Inorganic Chemistry

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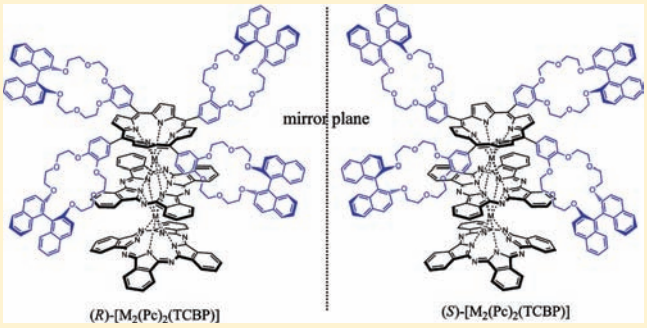
Optically Active Mixed (Phthalocyaninato)(Porphyrinato) Rare Earth Triple-Decker Complexes. Synthesis, Spectroscopy, and Effective Chiral Information Transfer

Jitao Lu,[‡] Yanhua Deng,[‡] Xiaomei Zhang,[*,‡] Nagao Kobayashi,[*,§] and Jianzhuang Jiang[*,†]

[†]Department of Chemistry, University of Science and Technology Beijing, Beijing 100083, China
[‡]Department of Chemistry, Shandong University, Jinan 250100, China
[§]Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan

S *Supporting Information*



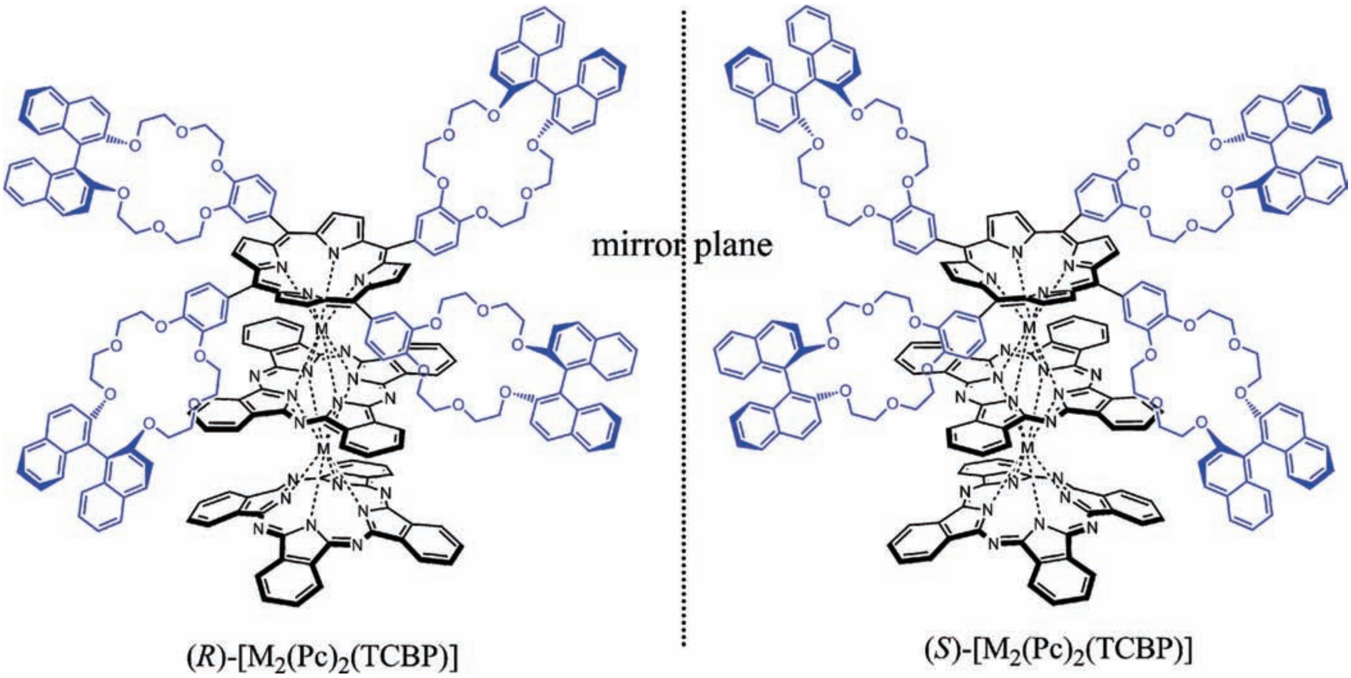
ABSTRACT: With the view to creating novel sandwich-type tetrapyrrole rare earth complexes toward potential applications in material science and chiral catalysis, two new optically active mixed (phthalocyaninato)(porphyrinato) rare earth triple-decker complexes with both (*R*)- and (*S*)-enantiomers [M$_2$(Pc)$_2$(TCBP)] {TCBP = Meso-tetrakis [3,4-(11,12:13,14-di(1′,2′-naphtho)-1,4,7,10,15,18-hexaoxacycloeicosa-2,11,13-triene)-phenyl] porphyrinate; M = Eu (**1**), Y (**2**)} have been designed and prepared by treating optically active metal free porphyrin (*R*)-/(*S*)-H$_2$TCBP with M(Pc)$_2$ in the presence of corresponding M(acac)$_3$·*n*H$_2$O (acac = acetylacetonate) in refluxing 1,2,4-trichlorobenzene (TCB). These novel mixed ring rare earth triple-decker compounds were characterized by a wide range of spectroscopic methods including MS, ^{1}H NMR, IR, electronic absorption, and magnetic circular-dichroism (MCD) spectroscopic measurements in addition to elemental analysis. Perfect mirror image relationship was observed in the Soret and Q absorption regions in the circular-dichroism (CD) spectra of the (*R*)- and (*S*)-enantiomers, indicating the optically active nature of these two mixed (phthalocyaninato)(porphyrinato) rare earth triple-decker complexes. This result reveals the effective chiral information transfer from the peripheral chiral binaphthyl units to the porphyrin and phthalocyanine chromophores in the triple-decker molecule because of the intense $\pi-\pi$ interaction between porphyrin and phthalocyanine rings. In addition, their electrochemical properties have also been investigated by cyclic voltammetry (CV).

INTRODUCTION

Chirality is one of the most fascinating and complicated features in nature.[1] Inspired by the elegance of natural chiral structures with biological activity, numerous artificial chiral compounds including optically active porphyrins and phthalocyanines have been developed depending on various asymmetric synthetic methods.[2] However, optically active sandwich-type phthalocyaninato and/or porphyrinato metal complexes remain extremely rare thus far.[3] In 1997, Aida and collaborators synthesized and realized the optical resolution of the chiral homoleptic bis(porphyrinato) zirconium and cerium compounds with a D_2 symmetry.[4] Shinkai et al. successfully induced optical activity into the sandwich double-decker compounds by means of hydrogen bonding between chiral dicarboxylic acids or saccharides and the pyridyl nitrogen atoms of bis[tetrakis(4-pyridyl)porphyrinato] cerium through positive homotropic allosterism.[5] With the help of phthalocyanine ligand with planar asymmetry, mixtures containing both *R*- and *S*-isomers of heteroleptic (phthalocyaninato)(naphthalocyaninato) and bis(phthalocyaninato) rare earth double-decker complexes [Lu^{III}(Pc)(Nc*)] (Nc* = the C_S isomer of 1,2-naphthalocyaninate) and M(Pc)[Pc(α-OC$_5$H$_{11}$)$_4$] [Pc(α-OC$_5$H$_{11}$)$_4$ = 1,8,15,22-tetrakis(3-pentyloxy)phthalocyaninate] have been prepared by Simon and Jiang.[6] However, optical resolution of the two enantiomers had not yet been successful. Fortunately, optically active homoleptic and heteroleptic bis(phthalocyaninato) rare earth double-decker complexes were obtained very recently by employing the phthalocyanine bearing four chiral menthol moieties at the peripheral positions by Jiang and co-workers.[7] Nevertheless, successful optical resolution of the mixed (phthalocyaninato)(porphyrinato) rare earth double-decker complexes [HM^{III}{Pc(α-3-OC$_5$H$_{11}$)$_4$}{TOAPP}] [Pc(α-3-OC$_5$H$_{11}$)$_4$ = 1,8,15,22-tetrakis(3-pentyloxy)-phthalocyaninate; TOAPP = meso-tetrakis(4-octylamino-phenyl)porphyrinate; M = Y, Ho] was also reached by this group by means of a chiral HPLC technique in combination with the formation of their diastereomeric mixture using L-Boc-Phe-OH as the chiral resolving agent.[8] In addition to inducing chirality into the sandwich-type mixed (phthalocyaninato)(porphyrinato) rare earth double-decker molecules by utilizing the phthalocyanine ligand with planar

Received: November 30, 2010
Published: February 04, 2011

Scheme 1. Schematic Molecular Structures of Optically Active Mixed (Phthalocyaninato)(Porphyrinato) Rare Earth Triple-Decker Complexes (*R*)- and (*S*)-[$M_2(Pc)_2(TCBP)$] (M = Eu, Y) (1, 2)



asymmetry,[9] optical activity could also be effectively induced into the mixed (phthalocyaninato)(porphyrinato) rare earth double-decker complexes by linking optically active aromatic moieties onto the peripheral positions of phthalocyanine ring.[10] With this idea in mind, in the present study, optically active metal free tetra(aryl)porphyrin with four chiral binaphthyl moieties attached at the *meso*-phenyl groups through crown ether linkage was employed for the purpose of synthesizing mixed (phthalocyaninato)(porphyrinato) rare earth triple-decker complexes.

In this paper, two new chiral sandwich-type mixed (phthalocyaninato)(porphyrinato) rare earth triple-decker complexes, namely (*R*)- and (*S*)-[$M_2(Pc)_2(TCBP)$] {TCBP = Meso-tetrakis [3,4-(11,12:13,14-di(1′,2′-naphtho)-1,4,7,10,15,18-hexaoxacycloeicosa-2,11,13-triene)-phenyl] porphyrinate; M = Eu (**1**), Y (**2**)} were synthesized, Scheme 1. Observation of CD signals in the Soret and Q regions of both porphyrin and phthalocyanine chromophores indicates the effective chiral information transfer from the peripheral chiral binaphthyl side units to the porphyrin and phthalocyanine chromophores in the triple-decker molecule because of the intense $\pi-\pi$ interaction between porphyrin and phthalocyanine rings. This, to the best of our knowledge, represents the first example of optically active mixed (phthalocyaninato)(porphyrinato) rare earth triple-decker complexes.

RESULTS AND DISCUSSION

Synthesis and Spectroscopic Characterization. Several possible synthetic pathways have been developed to mixed (phthalocyaninato)(porphyrinato) rare earth triple-decker complexes.[3,11] In the present study, the target triple-decker complexes (*R*)- and (*S*)-[$M_2(Pc)_2(TCBP)$] (M = Eu, Y) (**1, 2**) were obtained with good yield from the reaction between optically active metal free porphyrin (*R*)- or (*S*)-H_2TCBP and $M(Pc)_2$ (M = Eu, Y) in the presence of $M(acac)_3 \cdot nH_2O$ (M = Eu, Y) in refluxing TCB. It is worth pointing out that racemization of the porphyrin at such high temperature over 218 °C under the present reaction condition did not occur.[12]

After repeated column chromatography and recrystallization, satisfactory elemental analysis results were obtained for both the two newly prepared optically active triple-decker complexes **1** and **2**, Table 1, which have good solubility in common organic solvents such as $CHCl_3$, CH_2Cl_2, and toluene. These two triple-decker complexes were also characterized by MALDI-TOF mass spectra and ^1H NMR spectroscopy. The MALDI-TOF mass spectra of these two compounds clearly showed intense signals for the protonated molecular ion $[M+H]^+$ for **1** and $[M+2H]^{2+}$ for **2**, respectively. The isotopic pattern closely resembles the simulated one as exemplified by the spectrum of **2** given in Figure S1 (Supporting Information).

The ^1H NMR spectra of **1** and **2** were recorded in $CDCl_3$, and the data are summarized in Table 2. The ^1H NMR spectrum for the europium triple-decker complex **1** spreads into a relatively wider region in comparison with that for the yttrium analogue **2** because of the paramagnetic nature of the europium ion. However, assignment of the ^1H NMR spectra for both compounds could be reached depending on the integration and multiplicity of the signals and by reference to the previous results for similar analogues.[13] The two complexes showed four multiplets at δ12.96 (broad), 11.06−11.18, 10.22−10.49, and 8.80−9.05 for **1**, 9.16−9.27, 8.53−8.62, 8.53−8.62, and 8.17−8.30 for **2**, respectively. The former two multiplets are attributed to α ring protons of Pc, while the latter two are the signals of β ring protons of Pc. In the high-field region, a multiplet signal appears at 3.12−3.90 for **1** and 2.84−3.26 for **2**, respectively, which can be assigned to the β proton of the Por ring. In addition, the ^1H NMR spectra of **1** and **2** also present one multiplet signal in the region of δ 6.99−8.78 for **1** and 7.06−8.07 for **2**, respectively, assigning to the protons from binaphthyl units and meso-phenyl

Table 1. Analytical and Mass Spectroscopic Data for the Triple-Decker Complexes[a]

compound	(*m*/*z*)[b]	analysis (%)		
		C	H	N
$Eu_2(Pc)_2(TCBP)$ (1)[c]	3647.6 (3648.4)	68.74 (68.80)	4.52 (4.32)	6.39 (6.48)[c]
$Y_2(Pc)_2(TCBP)$ (2)[d]	3373.7 (3375.4)	72.37 (72.08)	4.50 (4.53)	6.83 (6.80)[d]

[a] Calculated values given in parentheses. [b] By MALDI-TOF mass spectrometry and the value corresponds to the most abundant isotopic peak of the molecular ion $(M+H)^+$ for **1** and $(M+2H)^+$ for **2**, respectively. [c] Contains 1 equiv of solvated $CHCl_3$. [d] Contains 0.5 equiv of solvated $CHCl_3$.

Table 2. ^1H NMR Spectroscopic Data (δ) for the Triple-Deckers **1** and **2** Recorded in $CDCl_3$[a]

compound	Pc-α	Pc-β	Por-β	Por binaphthyl and Ph	Por Crown ether
1	12.96 (br, 8H) 11.06−11.18 (br, 8H)	10.22−10.49 (m, 8H) 8.80−9.05 (m, 8H)	3.12−3.90 (m, 8H)	6.99−8.78 (m, 60H)	4.02−5.97 (m, 64H)
2	9.16−9.27 (m, 8H) 8.53−8.62 (m, 8H)	8.53−8.62 (m, 8H) 8.17−8.30 (m, 8H)	2.84−3.26 (m, 8H)	7.06−8.07 (m, 60H)	3.49−4.87 (m, 64H)

[a] Multiplicities: br = broad, m = multiplet.

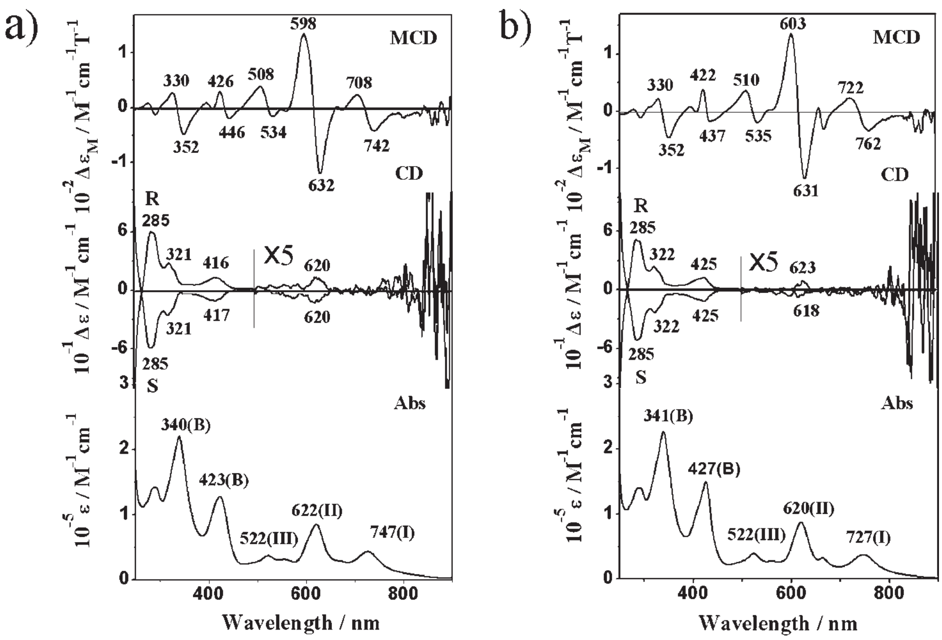


Figure 1. Electronic absorption, MCD, and CD spectra of $[Eu_2(Pc)_2(TCBP)]$ (a) and $[Y_2(Pc)_2(TCBP)]$ (b). MCD and CD spectra beyond about 800 nm are noisy because of the instrumental limitation and therefore unreliable.

substituents of the Por. The protons for crown ether moieties at δ 4.02−5.97 for **1** and 3.49−4.87 for **2** are also observed.

IR spectroscopy is a useful tool to reveal the nature of phthalocyaninato ligands in their sandwich-type rare earth complexes.[3b] Systematic study over the IR characteristics of several series of phthalocyaninato and/or porphyrinato rare earth double- and triple-decker compounds revealed that an intense band observed at 1312−1323 cm^{-1} for neutral bis(phthalocyaninato) and mixed (phthalocyaninato)(porphyrinato) rare earth(III) double-decker complexes can be attributed to the $Pc^{\bullet-}$ IR marker band.[14] This band was shifted to about 1329 cm^{-1} as a moderately strong band for $Ce^{IV}(Pc)_2$ containing dianionic phthalocyanine rings and therefore regarded as the characteristic IR band for Pc^{2-}.[14] As can be seen in Figure S2 (Supporting Information), both **1** and **2** showed a relatively intense band at 1326−1330 cm^{-1}, unambiguously verifying the dianionic nature of the phthalocyaninato ligands in these two triple-decker complexes. The asymmetric C−O−C stretching for **1** and **2** is observed at about 1257−1259 cm^{-1}.[15] Meanwhile, the IR spectra for **1** and **2** also show several strong bands in the region from 2850 to 2920 cm^{-1} because of the C−H stretching vibrations of the $-CH_2-$ groups of crown-ether chains.

Electronic Absorption, MCD, and CD Spectra of $[M_2(Pc)_2(TCBP)]$ (M = Eu, Y) (1, 2). The electronic absorption, magnetic circular-dichroism (MCD), and CD spectra of triple-decker complexes **1** and **2** were measured in $CHCl_3$, Figure 1, and the electronic absorption data are compiled in Table 3. As can be seen from Figure 1, both compounds **1** and **2** show a typical molecular electronic absorption spectrum with the maximum absorption peaks appearing at 340 and 341 nm, a B (or Soret) band originating primarily from the Pc moiety, 423 and 427 nm, a B (or Soret) band originating primarily from the TCBP porphyrin

Table 3. Electronic Absorption Data for Triple-Decker Complexes 1 and 2 in $CHCl_3$

compound	λmax/nm (log ε)				
$Eu_2(Pc)_2(TCBP)$ (1)	340 (5.24)	423 (5.00)	522 (4.43)	622 (4.83)	747 (4.53)
$Y_2(Pc)_2(TCBP)$ (2)	341 (5.22)	427 (5.00)	522 (4.46)	620 (4.83)	727 (4.46)

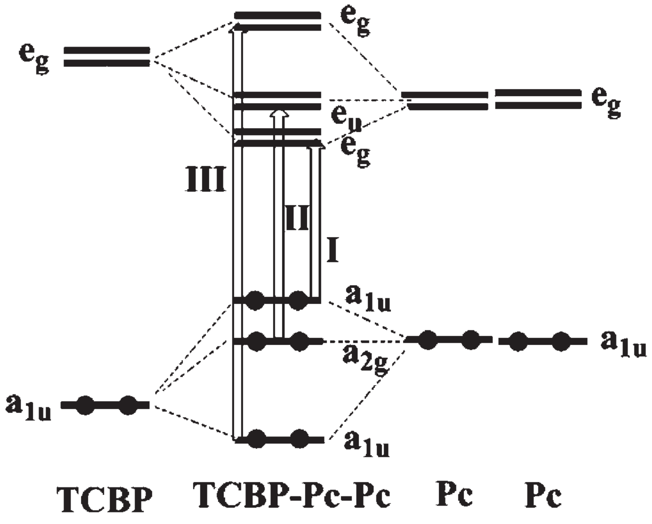


Figure 2. Partial molecular-orbital diagram for $[M_2(Pc)_2(TCBP)]$.

moiety, 522 nm denoted as band III, 622 and 620 nm denoted as band II, and 747 and 727 nm denoted as band I, respectively. Meanwhile, the intense band below 280 nm was also observed, which can be attributed to the absorption of binaphthyl groups.[16]

Investigation reveals that in the mixed ring rare earth triple-decker complexes $[M_2(Pc)_2(TClPP)]$ [TClPP=tetrakis(4-chloro)-phenylporphyrinate, M = Y, La−Er except Ce and Pm],[11d] close consanguinity of the three conjugated π-systems in a face-to-face configuration induces a splitting of the monomer (Pc and TClPP) molecular orbitals. As can be seen from Figure 2, interactions of the doubly degenerate e_g lowest unoccupied molecular orbitals (LUMOs) of both ligands, the a_{1u} highest occupied molecular orbitals (HOMOs) of Pc's, and the a_{1u} HOMO of TCBP result in the formation of three doubly degenerate lowest-unoccupied molecular orbitals (the e_g bonding LUMO, second non-bonding e_u LUMO, and third e_g anti-bonding LUMO), as well as three non-degenerate HOMOs (the a_{1u} third bonding HOMO, second a_{2g} non-bonding HOMO, and first a_{1u} anti-bonding HOMO) of triple-decker compounds **1** and **2**.[17] Because of the intrinsic difference in the molecular orbital energy, the a_{1u} orbital of Pc's is higher in energy than that of TCBP, while the e_g orbitals of Pc's are lower than those of TCBP. As a result, the first a_{1u} anti-bonding HOMO and the first e_g bonding LUMO are mainly from the phthalocyaninato ligands, while the third a_{1u} bonding HOMO and third e_g anti-bonding LUMO have higher porphyrin character. Nevertheless, the non-bonding LUMO is a pure Pc orbital. These results therefore suggest that the lowest-energy absorption band, with the maximum at 747 and 727 nm for **1** and **2**, respectively, can be attributed to the electronic transition from the anti-bonding HOMO to the bonding LUMO, which is mainly from the phthalocyaninato ligands. The second-lowest-energy absorption band with the maximum at 622 and 620 nm for both complexes can be ascribed to the transition from the second non-bonding HOMO to the second non-bonding LUMO. Clearly, this absorption peak remains essentially unchanged for the two compounds. The Soret bands at 423 and 427 nm for complexes **1** and **2** are clearly derived from transitions involving molecular orbitals with mixed phthalocyanine and porphyrin character. However, it is noteworthy that the Soret bands at 340 and 341 nm for **1** and **2** should also involve non-bonding orbitals mainly with a pure Pc character.

However, as can be seen from Figure 1, perfect mirror-image circular dichroism (CD) spectra were observed in the whole spectral region of the optically pure isomers of both europium and yttrium compounds **1** and **2**. This indicates the effective chiral information transfer from the peripheral chiral binaphthyl units to the porphyrin and phthalocyanine chromophores in the triple-decker molecules because of the intense $\pi-\pi$ interaction between porphyrin and phthalocyanine rings. With the exception of wavelengths shorter than 280 nm, the CD intensity is primarily due to induced CD (ICD) associated with the presence of the optically active binaphthyl moiety. In binaphthyl linked monomeric Pc systems reported previously,[18] enantiomers with an (*R*)-binaphthyl moiety (left-handed conformer) exhibited a positive ICD sign in the 280−750 nm region, while the enantiomers with an (*S*)-binaphthyl moiety (right-handed conformer) exhibited the opposite sign pattern. In the present system, ICD sign was positive in the 300−500 nm region while negative in the 520−670 nm region for the (*R*)-enantiomer, and an opposite sign pattern was observed for the (*S*)-enantiomer. The sign of the ICD signal is dependent on the direction of the electronic transition moment ($\boldsymbol{\mu}$) of the porphyrin or phthalocyanine (Pc) chromophores ($\boldsymbol{\mu}_P$) and the $\boldsymbol{\mu}$ and magnetic transition moment ($\mathbf{m}$) of the binaphthyl moieties ($\boldsymbol{\mu}_N$ and $\mathbf{m}_N$, respectively). Since the ICD sign in the 300−500 nm of the (*R*) enantiomer spectrum is positive as is also the case with monomeric Pc systems containing an (*R*) binaphthyl unit on the ligand periphery, the $\boldsymbol{\mu}_P$'s of the porphyrin and Pc Soret bands are believed to lie in the plane of the ligand π-system. In contrast, the direction of $\boldsymbol{\mu}_P$'s of the band at around 620 nm probably deviates slightly from this alignment because of configurational interaction between the relevant $\pi\pi^*$ state and a CT state, which has a moment aligned along the *z*-axis normal to the ligand plane. ICD intensity becomes weaker for the bands lying at longer wavelength, since it is inversely proportional to $(\nu_N^2 - \nu_P^2)R$,[18] where ν_N and ν_P are the frequencies of the absorption by naphthalene and the chromophore (either porphyrin or phthalocyanine in this context), respectively, and R is the distance between the approximate center of the binaphthyl moiety and the chromophores. Since the long-axis polarized ^1B_b band of naphthalene lies at about 45500 cm^{-1} (ca. 220 nm), the ICD of the bands that lie at longer wavelengths is much weaker. For this reason, no meaningful ICD could be detected for the 727 and 747 nm bands of **1** and **2**, respectively, even when the concentration of the solution is markedly increased.

Associated with their electronic absorption peaks, the MCD spectra of **1** and **2** show apparently dispersion type Faraday *A* terms with crossover points corresponding to the band centers of the main absorption bands (Figure 1), suggesting that these are corresponding to transitions to the nearly degenerate excited states, Figure 2.[19]

Table 4. Half-Wave Redox Potentials of 1 and 2 (V vs SCE) in CH_2Cl_2 Containing 0.1 M $[NBu_4][ClO_4]$

compound	Oxd_2	Oxd_1	Red_1	Red_2	$\Delta E°_{1/2}$[a]
$Eu_2(Pc)_2(TCBP)$ (**1**)	0.90	0.47	−0.64	−1.06	1.11
$Y_2(Pc)_2(TCBP)$ (**2**)	0.83	0.41	−0.64	−1.08	1.05

[a] $\Delta E°_{1/2}$ is the potential difference between the first oxidation (Oxd_1) and first reduction (Red_1) processes, that is the HOMO−LUMO gap of corresponding molecule.

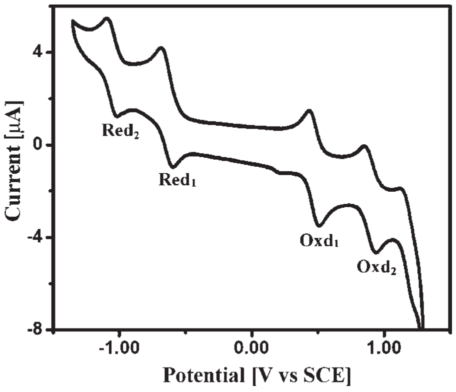


Figure 3. Cyclic voltammogram of compound **1** in CH_2Cl_2 containing 0.1 M $[NBu_4][ClO_4]$ at a scan rate of 20 mV s^{-1}.

Electrochemical Properties. The electrochemical behavior of **1** and **2** was investigated by cyclic voltammetry (CV) in CH_2Cl_2. The half-wave potentials of the two complexes **1** and **2** are summarized in Table 4. Figure 3 shows the cyclic voltammograms of $[Eu_2(Pc)_2(TCBP)]$ (**1**) as a typical representative of these two compounds. According to the CV result, within the electrochemical window of CH_2Cl_2, both the two compounds exhibit two quasi-reversible one-electron oxidations labeled as Oxd_1 and Oxd_2 and two quasi-reversible one-electron reductions labeled as Red_1 and Red_2. All the processes can be attributed to the successive removal of an electron and addition of an electron to the ligand-based orbitals as the oxidation state of the central tervalent rare earth metals in the triple-decker complexes does not change. In comparison with compound **1**, the half-wave potentials of the first (Oxd_1) and second oxidation (Oxd_2) processes for **2**, which involve the removal of electrons from the HOMO, are obviously smaller, Table 4. However, the two reduction processes (Red_1 and Red_2) for both compounds **1** and **2** remain virtually unchanged, suggesting that the energy level of the LUMO remains relatively constant for the two compounds. As a consequence, the energy separation between the HOMO and the LUMO for compound **2** is smaller than that of **1**, in accord with the red-shift of the longest-wavelength absorption band of the former compound. This result is just in line with the electronic absorption result as detailed above, Figure 1.

CONCLUSION

In summary, two novel optically active mixed (phthalocyaninato)(porphyrinato) rare earth triple-decker complexes with both (*R*)- and (*S*)-enantiomers $M_2(Pc)_2(TCBP)$ (M = Eu, Y) have been designed, synthesized, and spectroscopically characterized. Perfect mirror-image CD signals observed in the Soret and Q absorption regions in the CD spectra of the (*R*)- and (*S*)-enantiomers for **1** and **2** reveal that the chirality of the binaphthyl moiety is effectively transferred to the porphyrin and phthalocyanine moieties. The present result, representing part of our continuous effort toward the design and preparation of chiral sandwich-type tetrapyrrole rare earth complexes, will be helpful in providing new insight into novel sandwich type tetrapyrrole rare earth compounds with potential applications in the fields of nonlinear optics and chiral catalysis.

EXPERIMENTAL SECTION

General Procedures. 1,2,4-Trichlorobenzene (TCB) was distilled from anhydrous CaH_2 under reduced pressure prior to use. Dimethylformamide (DMF) was freshly distilled from anhydrous $MgSO_4$ just before use. Dichloromethane was freshly distilled from CaH_2 under nitrogen. 3,4-Dihydroxybenzaldehyde was purchased from Shanghai Zhixin Co. Both chloroform and methanol (HPLC grade) were purchased from Tianjin Kermel Co. Column chromatography was carried out on silica gel (Merck, Kieselgel 60, 70−230 mesh) with the indicated eluents. Optically pure (*R*)- and (*S*)-2,2′-dihydroxy-1,1′-binaphthyl (>99% ee) were obtained from Dalian Reagent Company. All other reagents and solvents were of reagent grade and used as received. The compounds of optically active metal free porphyrin (*R*)- and (*S*)-H_2TCBP,[20] $Eu(acac)_3\cdot nH_2O$,[21] and $Eu(Pc)_2$[22] were prepared according to literature procedures. The optically active triple-decker complexes [(*R*)- and (*S*)-$M_2(Pc)_2(TCBP)$] (M = Eu, Y) (**1**, **2**) were prepared according to the reported procedure as detailed below.

Measurements. ^1H NMR spectra were measured on a Bruker DPX 300 spectrometer (300 MHz) in $CDCl_3$. Electronic absorption spectra were recorded on a Hitachi U-4100 spectrophotometer. MALDI-TOF mass spectra were taken on a Bruker BIFLEX III ultrahigh resolution instrument. Elemental analyses were performed on an Elementar Vavio El III Fourier transform infrared spectra were recorded in KBr pellets with 2 cm^{-1} resolution using an αALPHA-T spectrometer. MCD and CD measurements were made on a JASCO J-725 spectropolarimeter in the presence and absence of magnetic field (1.09 T), respectively.

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 silverwire counter electrode. The reference electrode was Ag/Ag^+ (a solution of 0.01 M $AgNO_3$ and 0.1 M TBAP in acetonitrile), 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 saturated calomel electrode (SCE). Typically, a 0.1 M solution of $[NBu_4][ClO_4]$ in CH_2Cl_2 containing 0.5 mM of sample was purged with nitrogen for 10 min, and then the voltammograms were recorded at ambient temperature. The scan rate was 20 mV s^{-1} for CV.

Preparation of (*R*)- and (*S*)-$Eu_2(Pc)_2(TCBP)$ [(*R*)- and (*S*)-1]. A mixture of $Eu(acac)_3\cdot nH_2O$ (23 mg, 0.05 mmol), $Eu(Pc)_2$ (59 mg, 0.05 mmol), and (*R*)- or (*S*)-H_2TCBP (122 mg, 0.05 mmol) in TCB (6 mL) was heated to reflux for 7 h. After being cooled to room temperature, the solvent was evaporated under reduced pressure, and the residue was subjected to chromatography on a silica-gel column with $CHCl_3$ as eluent. A small amount of unreacted $Eu(Pc)_2$ were collected as the first fraction and then the target mixed (phthalocyaninato)(porphyrinato) europium triple-decker product $Eu_2(Pc)_2(TCBP)$ was collected as the second fraction. The small amount of unreacted H_2TCBP was collected as the third fraction. Repeated chromatography followed by recrystallization from $CHCl_3$ and MeOH gave pure compounds of (*R*)- and (*S*)-**1** as a darkish-blue solid (70.0 mg, 38%).

Preparation of (*R*)- and (*S*)-$Y_2(Pc)_2(TCBP)$ [(*R*)- and (*S*)-2]. The procedure described above for (*R*)- and (*S*)-**1** with Eu_2 complexes was used in the presence of $Y(acac)_3\cdot nH_2O$ (20 mg, 0.05 mmol) instead of Eu(acac)$_3$·nH$_2$O as starting material, Y$_2$ compounds (R)- and (S)-**2** were obtained after recrystallization from CHCl$_3$ and MeOH (60.5 mg, 36%).

■ ASSOCIATED CONTENT

Supporting Information. (A) Experimental and (a) simulated isotopic patterns for the molecular ion of triple-decker compound **1**; IR spectra of complexes **1** and **2** in the region of 400−3800 cm^{-1} with 2 cm^{-1} resolution. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: jianzhuang@ustb.edu.cn.

■ ACKNOWLEDGMENT

Financial support from the Natural Science Foundation of China, Ministry of Education of China, Shandong Province (Grant Q2008B01), Beijing Municipal Commission of Education, and University of Science and Technology Beijing to J.J. and that by a Grant-in-Aid for Scientific Research on Innovative Areas (π-Space, No. 20108007) to N.K. is gratefully acknowledged.

■ REFERENCES

(1) (a) Garoff, R. A.; Litzinger, E. A.; Connor, R. E.; Fishman, I.; Armitage, B. A. *Langmuir* **2002**, *18*, 6330–6337. (b) Wang, M.; Silva, G. L.; Armitage, B. A. *J. Am. Chem. Soc.* **2000**, *122*, 9977–9986. (c) Pasternack, R. F.; Giannetto, A.; Pagano, P.; Gibbs, E. J. *J. Am. Chem. Soc.* **1991**, *113*, 7799–7780.

(2) (a) *Phthalocyanine: Properties and Applications*; Lever, A. B. P., Leznoff, C. C., Eds.; VCH: New York, 1989−1996; Vols. 1−4. (b) *Phthalocyanines Materials: Synthesis, Structure and Function*; McKeown, N. B., Ed.; Cambridge University Press: New York, 1998. (c) *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: San Diego, CA, 2000 and 2003; Vols. 1−20. (d) Senge, M. O.; Fazekas, M.; Notaras, E. G. A.; Blau, W. J.; Zawadzka, M.; Locos, O. B.; Ni Mhuircheartaigh, E. M. *Adv. Mater.* **2007**, *19*, 2734–2774. (e) Kobayashi, N. *Coord. Chem. Rev.* **2001**, 99–123. (f) Bellacchio, E.; Lauceri, R.; Gurrieri, S.; Scolaro, L. M.; Romeo, A.; Purrello, R. *J. Am. Chem. Soc.* **1998**, *120*, 12353–12354. (g) Galardon, E.; Lukas, M.; Le Maux, P.; Simonneaux, G. *Tetrahedron Lett.* **1999**, *40*, 2753–2756. (h) Boitrel, B.; Baveux-Chambenoit, V.; Richard, P. *Eur. J. Org. Chem.* **2001**, 4213–4221. (i) Liang, J.-L.; Huang, J.-S.; Yu, X.-Q.; Zhu, N.; Che, C.-M. *Chem.—Eur. J.* **2002**, *8*, 1563–1572. (j) Zhang, R.; Yu, W.-Y.; Sun, H.-Z.; Liu, W.-S.; Che, C.-M. *Chem.—Eur. J.* **2002**, *8*, 2495–2507. (k) Engelkamp, H.; Middlebeek, S.; Nolte, R. J. M. *Science* **1999**, *284*, 785–788.

(3) (a) Jiang, J.; Ng, D. K. P. *Acc. Chem. Res.* **2009**, *42*, 79–88. (b) Jiang, J.; Bao, M.; Rintoul, L.; Arnold, D. P. *Coord. Chem. Rev.* **2006**, *250*, 424–448. (c) Jiang, J.; Liu, W.; Arnold, D. P. *J. Porphyrins Phthalocyanines* **2003**, *7*, 459–473. (d) Jiang, J.; Kasuga, K.; Arnold, D. P. In *Supramolecular Photosensitive and Electroactive Materials*; Nalwa, H. S., Ed.; Academic Press: New York, 2001; Chapter 2, pp 113−210. (e) Ng, D. K. P.; Jiang *J. Chem. Soc. Rev.* **1997**, *26*, 433–442.

(4) (a) Tashiro, K.; Konishi, K.; Aida, T. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 856–858. (b) Tashiro, K.; Fujiwara, T.; Konishi, K.; Aida, T. *Chem. Commun* **1998**, 1121–1122. (c) Tashiro, K.; Konishi, K.; Aida, T. *J. Am. Chem. Soc.* **2000**, *122*, 7921–7926.

(5) (a) Takeuchi, M.; Imada, T.; Shinkai, S. *Angew. Chem., Int. Ed.* **1998**, *37*, 2096–2099. (b) Sugasaki, A.; Ikeda, M.; Takeuchi, M.; Shinkai, S. *Angew. Chem., Int. Ed.* **2000**, *39*, 3839–3842. (c) Takeuchi, M.; Ikeda, M.; Sugasaki, A.; Shinkai, S. *Acc. Chem. Res.* **2001**, *34*, 865–873. (d) Ikeda, M.; Takeuchi, M.; Shinkai, S.; Tani, F.; Naruta, Y.; Sakamoto, S.; Yamaguchi, K. *Chem.—Eur. J.* **2002**, *8*, 5541–5550.

(6) (a) Negrimovskii, V. M.; Bouvet, M. M.; Luk'yanets, E A.; Simon, J. J. *Porphyrins Phthalocyanines* **2001**, *5*, 423–427. (b) Bian, Y.; Wang, R.; Wang, D.; Zhu, P.; Li, R.; Dou, J.; Liu, W.; Choi, C.-F.; Chan, H.-S.; Ma, C.; Ng, D. K. P.; Jiang, J. *Helv. Chim. Acta* **2004**, *87*, 2581–2596. (c) Bian, Y.; Wang, R.; Jiang, J.; Lee, C.-H.; Wang, J.; Ng, D. K. P. *Chem. Commun.* **2003**, 1194–1195.

(7) Lv, W.; Zhu, P.; Bian, Y.; Ma, C.; Zhang, X.; Jiang, J. *Inorg. Chem.* **2010**, *49*, 6628–6635.

(8) Zhou, Y.; Zhang, Y.; Wang, H.; Jiang, J.; Bian, Y.; Muranaka, A.; Kobayashi, N. *Inorg. Chem.* **2009**, *48*, 8925–8933.

(9) Wang, R.; Li, R.; Li, Y.; Zhang, X.; Zhu, P.; Lo, P.-C.; Ng, D. K. P.; Pan, N.; Ma, C.; Kobayashi, N.; Jiang, J. *Chem.—Eur. J.* **2006**, *12*, 1475–1485.

(10) Zhang, X.; Muranaka, A.; Lv, W.; Zhang, Y.; Bian, Y.; Jiang, J.; Kobayashi, N. *Chem.—Eur. J.* **2008**, *14*, 4667–4674.

(11) (a) Kirin, I. S.; Moskalev, P. N.; Makashev, Y. A. *Russ. J. Inorg. Chem.* **1965**, *10*, 1065–1066. (b) Buchler, J. W.; Ng, D. K. P. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: San Diego, CA, 2000; Vol. 3, pp 245−294. (c) Sun, X.; Cui, X.; Arnold, D. P.; Choi, M. T. M.; Ng, D. K. P.; Jiang, J. *Eur. J. Inorg. Chem.* **2003**, *8*, 1555–1561. (d) Sun, X.; Li, R.; Wang, D.; Dou, J.; Zhu, P.; Lu, F.; Ma, C.; Choi, Ch-F.; Cheng, D. Y. Y.; Ng, D.K. P.; Kobayashi, N.; Jiang, J. *Eur. J. Inorg. Chem.* **2004**, *19*, 3806–3813.

(12) To detect whether racemization of optically active porphyrin in refluxing TCB occurs, unreacted metal-free porphyrin after synthesizing the europium and yttrium mixed ring triple-decker complexes was recovered and purified. CD spectroscopic measurement results reveal that both the CD spectra and the coefficients of CD curves for both (R)- or (S)-H$_2$TCBP do not change.

(13) Lu, G.; Chen, Y.; Zhang, Y.; Bao, M.; Bian, Y.; Li, X.; Jiang, J. *J. Am. Chem. Soc.* **2008**, *130*, 11623–116320.

(14) (a) Jiang, J.; Arnold, D. P.; Yu, H. *Polyhedron* **1999**, *18*, 2129–2139. (b) Lu, F.; Bao, M.; Ma, C.; Zhang, X.; Arnold, D. P.; Jiang, J. *Spectrochim. Acta. A* **2003**, *59*, 3273–3286. (c) Bao, M.; Pan, N.; Ma, C.; Arnold, D. P.; Jiang, J. *Vib. Spectrosc.* **2003**, *32*, 175–184.

(15) Sheng, N.; Li, R.; Choi, C.; Su, W.; Ng, D. K. P.; Cui, C.; Yoshida, K.; Kobayashi, N.; Jiang, J. *Inorg. Chem.* **2006**, *45*, 3794–3802.

(16) (a) Kobayashi, N.; Kobayashi, Y.; Osa, T. *J. Am. Chem. Soc.* **1993**, *115*, 10994–1099. (b) Kobayashi, N. *Chem. Commun.* **1998**, *4*, 487–488.

(17) (a) Stillman, M. J.; Nyokong, T. In *Phthalocyanines: Properties and Applications*; Leznoff, C. C., Lever, A. B. P., Eds.; VCH: New York, 1989; Vol. 1, pp 133−290. (b) Orti, E.; Bredas, J. L. *J. Chem. Phys.* **1990**, 92, 1228–1236. (c) Rousseau, R.; Aroca, R.; Rodriguez-Mendez, M. L. *J. Mol. Struct.* **1995**, *356*, 49–62. (d) Ishikawa, N. *J. Porphyrins Phthalocyanines* **2001**, *5*, 87–101.

(18) Kobayashi, N.; Higashi, R.; Titeca, B. C.; Lamote, F.; Ceulemans, A. *J. Am. Chem. Soc.* **1999**, *121*, 12018–12028.

(19) Muranaka, A.; Matsumoto, Y.; Uchiyama, M.; Jiang, J.; Bian, Y.; Ceulemans, A.; Kobayashi, N. *Inorg. Chem.* **2005**, *44*, 3818–3826.

(20) Lu, J.; Wu, L.; Zhang, X.; Jiang, J. *Eur. J. Inorg. Chem.* **2010**, 4000–4008.

(21) Stites, J. G.; McCarty, C. N.; Quill, L. L. *J. Am. Chem. Soc.* **1948**, *70*, 3142–3143.

(22) Jiang, J.; Liu, R. C. W.; Mak, T. C. W.; Chan, T. W. D.; Ng, D. K. P. *Polyhedron* **1997**, *16*, 515–520.