under various experimental conditions.[28] Surprisingly, when **1**·L-Phe-Boc was applied to a chiral HPLC column (ChiralPak IA) with $CHCl_3$/hexane (1:1, v/v) as the eluent, two well-separated peaks having retention times of 8.04 and 11.32 min, with comparable areas, were observed in the chromatogram, Figure 3. The two eluted fractions corresponding to the two peaks show identical electronic absorption spectra and magnetic circular dichroism (MCD) spectra, as well as perfect mirror images in their CD spectra over the whole spectral region, Figure 4A. This indicates successful resolution of the two

(28) Normal phase analytic high-performance liquid chromatography (HPLC) was performed at 20 °C using a φ4.6 × 150 mm HiQ SIL (KYA Tech. Co.) column with hexane/$CHCl_3$ (1:3 to 1:1, v/v) as an eluent at a flow rate of 0.5 or 1.0 mL min^{-1}, monitored by a UV detector at 400 nm.

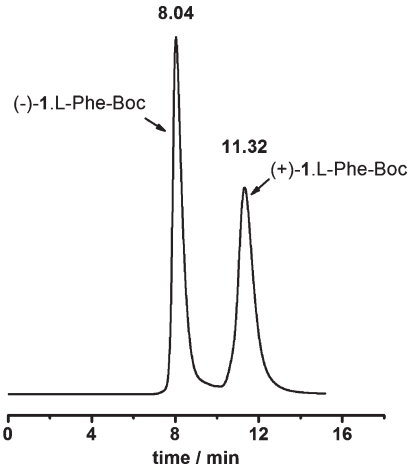

Figure 3. Chromatogram of **1**·L-Phe-Boc monitored at 400 nm.

diastereoisomers of chiral **1**·L-Phe-Boc. The first and second fractions display the most intense CD signal at 493 nm in $CHCl_3$ with negative and positive signs denoted as (−)-**1**·L-Phe-Boc and (+)-**1**·L-Phe-Boc, respectively. Similarly, **2**·L-Phe-Boc was also successfully resolved and the electronic absorption, CD, and MCD spectra of the diastereoisomers recorded, which are similar to those of **1**·L-Phe-Boc, Figure S4 (Supporting Information).

It is worth noting that partial resolution of **1**·L-Phe-Boc and **2**·L-Phe-Boc can also be achieved by means of the reprecipitation method. As revealed by CD measurements, (−)-**2**·L-Phe-Boc was enriched in precipitates obtained from a mixed solvent of $CHCl_3$ and CH_3OH (1:9, v/v), Figure S5 (Supporting Information). However, this method is time-consuming and inefficient in comparison to the chiral HPLC technique.

In concluding this section, it is worth noting that the two enantiomers of a chiral compound are usually chromatographically resolved by using a chiral-phase column, while diastereomers of a chiral compound are usually separated by achiral-phase chromatography or a recrystallization procedure. However, this is not the case in the present work. The double-deckers **1** and **2** with chirality originating from the single-handed rotational arrangement of 3-pentyloxy substituents in the Pc ring are quite different from traditional optically active compounds with chirality derived from chiral centers (carbon or other atoms), chiral binaphthyls, or other axial or planar chiral units. Chiral HPLC columns were unable to achieve resolution for **1** and **2** together with other related analogues.[12d,18−20] Nevertheless, the diastereomeric mixture of their homochiral amino acid modified species, **1**·L-Phe-Boc and **2**·L-Phe-Boc, could not be effectively separated by achiral-phase chromatography or recrystallization procedures. In strong contrast, the diastereomeric mixtures of both **1**·L-Phe-Boc and **2**·L-Phe-Boc have been successfully separated by the chiral HPLC technique, revealing the potential application of this procedure in realizing a resolution of compounds with chirality originating in a similar manner.

Absolute Configuration Assignment. In order to directly correlate the isomeric structure with the CD sign, a large amount of effort has been made to prepare single crystals from (−)-**1**·L-Phe-Boc, (+)-**1**·L-Phe-Boc, (−)-**2**·L-Phe-Boc, and (+)-**2**·L-Phe-Boc. However, due to the poor

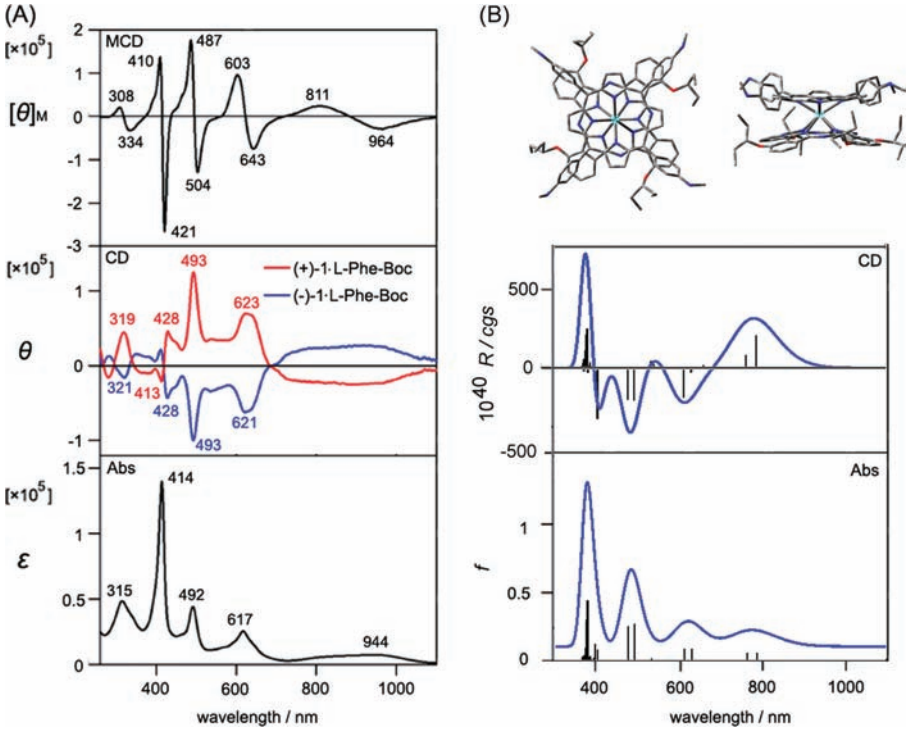

Figure 4. (A) Electronic absorption, CD, and MCD spectra of (−)-**1**·L-Phe-Boc and (+)-**1**·L-Phe-Boc measured in $CHCl_3$. (B) Simulated electronic absorption and CD spectra of (*R*)-[Y^{III}{Pc(α-$OC_5H_{11})_4$}{TMAPP}]$^-$; Gaussian bands with half-bandwidths of 2000 cm^{-1} were used. The inset show the optimized geometry of (*R*)-[Y^{III}{Pc(α-$OC_5H_{11})_4$}{TMAPP}]$^-$.

Table 1. Comparison of the Structural Data for **1** and **2.**

	1	**2**
average M−N(Por) bond distance (Å)	2.422	2.425
average M−N[Pc(α-$OC_5H_{11})_4$] bond distance (Å)	2.495	2.498
M−N_4(Por) plane distance (Å)	1.266	1.257
M−N_4[Pc(α-$OC_5H_{11})_4$] plane distance (Å)	1.520	1.514
interplanar distance (Å)	2.786	2.771
dihedral angle between the two N_4 planes (deg)	0.60	1.32
average dihedral angle φ for the Por ring (deg)[a]	12.32	12.03
average dihedral angle φ for the Pc(α-$OC_5H_{11})_4$ ring (deg)[a]	15.55	15.52
average twist angle θ (deg)[b]	38.68	39.37

[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.

crystallinity of the pure isomers, all attempts were unsuccessful. Fortunately, TD-DFT calculations have been shown to be useful in the study of the molecular and electronic structures of bis(tetrapyrrole) rare earth complexes.[12f,16,29] In particular, the simulated electronic absorption and CD spectra of optically active mixed (phthalocyaninato)(porphyrinato) rare earth complexes using the TD-DFT method reproduce the experimental data well in different solvents, allowing clarification of the solvent-dependent conformational changes for (*S*)-[HY^{III}-{Pc-$(OBNP)_2$}(TClPP)].[16] As a consequence, in the present work, calculations using the TD-DFT method have been applied in order to simulate the electronic absorption and CD spectra of [HY^{III}{Pc(α-3-$OC_5H_{11})_4$}{TOAPP}] (**1**) for the purpose of realizing absolute configuration assignments. It is worth noting that the configuration of enantiomers of the sandwich double-decker complexes with C_4 chirality in this work is tentatively defined according to the rotational direction from the phenyl rings to the alkoxy substituents at the Pc ligand. Viewed from the Por side, the species with the alkoxy substituents arranged clockwise is defined as the (*R*)- enantiomer, and that with anticlockwise-arranged alkoxy substituents as the (*S*)- enantiomer, Chart 1.

Obviously, the observation of CD signals for (−)-**1**·L-Phe-Boc, (+)-**1**·L-Phe-Boc, (−)-**2**·L-Phe-Boc, and (+)-**2**·L-Phe-Boc in the region of 300−1100 nm originates from the C_4 chirality of the sandwich double-decker part in these molecules and is independent of the homochiral amino acid substituents. Both **1**·L-Phe-Boc and **2**·L-Phe-Boc display very similar features to those of **1** and **2** in their electronic absorption spectra, indicating negligible electronic interaction between the central double-decker core and the L-Phe-Boc moieties in **1**·L-Phe-Boc and **2**·L-Phe-Boc. On the other hand, previous calculations indicate that the anionic forms of double-decker complexes give better results in simulating the experimental electronic absorption and CD spectra compared to the protonated derivatives.[12f,16] As a consequence, TD-DFT calculations on [Y^{III}{Pc(α-3-$OC_5H_{11})_4$}{TOAPP}]$^-$ (**1**$^-$) were conducted. To further simplify the calculations, the anionic form of the yttrium complex [(*R*)-Y^{III}{Pc(α-3-$OC_5H_{11})_4$}-{TMAPP}]$^-$ [TMAPP = meso-tetrakis(4-methylaminophenyl) porphyrinate] instead of **1**$^-$ was subjected to TD-DFT calculations at the B3LYP/6-31G* (LANL2DZ for Y) level.[16]

In a manner similar to that for [Y^{III}(Pc)(Por)]$^-$ (Pc = unsubstituted phthalocyaninate),[12f] the electronic

(29) (a) Zhang, Y.; Cai, X.; Zhou, Y.; Zhang, X.; Xu, H.; Liu, Z.; Li, X.; Jiang, J. *J. Phys. Chem. A* **2007**, *111*, 392–400. (b) Muranaka, A.; Matsumoto, Y.; Uchiyama, M.; Jiang, J.; Bian, Y.; Ceulemans, A.; Kobayashi, N. *Inorg. Chem.* **2005**, *44*, 3818–3826.

absorption and CD spectra of (*R*)-[Y^{III}{Pc(α-3-$OC_5H_{11})_4$}-{TMAPP}]$^-$ were calculated and simulated, as shown in Figure 4B. The electronic transitions of the main absorption bands are organized in Table S1, and the energy level scheme and maps of the molecular orbitals are summarized in Figure S6 in the Supporting Information. As seen in the simulated absorption spectrum, Figure 4B, two transitions with similar intensity constitute the major absorption bands, although the band at the longest wavelength was revealed to locate at a higher energy (763 and 787 nm) than the experimental observation of ca. 700−1000 nm, according to the calculation result. The configurations listed in Table S1 suggest a similar origin for these pairs of transitions, which are assigned to transitions to nearly degenerate unoccupied orbitals. Observation of the dispersion-type pseudo-Faraday A MCD terms corresponding to the absorption peaks lend further support to this assignment, Figure 4A. Judging from the configurations in Table S1 and the MCD intensity in Figure 4A, the experimental band at 700−1000 nm and peaks at ca. 620, 490, 414, and 315 nm (Figures 1 and 4A) might be assigned to the Q band of Pc, mainly charge transfer from the Pc to Por moiety, the Q band of Por, the Soret band of Por, and the Soret band of the Pc moiety, respectively. The simulated CD spectrum of (*R*)-[Y^{III}{Pc(α-3-$OC_5H_{11})_4$}{TMAPP}]$^-$, Figure 4B, basically reproduces the observed spectrum of (−)-**1**·L-Phe-Boc in $CHCl_3$, Figure 4A. As can be found in the simulated CD spectrum, the positive, negative, and negative troughs appear, respectively, corresponding to the observed band at 700−1000 nm, the peak at ca. 620 nm, and the peak at 490 nm. Nevertheless, even the minus/plus pattern in ascending energy is reproduced for the observed absorption peak at 414 nm due to the Soret band of the Por moiety. As a total result, almost across the whole spectral region, the CD signs in the calculated CD spectrum for (*R*)-[Y^{III}{Pc(α-3-$OC_5H_{11})_4$}{TMAPP}]$^-$ are in agreement with those observed for (−)-**1**·L-Phe-Boc, leading to the designation of (−)-**1**·L-Phe-Boc as the (*R*)- isomer, denoted as (*R*)-(−)-**1**·L-Phe-Boc, and (+)-**1**·L-Phe-Boc as (*S*)-(+)-**1**·L-Phe-Boc. This is also true for **2**·L-Phe-Boc.

Conclusions

In summary, two novel optically active mixed (phthalocyaninato)(porphyrinato) rare earth double-decker complexes **1** and **2** with C_4 chirality have been designed and prepared. In particular, resolution was achieved for the first time for a sandwich tetrapyrrole rare earth complex by combining the chiral HPLC technique with formation of their diastereoisomers using a homochiral amino acid as the chiral resolving agent. Absolute configuration assignment was performed on the basis of TD-DFT calculations.

Experimental Section

General. *n*-Octanol was distilled from sodium under nitrogen. Dichloromethane was freshly distilled from CaH_2 under nitrogen. Column chromatography was carried out on silica gel (Merck, Kieselgel 60, 70−230 mesh) and biobeads (BIORAD S-X1, 200−400 mesh) with the eluents indicated. Optically pure N-(tert-butoxycarbonyl)-L-phenylalanine (Boc-L-Phe-OH) and 3-nitrophthalonitrile were obtained from GL Biochem, Ltd. and Aldrich, respectively. All other reagents and solvents were used as received. The compounds [M(acac)$_3$]·$n$$H_2O$ (M = Y, Ho),[30] H_2Pc(α-3-$OC_5H_{11})_4$,[8b,17] and H_2TAPP[31] were prepared according to literature procedures.

^{1}H NMR spectra were recorded on a Bruker DPX 300 spectrometer (300 MHz). Spectra were referenced internally using the residual solvent resonances relative to $SiMe_4$. Electronic absorption spectra were recorded by using a Hitachi U-4100 spectrophotometer. MALDI-TOF mass spectra were recorded by using a Bruker BIFLEX III ultra-high-resolution Fourier transform ion cyclotron resonance mass spectrometer with α-cyano-4-hydroxycinnamic acid as the matrix. Elemental analyses were performed by the Institute of Chemistry at the Chinese Academy of Sciences. CD and MCD spectra were recorded in the range 300−900 nm with a JASCO J-725 spectrodichrometer equipped with a JASCO electromagnet which produces parallel and antiparallel magnetic fields of 1.09 T, and in the near-IR region (800−2000 nm) with a JASCO J-730 spectrodichrometer equipped with a JASCO electromagnet which produces magnetic fields of 1.5 T. The CD and MCD spectra were combined in the region where there are no intense absorption bands. The magnitude of the MCD signal is expressed in terms of molar ellipticity per tesla $[\theta]_M$/deg mol^{-1} dm^3 cm^{-1} T^{-1}.

[Y^{III}H{Pc(α-$OC_5H_{11})_4$}{TOAPP}] (1). A mixture of [Y(acac)$_3$]·$n$$H_2O$ (44.4 mg, 0.11 mmol) and H_2TAPP (67.5 mg, 0.10 mmol) in *n*-octanol (4 mL) was heated to reflux under nitrogen for 48 h. After the mixture was cooled to room temperature, H_2Pc(α-3-$OC_5H_{11})_4$ (86.0 mg 0.10 mmol) was added and then heated to reflux for another 2 h. After a brief cooling, the solvent was evaporated under reduced pressure, and the residue was dissolved in 10 mL $CHCl_3$/CH_3OH (1:1, v/v). Then, 0.5 mL of hydrazine hydrate was added, and the mixture was rotary evaporated to dryness. The residue was subjected to chromatography on a silica-gel column. A small amount of metal-free H_2TOAPP was separated by using $CHCl_3$/hexane (1:2) as the eluent, and then the column was eluted with $CHCl_3$. A small green band containing metal-free phthalocyanine followed by another green band containing the protonated double-decker was developed. Repeated chromatography followed by recrystallization from $CHCl_3$/MeOH gave pure **1** (93 mg, 45%). ^{1}H NMR (300 MHz, $CDCl_3$/[D_6]DMSO (1:1) with ca. 1% hydrazine hydrate, 295.9 K, TMS): δ 8.71 (d, J = 7.5 Hz, 4H; Pc $H_α$), 8.14 (d, J = 4.5 Hz, 4H; Por $H_{β'}$), 8.01 (d, J = 4.5 Hz, 4H; Por $H_{β'}$), 7.89 (t, J = 7.5 Hz, 4H; Pc $H_β$), 7.49 (d, J = 7.8 Hz, 4H; Pc $H_γ$), 7.25 (d, J = 6.9 Hz, 4H; Por *endo*-H_o), 6.84 (d, J = 6.9 Hz, 4H; Por *exo*-H_o), 6.43 (d, J = 7.5 Hz, 4H; Por *endo*-H_m), 6.33 (d, J = 7.5 Hz, 4H; *exo*-H_m), 5.55 (m, J = 6.0 Hz, 4H; OCH), 5.05 (brd, 4H; Por NH), 3.29 (t, J = 6.6 Hz, 8H; Por NCH_2), 2.56 (m, J = 7.2 Hz, 8H; Por $NCH_2CH_2C_6H_{13}$), 2.18 (m, J = 6.6 Hz, 8H; Pc *endo*-CH_2), 1.82 (m, J = 6.6 Hz, 8H; Pc *exo*-CH2), 1.69 (t, J = 7.5 Hz, 12H; Pc *endo*-CH_3), 1.59−1.40 (brd, 40H; Por $NCH_2CH_2C_5H_{10}CH_3$), 1.24 (t, J = 7.5 Hz, 12H; Pc *exo*-CH_3), 0.97 ppm (t, J = 6.6 Hz, 12H; Por CH_3). UV−vis−NIR ($CHCl_3$): $λ_{max}$ (log ε) 311 (4.84), 414 (5.19), 489 (4.93), 568 (4.38), 618 (4.48), 645 (4.36), 854 nm (3.95). MALDI-TOF-MS m/z calcd. for $C_{128}H_{153}N_{16}O_4Y$: (M^+) 2067.1. Found: 2066.9. Elem anal. calcd (%) for $C_{128}H_{153}N_{16}O_4Y$: C, 74.32; H, 7.46; N, 10.83. Found: C, 73.85; H, 7.45; N, 10.92.

[Ho^{III}H{Pc(α-$OC_5H_{11})_4$}{TOAPP}] (2). By using the procedure described above for **1** with [Ho(acac)$_3$]·$n$$H_2O$ (53 mg, 0.11 mmol) instead of [Y(acac)$_3$]·$n$$H_2O$ as the starting material, compound **2** was obtained (86 mg, 40%). UV−vis−NIR ($CHCl_3$): $λ_{max}$ (log ε) 311 (4.86), 414 (5.17), 490 (4.88), 565 (4.43), 617 (4.49), 643 (4.34), 855 nm (3.88). MALDI-TOF-MS

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Table 2. Crystallographic Data for **1** and **2**

	1	**2**
molecular formula	$C_{128}H_{152}N_{16}O_4Y$	$C_{128}H_{152}N_{16}O_4Ho$
M	2067.57	2143.59
cryst syst	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a/Å	13.784(3)	13.771(3)
b/Å	16.728(3)	16.777(4)
c/Å	27.926(6)	27.932(7)
α/deg	96.307(2)	96.396(4)
β/deg	103.4020(10)	103.210(4)
γ/deg	112.204(2)	112.077(4)
V/Å^3	5658.3(19)	5681(2)
Z	2	2
F(000)	2206	2262
D_c/Mg m^{-3}	1.214	1.253
μ/mm^{-1}	0.577	0.757
data collection range/deg	0.77 to 25.00	1.91 to 25.00
reflns collected	28398	29415
independent reflns	19780 [R(int) = 0.0704]	19511 [R(int) = 0.0432]
params	1342	1355
R_1 [$I > 2\sigma(I)$]	0.1070	0.1088
wR_2 [$I > 2\sigma(I)$]	0.2750	0.2848
goodness of fit	0.993	1.155

m/z calcd. for $C_{128}H_{153}N_{16}O_4Ho$: ($M^+$) 2143.2. Found: 2143.3. Elem anal. calcd (%) for $C_{128}H_{153}N_{16}O_4Ho$: C, 71.68; H, 7.19; N, 10.45. Found: C, 70.99; H, 7.23; N, 10.38.

Synthesis of N-(*tert*-Butoxycarbonyl)-L-phenylalanine Modified Double Deckers. Compound **1** (or **2**) (0.2 mmol) and Boc-L-Phe-OH (1.6 mmol) were dissolved in 10 mL of dry CH_2Cl_2. The solution was cooled to 0 °C, and DCC (1.6 mmol) was added. The reaction mixture was stirred at 0 °C for 30 min and at 25 °C for 24 h. The mixture was rotary evaporated to dryness, and the residue was subjected to chromatography on a silica-gel column followed by an open GPC column with CH_2Cl_2 as the eluent. The corresponding modified double-deckers were obtained after evaporation of the solvent.

1·L-Phe-Boc (58 mg, 95%). UV−vis−NIR ($CHCl_3$): λ_{max} (log ε) 315 (4.86), 414 (5.33), 492 (4.81), 617 (4.58), 929 nm (4.04). MALDI-TOF-MS m/z calcd. for $C_{184}H_{221}N_{20}O_{16}Y$: ($M^+$) 3057.8. Found: 3057.9. Elem anal. calcd (%) for $C_{184}H_{221}N_{20}O_{16}Y \cdot CH_2Cl_2$: C, 70.70; H, 7.15; N, 8.91. Found: C, 70.32; H, 7.30; N, 8.79.

2·L-Phe-Boc (60 mg, 96%). UV−vis−NIR ($CHCl_3$): λ_{max} (log ε) 314 (4.84), 413 (5.29), 491 (4.78), 616 (4.56), 943 nm (4.00). MALDI-TOF-MS m/z calcd. for $C_{184}H_{221}N_{20}O_{16}Ho$: ($M^+$) 3133.8. Found: 3133.7. Elem anal. calcd (%) for $C_{184}H_{221}N_{20}O_{16}Y \cdot CH_2Cl_2$: C, 70.52; H, 7.11; N, 8.94. Found: C, 69.62; H, 7.13; N, 8.69

Resolution by HPLC. Analytical HPLC was performed at 25 °C using a 4.6 × 250 mm CHIRALPAK IA (Daicel Chemical) column on a JASCO PU-2086 Plus Intelligent Prep. Pump, equipped with a JASCO UV-2075 Plus Intelligent UV/vis detector, monitored at 400 nm.

(−)-1·L-Phe-Boc and (+)-1·L-Phe-Boc. A hexane/$CHCl_3$ (1/1 v/v) solution of **1**·L-Phe-Boc was subjected to analytical HPLC with hexane/$CHCl_3$ (1/1 v/v) as an eluent at a flow rate of 0.5 mL min^{-1}, where the first elution peak and the second elution peak, eluted at 8.01 and 11.32 min, were collected and evaporated to leave (−)-**1**·L-Phe-Boc and (+)-**1**·L-Phe-Boc, respectively (Figure 3).

(−)-2·L-Phe-Boc and (+)-2·L-Phe-Boc. A hexane/$CHCl_3$ (1/1 v/v) solution of **2**·L-Phe-Boc was subjected to analytical HPLC with hexane/$CHCl_3$ (1/1 v/v) as an eluent at a flow rate of 1.0 mL min^{-1}, where the first elution peak and the second elution peak, eluted at 4.10 and 5.01 min, were collected and evaporated to leave (−)-**2**·L-Phe-Boc and (+)-**2**·L-Phe-Boc, respectively, Figure S4A (Supporting Information).

X-Ray Crystallographic Analyses. Crystal data and details of data collection and structure refinement are given in Table 2. Data were collected on a Bruker SMART CCD diffractometer with a Mo Kα 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 the integration of intensity of reflections and scaling;[32] SADABS for absorption correction;[33] and SHELXL for space group and structure determination, refinements, graphics, and structure reporting.[34] CCDC-734407 and 734408 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.

Computational Details. The primal input structure of [(*R*)-Y^{III}{Pc(α-3-$OC_5H_{11})_4$}{TMAPP}]$^-$ was obtained by changing the octyl groups of 4-octylamino-phenyl in the crystal structure of [(*R*)-Y^{III}H{ Pc(α-3-$OC_5H_{11})_4$}{TOAPP}] (**1**) to methyls and changing the charge and spin multiple of the molecule to −1 and +1, respectively. With this input structure, electronic absorption and CD spectra of [(*R*)-Y^{III}{Pc(α-3-$OC_5H_{11})_4$}-{TMAPP}]$^-$ were calculated using the TD-DFT method, in which 30 singlet excited states were solved. In all cases, the hybrid density functional B3LYP (Becke−Lee−Young−Parr composite of the exchange-correlation functional) method[35] and the basis sets with LANL2DZ[36] for the Y atom and 6-31G*(d) for all other atoms were used. Wavelengths in the electronic absorption and CD spectra were scaled by a scaling factor of 1/0.9614. Gaussian bands with half-bandwidths of 2000 cm^{-1} were used for both the electronic absorption and CD spectra in Figure 4. All calculations were carried out using the Gaussian 03 program[37] on an IBM P690 system at the Shandong Province High Performance Computing Centre.

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Supporting Information Available: ^{1}H NMR spectrum of [Y^{III}H{Pc(α-$OC_5H_{11})_4$}{TOAPP}] (**1**); electronic absorption spectrum of [Ho^{III}H{Pc(α-$OC_5H_{11})_4$}{TOAPP}] (**2**) in $CHCl_3$; unit cell of [Y^{III}H{Pc(α-$OC_5H_{11})_4$}{TOAPP}] (**1**) showing one pair of enantiomers; chromatogram of **2**·L-Phe-Boc monitored at 400 nm; electronic absorption, CD, and MCD spectra of

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(−)-**2**·L-Phe-Boc and (+)-**2**·L-Phe-Boc measured in $CHCl_3$; CD spectra of a precipitate, in which (−)-**2**·L-Phe-Boc was enriched by reprecipitation of **2**·L-Phe-Boc five times, with a mixed solvent of $CHCl_3$ and CH_3OH (1:9, v/v), measured in $CHCl_3$; energy level scheme and maps of the molecular orbitals of (*R*)-[Y^{III}{Pc(α-3-$OC_5H_{11})_4$}{TOMPP}]$^-$; major contributions (in percent) from occupied−unoccupied orbital pairs to the transition dipole moments of some excitations of (*R*)-[Y^{III}{Pc(α-3-$OC_5H_{11})_4$}{TOMPP}]$^-$; complete ref 37; and crystallographic data of **1** and **2** (CIF). This material is available free of charge via Internet at http://pubs.acs.org.