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Optically Active Homoleptic Bis(phthalocyaninato) Rare Earth Double-Decker Complexes Bearing Peripheral Chiral Menthol Moieties: Effect of $\pi-\pi$ Interaction on the Chiral Information Transfer at the Molecular Level

Wei Lv,[‡] Peihua Zhu,[‡] Yongzhong Bian,[†] Changqin Ma,[‡] Xiaomei Zhang,*,[‡] and Jianzhuang Jiang*,[†],[‡]

[†]*Department of Chemistry, University of Science and Technology Beijing, Beijing 100083, People's Republic of China, and* [‡]*Department of Chemistry, Shandong University, Jinan 250100, People's Republic of China*

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With the view to creating novel sandwich-type phthalocyaninato rare earth complexes toward new applications in material science and catalysis, D- and L-enantiomers of a series of optically active homoleptic bis(phthalocyaninato) rare earth double-deckers with four chiral menthol moieties at the peripheral positions of the phthalocyanine ligand, $\mathrm{M}(Pc^*)_2$ [Pc^* = 2(3),9(10),16(17),23(24)-tetrakis(2-isopropyl-5-methylcyclohexoxyl)phthalocyanine; M = Eu, Y, Lu] (**1**−**3**), have been designed and prepared by treating (D)- or (L)-4-(2-isopropyl-5-methylcyclohexoxyl)-1,2-dicyanobenzene with the corresponding $\mathrm{M(acac)_3 \cdot}n\mathrm{H_2O}$ (acac = acetylacetonate) in the presence of the organic base 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in refluxing *n*-pentanol. For the purpose of comparative study, heteroleptic bis(phthalocyaninato) europium analogues (D)- and (L)-$\mathrm{Eu}(Pc)(Pc^*)$ (**4**) as well as the unsubstituted homoleptic bis(phthalocyaninato) europium counterpart $\mathrm{Eu}(Pc)_2$ (**5**) were also prepared. The novel synthesized bis(phthalocyaninato) rare earth double-deckers have been characterized by a wide range of spectroscopic methods including MS, ^{1}H NMR, IR, and electronic absorption spectroscopic measurements in addition to elemental analysis. In contrast to the CD silent monomeric metal-free 2(3),9(10),16(17),23(24)-tetrakis(2-isopropyl-5-methylcyclohexoxyl)phthalocyanine, observation of the CD signal in the N absorption region of **4** reveals the significant effect of intramolecular $\pi-\pi$ interaction on intensifying the asymmetrical perturbation of the chiral menthol units onto the phthalocyanine chromophore, which results in successful chiral information transfer from menthol moieties to the phthalocyanine chromophore at a molecular level in the heteroleptic double-decker compound **4** despite the lack of CD signal in the Soret and Q absorption regions of the phthalocyanine ligand. This is further supported by the optical activity of homoleptic bis(phthalocyaninato) rare earth double-deckers $\mathrm{M}(Pc^*)_2$ (**1**−**3**), as revealed by the CD signals even in the Soret and Q absorption regions according to the CD spectroscopic result, indicating the intensified asymmetrical perturbation of the chiral menthol units onto the phthalocyanine chromophores along with the increase in the chiral menthol substituent number from **4** to **1**−**3**. The present result at the molecular level is helpful for understanding the chiral information transfer mechanism at the supermolecular level. In addition, the electrochemical properties of bis(phthalocyaninato) rare earth complexes have also been comparatively investigated by cyclic voltammetry and differential pulse voltammetry.

Introduction

Chirality is one of the most fascinating and complicated features commonly found in nature.[1] This is manifested by natural products including proteins, nucleic acids, sugars, amino acids, hormones, and antibiotics as well as synthetic chemicals, drugs, and foods.[2] These materials often exhibit specific activity and functionality depending on their chirality. As a result, great efforts have been paid to prepare various kinds of absolute configuration-determined chiral compounds and separate their enantiomers.[3] Among these, optically active porphyrins and phthalocyanines have attracted growing interest because of their extensive biological relevance and various

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*To whom correspondence should be addressed. E-mail: jianzhuang@ustb.edu.cn.

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potential applications.[4] In 1999 Katz and co-workers reported on the synthesis of optically active phthalocyanine containing four nonracemic helicene-fused pyrazinoporphyrazines. They found the helical stacking of these phthalocyanine molecules, due to the effect of chiral side chains, results in a notable increase in the second-order nonlinear optical response.[4h] In 2003, Kimura and collaborators prepared chiral fibrous assemblies of phthalocyaninato zinc complexes carrying chiral diol or chiral branched alkyl chains.[4i]

It is worth noting that sandwich tetrapyrrole metal complexes have also attracted great attention over the past century due to their potential applications in molecular electronics and magnets.[5] In particular, recently the synthesis and properties of the chiral sandwich phthalocyaninato and/or porphyrinato rare earth complexes have formed the research focus in this direction associated with their intriguing structures, properties, and potential wide range of applications.[6] The unique molecular structure with two or three tetrapyrrole ligands connected by one or two rare earth metal ion(s) renders it possible to induce chirality in these compounds by selecting different phthalocyanine and/or porphyrin ligands with special symmetry. As early as 1997, Aida and co-workers started to synthesize and optically resolve chiral homoleptic bis(porphyrinato) zirconium and cerium compounds with D_2 symmetry.[7] Almost at the same time, Shinkai et al. prepared bis[tetrkis(4-pyridyl)porphyrinato] cerium/dicarboxylic acids or saccharide complexes, which show CD activity in the whole spectral range.[8] Nevertheless, both Simon and Jiang prepared the racemic mixture of heteroleptic (phthalocyaninato)(naphthalocyaninato) lutetium(III) double-decker complex $[\mathrm{Lu^{III}}(Pc)(\mathrm{Nc^*})]$, where Nc* represents the Cs isomer.[9] However, optical resolution of these two enantiomers was not successful. Very recently, on the basis of a systematic study of a series of sandwich-type chiral mixed (phthalocyaninato)(porphyrinato) and heteroleptic phthalocyaninato rare earth double- and triple-decker complexes isolated also in the form of a racemic mixture,[9b,c,10] this group reported the optical resolution of the mixed (phthalocyaninato)(porphyrinato) rare earth double-decker complexes $[\mathrm{HM^{III}}\{Pc(\alpha\text{-}3\text{-}\mathrm{OC_5H_{11}})_4\}\{\mathrm{TOAPP}\}]$ $[Pc(\alpha\text{-}3\text{-}\mathrm{OC_5H_{11}})_4$ = 1,8,15,22-tetrakis(3-pentyloxy)phthalocyaninate; TOAPP = *meso*-tetrakis(4-octylaminophenyl)porphyrinate; M = Y, Ho] for the first time 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.[11] In addition, optically active mixed (phthalocyaninato)(porphyrinato) rare earth double-decker complexes $[\mathrm{HM^{III}}\{Pc(\mathrm{OBNP})_2\}(\mathrm{TClPP})]$ [TClPP = *meso*-tetrakis(4-chlorophenyl)porphyrinate; M = Y, Eu] were also synthesized by this group with the optically active metal-free phthalocyanine having a π-system with non-centrosymmetrical C_{2v} symmetry, (*S*)- and (*R*)-$\mathrm{H_2}\{Pc(\mathrm{OBNP})_2\}$, as starting material.[12] However, to the best of our knowledge, optically active sandwich-type phthalocyaninato and/or porphyrinato metal complexes with chiral atom centers in the peripheral substituents still remain unknown so far.

In addition, *it is of great importance to study small systems composed of a limited number of components before examining infinitely extended systems*. As reported recently by this group, the self-assembly properties of both the D- and L-enantiomers of a metal-free 2(3),9(10),16(17),23(24)-tetrakis(2-isopropyl-5-methylcyclohexoxyl)phthalocyanine were studied.[13] CD spectroscopy indicates the formation of one-dimensional helices containing infinite numbers of metal-free phthalocyanine molecules with left-handed and right-handed helical molecular arrangement, respectively. However, it is impossible to prepare, isolate, and investigate nanostructures or aggregates consisting of only two (three, four, or other limited number of) metal-free 2(3),9(10),16(17),23(24)-tetrakis(2-isopropyl-5-methylcyclohexoxyl)phthalocyanine molecules by means of self-assembly methods. As a consequence, for the purpose of clarifying and understanding the origin of chiral information transfer *at the supermolecular level*, small related systems including both heteroleptic and homoleptic bis(phthalocyaninato) rare earth complexes containing two

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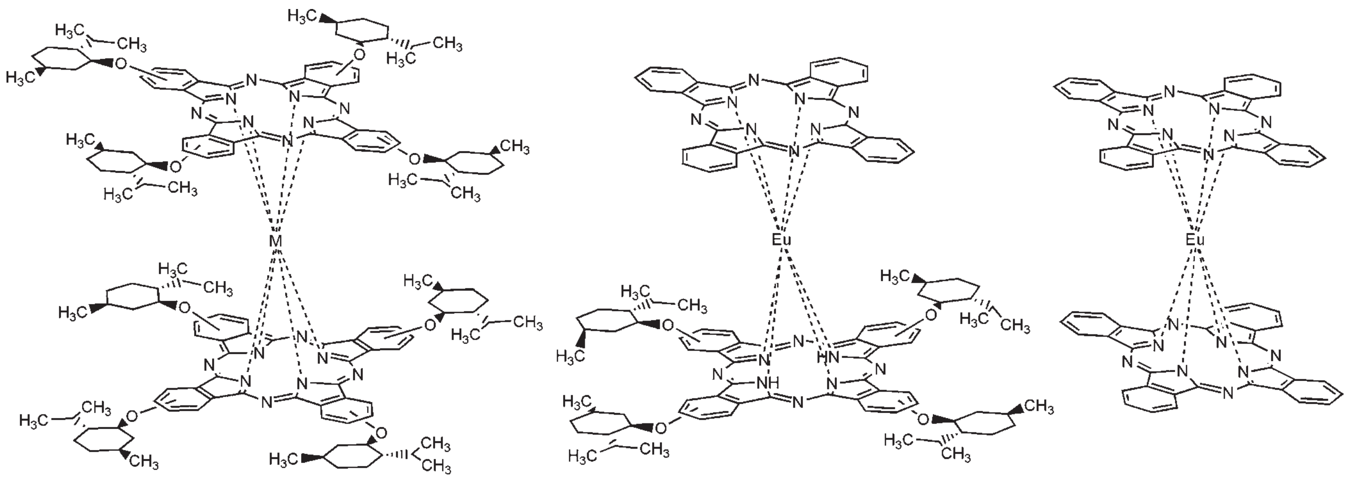
Scheme 1. Schematic Molecular Structures of Optically Active Homoleptic Tetra-β-substituted Bis(phthalocyaninato) Rare Earth Double-Decker Complexes (D)- and (L)-M(Pc*)$_2$ (M = Eu, Y, Lu) (**1**–**3**), Heteroleptic (D)- and (L)-Eu(Pc)(Pc*) (**4**), and Unsubstituted Homoleptic Eu(Pc)$_2$ (**5**)



(D)- / (L)-M(Pc*)$_2$ (M = Eu, Y, Lu) (1-3) **(D)- / (L)-Eu(Pc)(Pc*) (4)** **Eu(Pc)$_2$ (5)**

corresponding phthalocyanine components have been designed. In the present paper, we describe the synthesis and characterization of a new series of homoleptic tetra-β-substituted bis(phthalocyaninato) rare earth double-decker complexes bearing chiral menthol moieties at the peripheral positions of the phthalocyanine ligand (D)- and (L)-M(*Pc**)$_2$ (M = Eu, Y, Lu) (**1**–**3**) together with the heteroleptic bis(phthalocyaninato) europium analogues (D)- and (L)-Eu(*Pc*)(*Pc**) (**4**), Scheme 1. CD spectroscopy reveals an interesting experimental finding that the heteroleptic double-decker complex **4** displays a CD signal only in the N absorption region without any CD signal in the Soret and Q absorption regions of the phthalocyanine ligand, while the homoleptic analogues **1**–**3** show CD signals even in the Soret and Q absorption regions. Comparison with the optically silent monomeric metal-free 2(3),9(10),16(17),23(24)-tetrakis(2-isopropyl-5-methylcyclohexoxyl)phthalocyanine clearly reveals the significant effect of intense intramolecular π–π interaction on intensifying the asymmetrical perturbation of chiral substituents on the phthalocyanine chromophore and resulting in chiral information transfer at the molecular level. The present result, representing part of our continuous effort toward designing and preparing chiral sandwich-type tetrapyrrole rare earth complexes, will be helpful in providing new insight into chiral information transfer for synthetic conjugated systems at *molecular and also supermolecular levels.*

Results and Discussion

Molecular Design, Synthesis, and Spectroscopic Characterization. As mentioned above, chiral sandwich porphyrinato and/or phthalocyaninato metal complexes still remain extremely rare so far. Except for designing and preparing chiral sandwich-type tetrapyrrole rare earth complexes depending on their peculiar molecular structures, incorporating chiral groups (actually chiral discrimination information) onto the peripheral positions of tetrapyrrole rings also provides an alternative route to corresponding optically active sandwich-type tetrapyrrole rare earth compounds. As a consequence, four menthol units were incorporated onto the peripheral positions of the phthalocyanine ring for the purpose of preparing corresponding homoleptic and heteroleptic bis(phthalocyaninato) rare earth double-decker complexes, Scheme 1.

Homoleptic unsubstituted bis(phthalocyaninato) rare earth complexes M(*Pc*)$_2$ were usually prepared by cyclic tetramerization of corresponding phthalonitrile catalyzed by an organic base such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in the presence of rare earth salts.[14] This is also true for the homoleptic tetra/octa-β-substituted bis(phthalocyaninato) rare earth analogues including M^{III}[*Pc*(OR)$_4$]$_2$ and M^{III}[*Pc*(OR)$_8$]$_2$.[15] In the present study, both D- and L-enantiomers of the target homoleptic bis(phthalocyaninato) rare earth double-decker complexes, (D)- and (L)-M(*Pc**)$_2$ (M = Eu, Y, Lu) (**1**–**3**), were synthesized from cyclic tetramerization of (D)- or (L)-4-(2-isopropyl-5-methylcyclohexoxyl)-1,2-dicyanobenzene in the presence of catalyst DBU in *n*-pentanol. Because of the random location of four 2-isopropyl-5-methylcyclohexoxyl substituents at the peripheral positions of the phthalocyanine ring, both enantiomers of this series of bis(phthalocyaninato) rare earth double-deckers are actually a mixture of constitutional stereoisomers with different molecular symmetry. However, satisfactory elemental analysis results have been obtained for these newly prepared double-decker complexes (D)- and (L)-M(*Pc**)$_2$ (**1**–**3**) after repeated column chromatography and recrystallization.

A cyclic tetramerization method with a half-sandwich complex template was used for the preparation of the heteroleptic bis(phthalocyaninato) europium double-decker complex.[16] Reaction of H$_2$*Pc** and Eu(*Pc*)(acac) in refluxing

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Table 1. ^{1}H NMR Data (δ) for Double-Deckers **1**–**5** in $CDCl_3$/DMSO (1:1) in the Presence of ca. 1% Hydrazine Hydrate

compound	^{1}H NMR data (δ)
1	10.68–11.24 (m, 16H, *Pc**-H_α), 8.60–8.75 (m, 8H, *Pc**-H_β), 5.37–6.15 (m, 8H, OCH), 0.93–4.35 (m, 144H, H of menthol moieties)
2	8.46–8.84 (m, 16H, *Pc**-H_α), 7.68 (br, 8H, *Pc**-H_β), 4.55–4.84 (m, 8H, OCH) 0.94–3.40 (m, 144H, H of menthol moieties)
3	8.46–8.87 (m, 16H, *Pc**-H_α), 7.69 (br, 8H, *Pc**-H_β), 4.53–4.85 (m, 8H, OCH) 0.75–3.32 (m, 144H, H of menthol moieties)
4	11.21 (br, 8H, *Pc*-H_α), 10.67–11.07 (m, 8H, *Pc**-H_α), 9.13 (br, 8H, *Pc*-H_β) 8.67 (br, 4H, *Pc**-H_β), 5.69–5.99 (m, 4H, OCH), 0.80–4.41 (m, 72H, H of menthol moieties)
5^a	11.09–11.11 (m, 16H, *Pc*-H_α), 9.13–9.15 (m, 16H, *Pc*-H_β)

^{a} Cited from ref 19b.

n-octanol leads to the formation of Eu(*Pc*)(*Pc**) (**4**) in relatively good yield. For comparative studies, the homoleptic analogue Eu(Pc)$_2$ (**5**) was also prepared according to published methods.[17] The newly prepared heteroleptic bis(phthalocyaninto) europium complex **4** also gave satisfactory elemental analysis result. These five compounds were characterized by MALDI-TOF mass spectroscopic methods. The MALDI-TOF mass spectra of these compounds clearly showed intense signals for the protonated molecular ion $(M + H)^+$ or molecular ion M^+. The isotopic pattern closely resembled the simulated one, as exemplified by the spectrum of **1** given in Figure S1 (Supporting Information). The sandwich nature for both homoleptic **1**–**3** and heteroleptic **4** was further unambiguously confirmed by various spectroscopic methods including ^{1}H NMR spectroscopy as detailed below.

The ^{1}H NMR spectra of **1**–**4** were recorded in DMSO-*d*$_6$/$CDCl_3$ (1:1) in the presence of ca. 1% hydrazine hydrate, Figures S2–S5 (Supporting Information), and the data are summarized in Table 1. The hydrazine hydrate was used to reduce the paramagnetic neutral species to the respective monoanion in which both of the macrocycles are diamagnetic dianions.[18] As can be seen, because of the composition of constitutional stereoisomers of each enantiomer due to the random location of four chiral menthol substituents at the peripheral positions of the phthalocyanine ligand, both homoleptic and heteroleptic double-decker complexes **1**–**4** gave broad peaks in the whole range of ^{1}H NMR spectra. However, the identity of these compounds could still be reached by ^{1}H NMR spectroscopy. In particular, the homoleptic double-deckers M(Pc*)$_2$ gave two multiplets at δ 10.68–11.24 and 8.60–8.75 for **1**, 8.46–8.84 and 7.68 (broad) for **2**, and 8.46–8.87 and 7.69 (broad) for **3**, respectively, which can be assigned to the α and β ring protons of *Pc**, Figures S2, S3, and S4 (Supporting Information), while the heteroleptic analogue Eu(*Pc*)(*Pc**) (**4**) showed four multiplets at δ 11.21 (broad), 10.67–11.07, 9.13 (broad), and 8.67 (broad), respectively, Figure S5 (Supporting Information). The former two multiplets are attributed to α ring protons of *Pc* and *Pc**, respectively, while the latter two are the signals of β ring protons of *Pc* and *Pc**. In addition, the ^{1}H NMR spectra of **1**–**4** also present two multiplets in the region δ 5.37–6.15, 4.55–4.84, 4.53–4.85, and 5.69–5.99 for **1**–**4**, respectively, assigned to the OCH. As can be seen, the other protons of menthol moieties of **1**–**4** are partially overlapped at δ 0.93–4.35, 0.94–3.40, 0.75–3.32, and 0.80–4.41.

Similar to the unsubstituted double-decker counterpart **5**,[19g] the neutral sandwich nature for both homoleptic **1**–**3** and heteroleptic **4** was further unambiguously confirmed by their IR spectra. As can be seen in Figure S6 (Supporting Information), all four double-deckers showed an intense band at 1317–1321 cm^{-1}, which is a marker IR band for the phthalocyanine monoanion radical anion,[19] indicating the presence of an unpaired electron in one of the phthalocyanine ligands in these complexes. Similar to the IR spectra of the octakis(octyloxy) analogues M[*Pc*-$(OC_8H_{17})_8$]$_2$,[19] the asymmetric C–O–C stretching for **1**–**4** is observed at ca. 1263–1273 cm^{-1}. The spectra for **1**–**4** also showed several strong bands around 2922 cm^{-1}, which are attributed to the C–H stretching vibrations of the CH, CH_2, and CH_3 groups of the menthol moieties.

Electronic Absorption and Circular Dichroism (CD) Spectroscopy. The electronic absorption spectra of **1**–**5** were recorded in $CHCl_3$, and the data are summarized in Table 2. Figure 1 compares the electronic absorption spectra in the range 250–2000 nm of the five compounds. All the absorption spectra show a typical phthalocyanine N band around 287 nm (at 278 nm for **5**) due to the electronic transitions associated with deeply filled orbitals and the LUMO.[20] The Soret band of **1**–**5** appears at 322–331 nm with a shoulder at the lower-energy side, involving a couple of electronic transitions dealing with the third-occupied HOMO and the first LUMO. Similar slight splitting of the Soret band has also been observed for both homoleptic and heteroleptic bis(phthalocyaninato) rare earth(III) complexes.[17,21] The Q bands for these compounds are observed in the range 671–690 nm with one vibrational shoulder at 605–624 nm resulting from the transitions from the first semioccupied HOMO to the second LUMO or from the second fully occupied HOMO to the first LUMO.[22] In addition, one weak π-radical anion band at ca. 908–935 nm, together with a near-IR band at

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Table 2. Electronic Absorption Spectra and Near-IR Data of the Double-Decker Complexes **1**−**5** in $CHCl_3$

compound	λ_{max}/nm (log ε)							
1	287 (5.00)	331 (5.07)	365 (5.06)	475 (4.48)	624 (4.75)	690 (5.13)	928 (3.64)	1650 (4.19)
2	287 (4.95)	331 (5.03)	360 (5.05)	466 (4.44)	619 (4.67)	683 (5.12)	933 (3.75)	1579 (4.07)
3	287 (4.97)	328 (5.02)	360 (5.07)	468 (4.44)	615 (4.65)	679 (5.18)	935 (3.87)	1432 (4.14)
4	286 (4.89)	326 (5.02)	357 (5.19)	478 (4.42)	614 (4.54)	678 (5.10)	918 (3.66)	1602 (4.08)
5[a]	278 (4.86)	322 (4.78)	342 (4.60)	459 (4.17)	605 (4.21)	671 (4.93)	908 (3.37)	1601 (3.82)

[a] Cited from ref 19a.

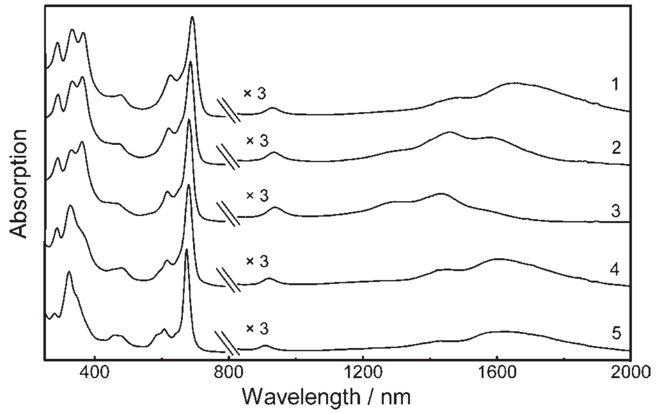

Figure 1. Electronic absorption spectra of double-decker complexes **1**−**5** in dilute chloroform solution.

1432−1650 nm, is also seen. The latter near-IR band is highly characteristic for tetrapyrrole rare earth(III) double-deckers that contain a hole in one of the ligands.[5,23]

In comparison with homoleptic unsubsituted bis(phthalocyaninato) europium complex **5**, except for the N absorption and near-IR band assigned to the transition from the second HOMO to the first semioccupied HOMO, the absorption positions of all the remaining bands of the heteroleptic bis(phthalocyaninato) europium analogue **4** seem to be red-shifted. Further red shifts in corresponding absorption bands were observed for the homoleptic bis(phthalocyaninato) rare earth(III) complexes **1**−**3** in comparison with the heteroleptic bis(phthalocyaninato) europium **4**, revealing the electron-donating nature of menthol substituents and indicating the effect of menthol substituent number on the absorption position. In addition, the intensity of some absorption peaks also seems to depend on the number of menthol units. For example, the shoulder of the Soret bands at the lower energy side of the heteroleptic bis(phthalocyaninato) europium complex **4** is stronger than that of the homoleptic bis(phthalocyaninato) europium counterpart **5**. For the homoleptic bis(phthalocyaninato) rare earth(III) complexex **1**−**3**, this absorption peak became equal or even more intense compared with the corresponding main Soret band. A similar change was also observed for the weak absorption band in the range 466−478 nm for **1**−**4**. These observations reveal that the electronic absorption spectra of these compounds are consanguineously correlative with the menthol moieties peripherally linked to the phthalocyanine ligand in the double-deckers. With increasing the menthol substituent number, the effect on the electronic absorption properties becomes gradually intense. This, together with the strong intramolecular π−π interaction between the two phthalocyanine rings, in turn induces intensified asymmetric perturbation from chiral menthol side chains, resulting in successful chiral expression in the phthalocyanine N absorption region in the heteroleptic bis(phthalocyaninato) europium complex **4** and even further into the phthalocyanine Soret and Q absorption regions in homoleptic bis(phthalocyaninato) rare earth(III) complexes **1**−**3** at the molecular level as verified by their CD spectroscopic results, as detailed below.

The CD spectra of bis(phthalocyaninato) rare earth(III) complexes **1**−**4** and monomeric metal-free 2(3),9(10),16(17),23(24)-tetrakis(2-isopropyl-5-methylcyclohexoxyl)phthalocyanine H_2Pc^* are shown in Figures 2 and S7 (Supporting Information). As can clearly be seen, subtle differences in the electronic absorption spectra of **1**−**4** were amplified in their CD spectra. The monomeric metal-free (D)- and (L)-2(3),9(10),16(17),23(24)-tetrakis(2-isopropyl-5-methylcyclohexoxyl)phthalocyanine H_2Pc^* shows no CD signal in the whole electronic absorption region due to the lack of effective asymmetrical perturbation of the chiral menthol units, Figure 2D. However, both D- and L-enantiomers of heteroleptic Eu(Pc)(Pc^*) (**4**) display a CD signal in the phthalocyanine N absorption region, Figure 2B,E, implying the effective chiral information transfer from the peripheral chiral menthol side chains to the phthalocyanine chromophore at the molecular level. Different from the heteroleptic counterpart Eu(Pc)(Pc^*), containing four peripheral chiral menthol substituents in one of the two phthalocyanine ligands, introduction of peripheral chiral menthol substituents onto both phthalocyanine ligands in homoleptic bis(phthalocyaninato) europium double-decker complexes leads to perfect mirroring CD signals observed not only in the N absorption region but also in the Soret and Q absorption regions of the phthalocyanine ligand for **1**−**3**, Figures 2C,F and S7 (Supporting Information). In detail, for (D)-**1**, (D)-**2**, and (D)-**3**, the sign of the CD is mainly positive over the main Soret and Q bands of phthalocyanine, while conversely (L)-**1**, (L)-**2**, and (L)-**3** show mainly negative CD signs. According to the chiral exciton theory,[24] (D)-**1**, (D)-**2**, and (D)-**3** are right-handed, while (L)-**1**, (L)-**2**, and (L)-**3** are left-handed on the basis of the CD pattern in the range 280−300 nm. This is also true for the two enantiomers of heteroleptic double-decker complex **4**, Figure 2B,E. At the end of this section, it is worth noting that in contrast to the findings that the monomeric metal-free 2(3),9(10),16(17),23(24)-tetrakis(2-isopropyl-5-methylcyclohexoxyl)phthalocyanine is optically silent in the whole phthalocyanine

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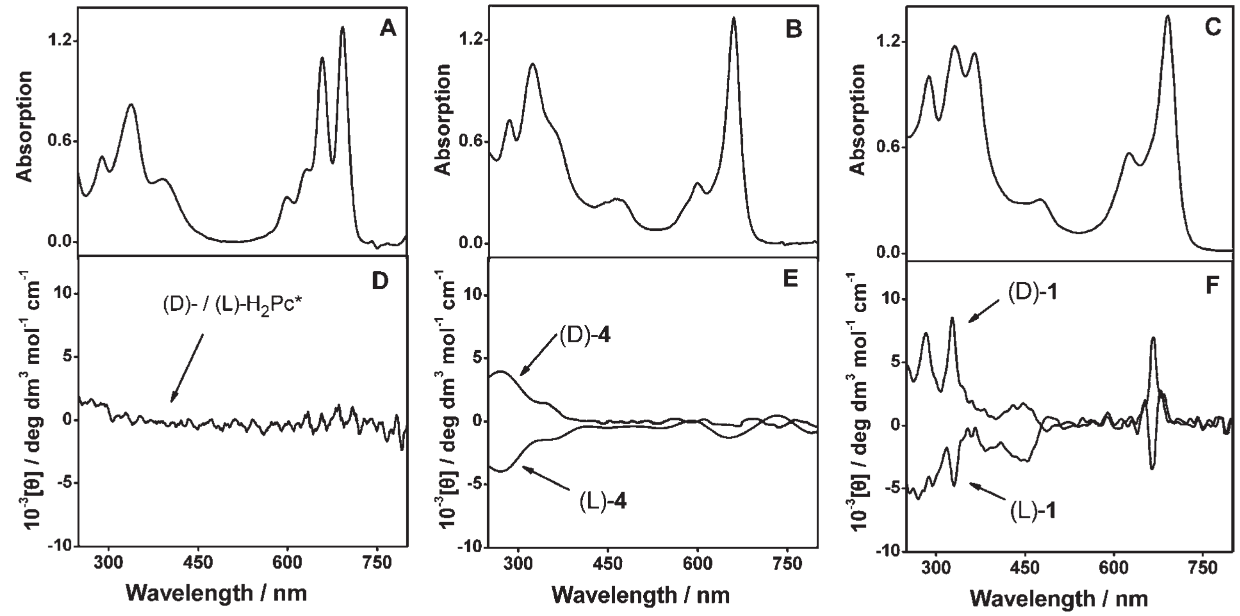

Figure 2. Electronic absorption spectra of monomeric metal-free 2(3),9(10),16(17),23(24)-tetrakis(2-isopropyl-5-methylcyclohexoxyl)phthalocyanine H_2Pc^* (A) and double-decker complexes **4** (B) and **1** (C) in dilute chloroform solution together with the CD spectra of H_2Pc^* (D), **4** (E), and **1** (F).

absorption region,[25] observation of a CD signal in the phthalocyanine N absorption region for the heteroleptic Eu(*Pc*)(*Pc**) (**4**) reveals the significant effect of intense intramolecular $\pi-\pi$ interaction on intensifying the asymmetrical perturbation of the chiral menthol units onto the phthalocyanine chromophore, which in turn induces effective chiral information transfer from the peripheral chiral menthol side chains to the phthalocyanine chromophore for **4**. In addition, incorporation of chiral menthol substituents onto both phthalocyanine rings in the bis(phthalocyaninato) europium double-decker molecule further intensifies the asymmetrical perturbation of the chiral menthol units onto the central phthalocyanine chromophore of $M(Pc^*)_2$ (**1**−**3**), indicating the effect of chiral sustituent number on chiral information transfer at the molecular level. The present result is not only beneficial for exploring the chiral transmission within the conjugated system *at the molecular level* but more importantly helpful for understanding the chiral information transfer mechanism of corresponding monomeric metal-free compounds *at the supermolecular level*: Cooperation of intermolecular $\pi-\pi$ interaction between phthalocyanine rings with chiral discrimination of peripheral chiral menthol side chains in the one-dimensional helices formed from metal-free 2(3),9(10),16(17),23(24)-tetrakis-(2-isopropyl-5-methylcyclohexoxyl)phthalocyanine induces intensified asymmetrical perturbation of the chiral menthol units onto the phthalocyanine chromophore, resulting in the optical activity for the self-assembled fibrous nanostructures of metal-free phthalocyanine over the whole absorption region of the phthalocyanine chromophore.[25]

Electrochemical Properties. The electrochemical behavior of the homoleptic bis(phthalocyaninato) rare earth double-deckers (**1**−**3**) and heteroleptic bis(phthalocyaninato) europium analogues (**4**) was investigated by cyclic voltammetry (CV) and then differential pulse voltammetry (DPV) in CH_2Cl_2. The half-wave redox potentials vs SCE for these complexes are summarized in Table 3. Figure 3 shows the cyclic voltammograms of $Eu(Pc^*)_2$ (**1**) as a typical representative of this series of rare earth compounds **1**−**4**. According to the CV and DPV results, within the electrochemical window of CH_2Cl_2 all the double-decker compounds **1**−**4** undergo one one-electron oxidation labeled as Oxd_1 and two one-electron reductions labeled Red_1 and Red_2 under the present conditions. The separation of the reduction and oxidation peak potentials for all the processes lies between 87 and 244 mV. All the processes of **1**−**4** can be attributed to successive removal from or addition of one electron to the ligand-based orbitals, as the oxidation state of the central tervalent rare earth ions in the double-decker complexes does not change. As shown in Table 3, the potential difference between Red_1 and Red_2 ($\Delta E^\circ_{1/2}$) decreases along with the decrease in central metal size from **1** to **3**. For comparison, the electrochemical properties of the unsubstituted homoleptic bis(phthalocyaninato) europium analogue (**5**) are also listed in Table 3. Comparison among these data reveals that with the increase in the number of menthol substituents, Red_1 and Red_2 are slightly shifted to the cathodic direction.

Table 3. Half-Wave Redox Potentials of Double-Deckers **1**−**5** in CH_2Cl_2 Containing 0.1M TBAP

compound	Oxd_1	Red_1	Red_2	$\Delta E^\circ_{1/2}$[a]
1	+0.35	−0.04	−1.23	1.19
2	+0.32	−0.10	−1.28	1.18
3	+0.29	−0.12	−1.21	1.09
4	+0.47	+0.06	−1.13	1.19
5[b]	+0.55	+0.12	−1.07	1.19

[a] $\Delta E^\circ_{1/2}$ is the potential difference between the first reduction and second reduction processes, i.e., the HOMO−LUMO gap of the corresponding molecule. [b] Cited from ref 26.

Conclusion

In summary, we describe the design, synthesis, and spectroscopic properties of a new series of homoleptic

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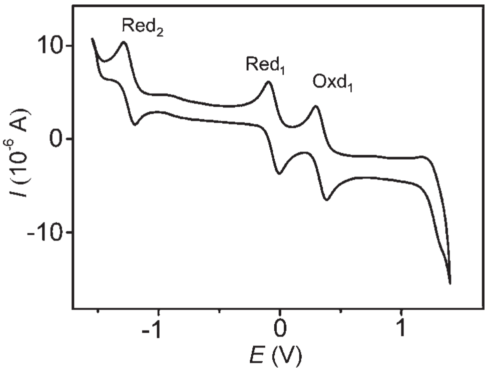

Figure 3. Cyclic voltammogram of **1** in CH_2Cl_2 containing 0.1 M $[NBu_4][ClO_4]$ at a scan rate 20 mV s^{-1}.

bis(phthalocyaninato) rare earth double-deckers (D)- and (L)-M(*Pc**)$_2$ and their heteroleptic analogues (D)- and (L)-Eu(*Pc*)(*Pc**). Observation of the CD signal in the phthalocyanine N absorption region of the heteroleptic double-decker reveals the important role of intense intramolecular $\pi-\pi$ interaction in intensifying the asymmetrical perturbation of the chiral menthol units onto the phthalocyanine chromophore in the heteroleptic double-decker molecule, which in turn induces the successful chiral information transfer from the peripheral chiral menthol side chains to the phthalocyanine chromophore. In addition, observation of the CD signals even in the Soret and Q absorption regions of the phthalocyanine ligand for homoleptic bis(phthalocyaninato) rare earth complexes reveals the further intensified asymmetrical perturbation of the chiral menthol units onto the phthalocyanine chromophore of homoleptic M(*Pc**)$_2$. The present result, representing part of our continuous effort toward design and preparation of chiral sandwich-type tetrapyrrole rare earth complexes, will be helpful in providing new insight into chiral information transfer for synthetic conjugated systems *at both the molecular and supermolecular level.*

Experimental Section

General Procedures. Anhydrous *n*-pentanol and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) were purchased from Aldrich. *n*-Pentanol, *n*-octanol, and DMF were freshly distilled just before use. Column chromatography was carried out on silica gel (Merck, Kieselgel 60, 70−230 mesh) with the indicated eluents. (D)- and (L)-Menthol (99% ee) were purchased from Alfa Aesar. All other reagents and solvents were of reagent grade form and used as received without further purification. The compounds $Eu(acac)_3\cdot H_2O$,[26] $Y(acac)_3\cdot nH_2O$,[26] $Lu(acac)_3\cdot nH_2O$,[26] (D)- or (L)-4-(2-isopropyl-5-methylcyclohexoxyl)-1,2-dicyanobenzene (**4**), and (D)- or (L)-2(3),9(10),16(17),23(24)-tetrakis(2-isopropyl-5-methylcyclohexoxyl)phthalocyanine were prepared as described in our previous paper.[25]

Measurements. ^{1}H NMR spectra were recorded on a Bruker Ultrashield Avance III 400 spectrometer (400 MHz). Spectra were referenced internally using the residual solvent resonances relative to $SiMe_4$. MALDI-TOF mass spectra were detected on a Bruker BIFLEX III ultrahigh-resolution Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer with α-cyano-4-hydroxycinnamic acid as matrix. Elemental analyses were performed on an Elementar Vavio El III. Electronic absorption spectra were obtained with a Hitachi U-4100 spectrophotometer. Circular dichroism measurements were carried out on a JASCO J-810 spectropolarimeter. Fourier transform infrared spectra were recorded in KBr pellets with 2 cm^{-1} resolution using a αALPHA-T spectrometer. Electrochemical measurements were carried out with a BAS CV-50W voltammetric analyzer. The cell comprised inlets for a glassy carbon disk working electrode of 3.0 mm in diameter and a silver-wire counter electrode. The reference electrode was Ag/Ag^+ (0.01 mol dm^{-3}), which was connected to the solution by a Luggin capillary, whose tip was placed close to the working electrode. It was corrected for junction potentials by being referenced internally to the ferrocenium/ferrocene (Fc^+/Fc) couple [$E_{1/2}(Fc^+/Fc) = 0.50$ V vs SCE]. Typically, a 0.1 mol dm^{-3} solution of $[Bu_4N][ClO_4]$inCH_2Cl_2 containing 0.5 mmol dm^{-3} of sample was purged with nitrogen for 10 min; then the voltammograms were recorded at ambient temperature. The scan rate was 20 and 10 mV s^{-1} for CV and DPV, respectively.[27]

Preparation of (D)- and (L)-M(*Pc)$_2$ [*Pc** = 2(3),9(10),16-(17),23(24)-tetrakis(2-isopropyl-5-methylcyclohexoxyl)phthalocyanine; M = Eu, Y, Lu] (1−3).** A mixture of (D)- or (L)-H$_2$*Pc** (100 mg, 0.35 mmol) and $M(acac)_3\cdot nH_2O$ (M = Eu, Y, Lu) (0.05 mmol) as the starting materials and DBU as a catalyst in *n*-pentanol (4 mL) was heated to reflux under nitrogen for 8−12 h. The solvent was then removed in vacuo, and the residue was subjected to chromatography on a silica gel column using pure chloroform as eluent. The crude product was purified by repeated chromatography followed by recrystallization from chloroform/methanol or chloroform/*n*-hexane, giving the pure target compounds as a dark black powder.

Yield for (D)- and (L)-Eu(*Pc**)$_2$ (**1**): 9.5 mg (9%), green solid. MS (MALDI-TOF): calcd for $C_{144}H_{176}N_{16}O_8Eu$ $(M + H)^+$ 2409.3; an isotopic cluster peaking at *m*/*z* 2409.3. Anal. Calcd (%) for $C_{144}H_{176}N_{16}O_8Eu$: C, 71.74; H, 7.36; N, 9.30. Found: C, 71.82; H, 7.17; N, 9.19.

Yield for (D)- and (L)-Y(*Pc**)$_2$ (**2**): 10 mg (10%), green solid. MS (MALDI-TOF): calcd for $C_{144}H_{176}N_{16}O_8Y$ $(M)^+$ 2346.3; an isotopic cluster peaking at *m*/*z* 2346.4. Anal. Calcd (%) for $C_{144}H_{176}N_{16}O_8Y$ (**2**$\cdot$1/3CHCl$_3$): C, 72.60; H, 7.44; N, 9.39. Found: C, 72.54; H, 7.50; N, 9.09.

Yield for (D)- and (L)-Lu(*Pc**)$_2$ (**3**): 11 mg (10%), green solid. MS (MALDI-TOF): calcd for $C_{144}H_{176}N_{16}O_8Lu$ $(M)^+$ 2432.3; an isotopic cluster peaking at *m*/*z* 2432.3. Anal. Calcd (%) for $C_{144}H_{176}N_{16}O_8Lu$ (**3**$\cdot$0.5C$_6$H$_{14}$): C, 71.28; H, 7.45; N, 9.05. Found: C, 71.53; H, 7.29; N, 8.68.

Preparation of (D)- and (L)-Eu(*Pc*)(*Pc) [*Pc** = 2(3),9(10),16-(17),23(24)-tetrakis(2-isopropyl-5-methylcyclohexoxyl)phthalocyanine] (4).** A mixture of (D)- or (L)-H$_2$*Pc** (11.2 mg, 0.01 mmol) and Eu(*Pc*)(acac)$_3$ (9.6 mg, 0.13 mmol) as the starting materials in *n*-octanol (3 mL) was heated to reflux under nitrogen for ca. 1−2 h. The solvent was then removed in vacuo, and the residue was first subjected to chromatography on a silica gel column using pure toluene as eluent. The crude product was purified by repeated chromatography followed by recrystallization from chloroform and methanol. Yield: 2.9 mg (25%), green solid. MS (MALDI-TOF): calcd for $C_{104}H_{104}N_{16}O_4Eu$ $(M)^+$ 1793.8; an isotopic cluster peaking at *m*/*z* 1794.2. Anal. Calcd (%) for $C_{104}H_{104}N_{16}O_4Eu$ (**4**$\cdot$3CH$_3$OH): C, 68.52; H, 6.08; N, 12.06. Found: C, 68.89; H, 6.29; N, 11.69.

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Supporting Information Available: (A) Experimental and (a) simulated isotopic patterns for the molecular ion of double-decker

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complex **1**. ^{1}H NMR spectrum of Eu(*Pc**)$_2$ (**1**) in $CDCl_3$/DMSO (1:1) in the presence of ca. 1% hydrazine hydrate. ^{1}H NMR spectrum of Y(*Pc**)$_2$ (**2**) in $CDCl_3$/DMSO (1:1) in the presence of ca. 1% hydrazine hydrate. ^{1}H NMR spectrum of Lu(*Pc**)$_2$ (**3**) in $CDCl_3$/DMSO (1:1) in the presence of ca. 1% hydrazine hydrate. ^{1}H NMR spectrum of Eu(*Pc*)(*Pc**) (**4**) in $CDCl_3$/DMSO (1:1) in the presence of ca. 1% hydrazine hydrate. IR spectra of homoleptic Eu(*Pc**)$_2$ (A), Y(*Pc**)$_2$ (B), Lu(*Pc**)$_2$ (C), and heteroleptic Eu(*Pc*)(*Pc**) (D) in the region 400−3100 cm^{-1} with 2 cm^{-1} resolution. CD spectra of double-decker complexes **2** (A) and **3** (B) in dilute chloroform solution together with the electronic absorption spectra of double-decker complexes **2** (C) and **3** (D) in dilute chloroform solution. This material is available free of charge via the Internet at http://pubs.acs.org.