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Optically Active Mixed Phthalocyaninato–Porphyrinato Rare-Earth Double-Decker Complexes: Synthesis, Spectroscopy, and Solvent-Dependent Molecular Conformations

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Abstract: Reaction between the optically active metal-free phthalocyanine with a π system with noncentrosymmetrical C_{2v} symmetry ((*S*)- and (*R*)-$H_2\{Pc(OBNP)_2\}$; OBNP = binaphthylphthalocyanine) and half-sandwich complexes $[M^{III}(acac)(TClPP)]$ (M = Y, Eu; TClPP = *meso*-tetrakis(4-chlorophenyl)porphyrinate; acac = acetylacetonate), which were generated in situ from $[M(acac)_3]\cdot nH_2O$ and $H_2(TClPP)$ in *n*-octanol at reflux, provided the first optically active protonated mixed phthalocyaninato–porphyrinato rare-earth double-decker complexes $[M^{III}H\{Pc(OBNP)_2\}(TClPP)]$ (M = Y, Eu) in good yield. In addition to electronic absorption spectroscopy and magnetic circular dichroism results, circular dichroism shows different spectroscopic features of these mixed-ring rare-earth double-decker compounds in different solvents, such as DMF and $CHCl_3$, which was well-reproduced on the basis of time-dependent density functional theory calculation results for the yttrium species (*S*)-$[Y^{III}\{Pc(OBNP)_2\}(Por)]^-$ (Por = porphyrinate, which is obtained by removing the four chlorophenyl groups from the TClPP ligand) in terms of the change in the rotation angle between the two macrocyclic ligands in the double-decker molecules. These results revealed the solvent-dependent nature of the molecular conformation of mixed-ring rare-earth double-decker complexes, which suggests a new way of tuning the optical and the electrochemical properties of sandwich-type bis(tetrapyrrole)–metal double-decker complexes in solution by changing the solvent.

Keywords: chirality · density functional calculations · phthalocyanines · porphyrinoids · rare-earth metals

Introduction

Porphyrins and phthalocyanines have been extensively studied over the past century owing to their wide range of biological relevance and industrial applications.[1] In particular, sandwich porphyrinato and phthalocyaninato metal complexes have attracted great attention as advanced materials due to their special optical, electrochemical, and magnetic properties associated with their unique molecular structure and strong π–π interactions between tetrapyrrole ligands.[2] Over the past few decades, optically active porphyrin and phthalocyanine derivatives have also been intensively studied,[3] however, chiral sandwich porphyrinato and phthalocyaninato metal complexes remain extremely rare to date. Through the sandwich staggered molecular structure of bis(tetrapyrrole)–metal compounds, Aida et al. have recently synthesized and optically resolved chiral homoleptic bis(porphyrinato)zirconium and cerium compounds with unusual D_2 symmetry.[4] Hydrogen bonding between chiral dicarboxylic acids or saccharides and the pyridyl nitrogen atoms of bis[tetrakis(4-pyridyl)porphyrinato]cerium through positive homotropic allosterism also induced optical activity into the sandwich double-decker compounds.[5] Very recently, the groups of Simon and Jiang have worked towards the synthesis of chiral bis(phthalocyaninato)–rare-earth complexes,

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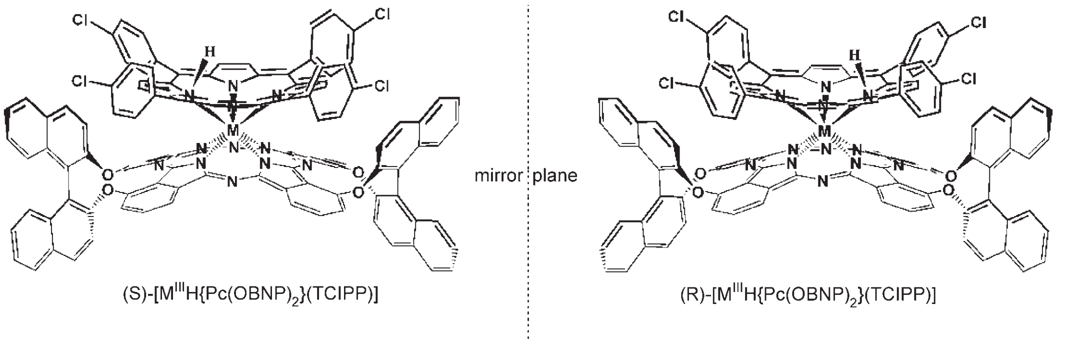

Scheme 1. Schematic molecular structures of **1** and **2**.

however, optical resolution of the two enantiomers for both [Lu^{III}(Pc)(Nc*)] (Nc* = the C_s isomer of 1,2-naphthalocyaninate) and [M(Pc){Pc(α-OC_5H_{11})$_4$}] (Pc(α-OC_5H_{11})$_4$ = 1,8,15,22-tetrakis(3-pentyloxy)phthalocyaninate) has not yet been successful.[6,7] Herein, we report the preparation and characterization of the first optically active mixed phthalocyaninato–porphyrinato rare-earth complexes [M^{III}H{Pc(OBNP)$_2$}(TClPP)] (M = Y (**1**), Eu (**2**); OBNP = binaphthylphthalocyanine, TClPP = *meso*-tetrakis(4-chlorophenyl)porphyrinate; Scheme 1). To enhance the asymmetric perturbation to the tetrapyrrole chromophores in the sandwich-type mixed phthalocyaninato–porphyrinato rare-earth double-decker molecules through dipole–dipole interactions, aromatic chiral binaphthyl units were introduced onto the nonperipheral positions of the phthalocyanine ring. In addition to electronic absorption and magnetic circular dichroism (MCD) spectroscopy results, circular dichroism (CD) reveals different spectroscopic features of these mixed-ring rare-earth double-decker compounds in different solvents. On the basis of time-dependent density functional theory (TD-DFT) results on the yttrium species (*S*)-[Y^{III}{Pc(OBNP)$_2$}(Por)]$^-$ in terms of different rotation angles between the two macrocyclic ligands in the double-decker molecules, different electronic absorption and CD spectroscopic features of (*S*)-[Y^{III}H{Pc(OBNP)$_2$}(TClPP)] in DMF and $CHCl_3$ were well reproduced, which revealed the solvent-dependent nature of the mixed-ring rare-earth double-decker complexes on the molecular conformation.

The fact that the electronic absorption spectra of mixed phthalocyaninato–porphyrinato rare-earth complexes, and other bis(tetrapyrrole)–rare-earth compounds, changes depending on the solvent has puzzled chemists in this field for a long time (Figures S1 and S2 in the Supporting Information).[8] Cofacial dimerization of the tetrapyrrole–metal double-decker compounds in solution, in a similar manner to planar, flat monomeric phthalocyanine compounds, was proposed to explain the spectroscopic change with solvent; however, this has never been verified. The present work reveals that the change in the optical spectroscopic spectra of mixed phthalocyaninato–porphyrinato rare-earth complexes with solvent (DMF and $CHCl_3$) is due to the change in the double-decker molecular conformation associated with different interactions between the double-decker and solvent molecules. This, to the best of our knowledge, represents the first effort to understand the change in the optical spectroscopic of bis(tetrapyrrole)–metal complexes with solvent.

Results and Discussion

Synthesis and characterization of [M^{III}H{Pc(OBNP)$_2$}(TClPP)] (M = Y (1) or Eu (2)): As mentioned above, to enhance the asymmetric perturbation of the phthalocyanine or porphyrin chromophores in the sandwich double-decker molecules,[9] phthalocyanine with aromatic chiral binaphthyl units at the nonperipheral positions (H_2{Pc(OBNP)$_2$}) were chosen to synthesize the target sandwich rare-earth complexes. However, efforts using H_2{Pc(OBNP)$_2$} to synthesize both homoleptic and heteroleptic bis(phthalocyaninato)–rare-earth complexes failed. Surprisingly, reaction of H_2{Pc(OBNP)$_2$} with the half-sandwich porphyrinato rare-earth complexes [M^{III}(acac)(TClPP)] (M = Y, Eu; acac = acetylacetonate), generated in situ from M(acac)$_3$·$n\,H_2O$ and H_2(TClPP) in *n*-octanol at reflux led to the isolation of optically active protonated mixed phthalocyaninato–porphyrinato rare-earth double-deckers (*S*)- and (*R*)-[M^{III}H{Pc(OBNP)$_2$}(TClPP)] (M = Y (**1**) or Eu (**2**)) in good yields. The isolation of protonated mixed-ring double-decker species is in accordance with previous results for 1,8,15,22-tetra- or 1,4,8,11,15,18,22,25-octakis-substituted phthalocyanine ligands with alkoxy groups at nonperipheral positions.[10] Racemization of the phthalocyanine did not occur at temperatures over 180° under the present reaction conditions.[11]

Satisfactory elemental analysis results were obtained for both the newly prepared protonated mixed-ring double-deckers **1** and **2**. These two compounds were further characterized by MALDI-TOF mass spectrometry and ^{1}H NMR spectroscopy. The MALDI-TOF mass spectra of these compounds clearly showed intense signals for the protonated molecular ion $[M+H]^+$. The isotopic pattern closely resembled that of the simulated one as exemplified by the spectrum of **2** given in Figure S3 in the Supporting Information. Yttrium compound **1** was EPR silent, which showed its diamagnetic property and revealed the protonated nature of these double-decker complexes. However, satisfactory NMR spectra could not be obtained for **1** and **2** probably due to the tautomerization of the acidic proton on the porphyrin ligand (note that the acid proton in the protonated mixed-ring double-decker should be on the porphyrin side according to our recent work).[12] Upon addition of approximately 1 % hydrazine hydrate, a well-resolved spectrum with virtually all of the expected signals was observed (Figure S4 in the Supporting Information). The IR spectra of **1** and **2** had an intense band at around $\tilde{\nu} = 1322\ \text{cm}^{-1}$, which is a characteristic signal for dianionic phthalocyaninato ligands.[2d] This result confirms the protonated nature of these two mixed-ring double-decker complexes.

Electronic absorption, MCD, and CD spectra of 1 and 2 recorded in DMF and $CHCl_3$: The electronic absorption, MCD, and CD spectra of **1** and **2** were recorded in DMF (Figure 1 and Figure S5 in the Supporting Information). Similar to those of $[M^{III}H\{Pc(\alpha\text{-}OC_5H_{11})_4\}(TClPP)]$ (M = Y, Sm, Eu; $Pc(\alpha\text{-}OC_5H_{11})_4$ = 1,8,15,22-tetrakis(3-pentyloxy)phthalocyaninate) and $[Y^{III}H\{Pc(\alpha\text{-}OC_4H_9)_8\}(TClPP)]$ ($Pc(\alpha\text{-}OC_4H_9)_8$ = 1,4,8,11,15,18,22,25-octakis(1-butyloxy)phthalocyaninate),[10] both complexes **1** and **2** have five absorption bands in their electronic absorption spectra, a typical feature of the protonated mixed phthalocyaninato–porphyrinato rare-earth double-decker complexes. Compounds **1** and **2** display medium to strong phthalocyanine (338 nm) and porphyrin (419–424 nm) Soret bands and several Q bands in the region of 616 to 842 nm in the spectra recorded in DMF. The spectrum also displays a medium band at 485 to 488 nm. However, the absence of the characteristic near-IR absorption at around 1200 nm for the neutral species in the electronic absorption spectra of both compounds again indicates the protonated nature of these double-deckers.[2a–c] Associated with absorption peaks, the MCD spectra apparently showed dispersion-type Faraday *A* terms, which suggested that these correspond to transitions to the almost degenerate excited states.[13] As shown in Figure 1a and Figure S5 in the Supporting Information, the optically pure isomers of both yttrium and europium compounds show perfect mirror-image CD spectra of each other in the whole spectral region. For both of the *S* isomers, the CD sign is positive between 370 and 420 nm and beyond approximately 630 nm, whereas the sign is negative between approximately 310 and 370 nm and 420 and 630 nm. Their CD intensities are $[\theta] = 0.5\times10^5$ to 6×10^5, which are comparable with those of the optically active sandwich bis(porphyrinato)–metal complexes previously reported.[4,5] The intense and sharp CD signal observed at 343 nm is characteristic of the CD of the monomeric binaphthyl-linked phthalocyanine.[9]

In accordance with the findings for [Y(Pc)(TClPP)] (Pc = unsubstituted phthalocyaninate) and $[YH\{Pc(\alpha\text{-}OC_4H_9)_8\}(TClPP)]$,[8,10] the electronic absorption spectra for these two protonated mixed-ring double-decker complexes

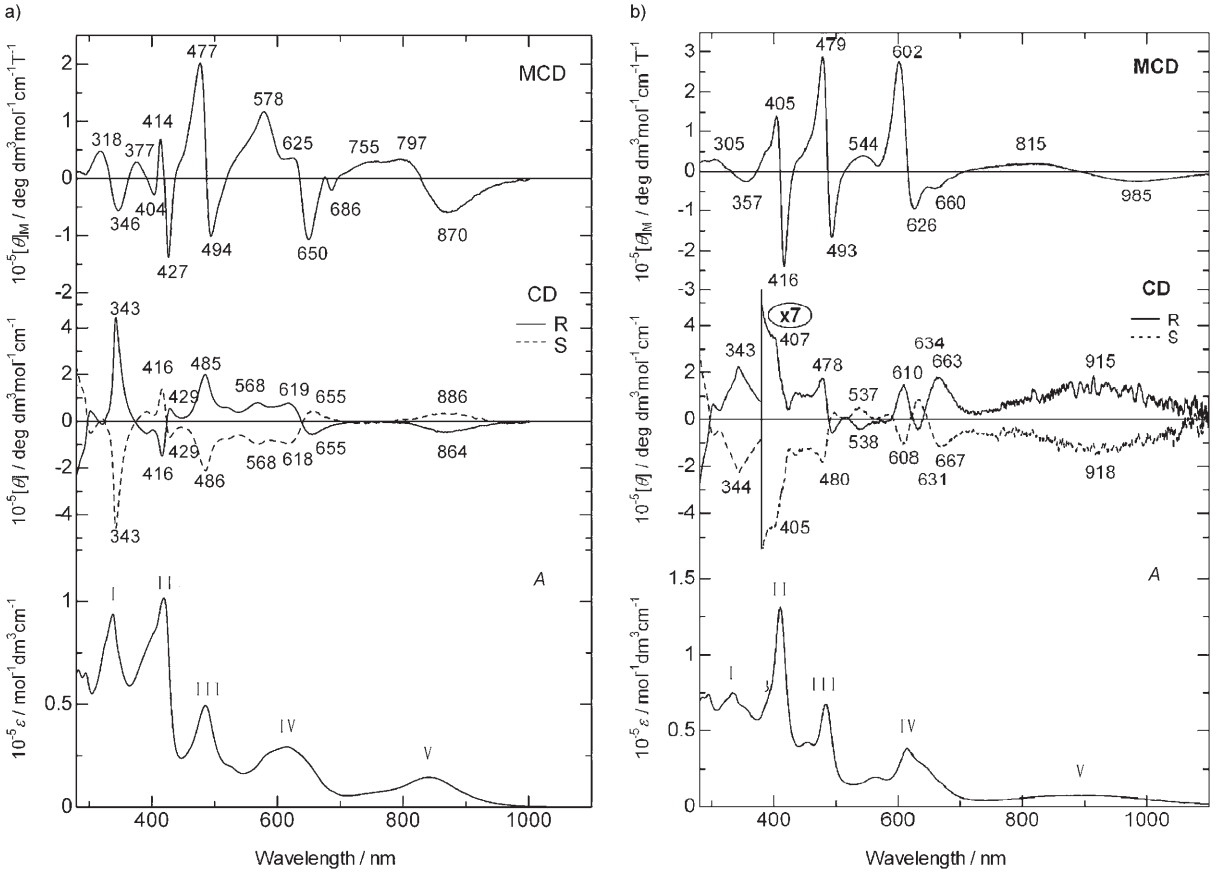

Figure 1. Electronic absorption, MCD, and CD spectra of **1** measured in a) DMF and b) $CHCl_3$.

[$M^{III}H\{Pc(OBNP)_2\}(TClPP)$] (M = Y, Eu) (**1**, **2**) change depending on the solvent. As shown in Figure 1 (and Figures S5 and S6 in the Supporting Information), despite the overall similar spectroscopic features, clear differences in the electronic absorption spectra of these two double-decker compounds recorded in $CHCl_3$ can be observed from those recorded in DMF. For example, both the phthalocyanine and porphyrin Soret bands of **1** and **2** shift from 338 and 420–424 nm in DMF to higher energy positions (333 and 410–415 nm) in $CHCl_3$. In contrast, the lowest-energy absorption band at 820 to 842 nm in DMF for **1** and **2** appears to become weaker and extends to longer wavelengths between 848–888 and 1100 nm in $CHCl_3$. Additionally, the broad absorption at 616–630 nm in DMF for **1** and **2** splits into two absorptions at 562–564 and 615 nm in $CHCl_3$. Associated with the change in the electronic absorption spectra, pseudo-Faraday *A* terms corresponding to the porphyrin Soret band at 410–415 nm, the porphyrin Q band at 484 nm, and the absorption at 615 nm in the MCD spectra recorded in $CHCl_3$ become sharper than those in DMF. More importantly, corresponding with the changes in the electronic absorption and MCD spectra, the CD spectra of the optical isomers for both complexes, in particular the yttrium compound, are completely different from those recorded in DMF in shape and the intensity becomes much weaker (about one third of that in DMF; see Figure 1, Figures S5 and S6 in the Supporting Information). It should be noted that both of the (*S*)-isomers exhibited a negative CD signal for the lowest-energy transition, in contrast to the positive CD in DMF.

All of the results described above appear to suggest a change in the molecular conformation of mixed phthalocyaninato–porphyrinato rare-earth complexes upon changing the solvent from DMF to $CHCl_3$. This is confirmed by the fact that the electronic absorption spectra of double-deckers change with a set of isosbestic points along with changing the ratio of DMF and $CHCl_3$, but maintaining a constant sample concentration (Figure 2 and Figure S7 in the Supporting Information). As mentioned in the Introduction, cofacial dimerization of any sandwich-type bis(tetrapyrrole)–rare-earth double-decker compounds with two outwardly oriented tetrapyrrole ligands in the molecule through π–π interactions between two double-decker molecules has not been reported in any solution thus far. This, in combination with the fact that all of the absorption bands in **1** and **2** do not simultaneously take a blue- or redshift along with changing the solvent, such as from DMF to $CHCl_3$, indicates the transformation of nonaggregated molecular conformations in these two solvents.

NMR spectroscopy has been a powerful method in determining molecular structure and geometry in solvent. However, as mentioned above, in the present case satisfactory ^1H NMR spectra for complexes **1** and **2** could not be obtained in either [D_7]DMF or $CDCl_3$, or in any deuterated solvents available without the addition of the reducing agent hydrazine hydrate, probably owing to tautomerization of the acidic proton over the porphyrin ligand of the double-decker molecules. This is in accordance with previous results for other protonated mixed phthalocyaninato–porphyrinato rare-earth complexes.[10] As documented in a very recent publication,[12] the location of the acidic proton in a protonated mixed phthalocyaninato–porphyrinato rare-earth (III) complex has not been solved due to the failure of ^1H NMR spectroscopy and other experimental techniques in dealing with this problem. Very recently, with the help of DFT calculations, the acidic proton in protonated mixed phthalocyaninato–porphyrinato rare-earth complexes was concluded to localize on the porphyrin rather than the phthalocyanine ring. As a result, NMR spectroscopy is unable to provide any information on the molecular geometry of complexes **1** and **2** in DMF, $CHCl_3$, or a mixture of both solvents.

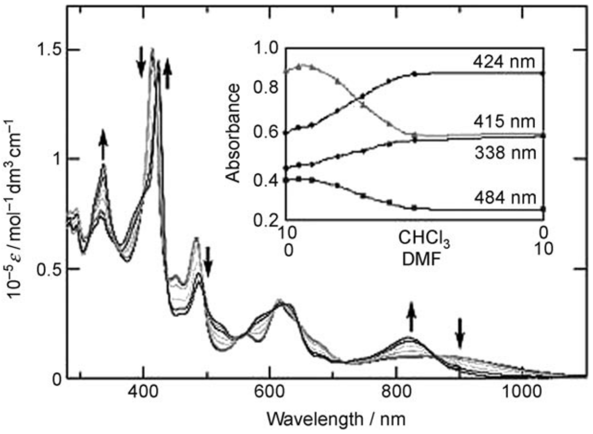

Figure 2. Solvent effect on the electronic absorption spectra of **1**. The inset shows the change in the absorbance corresponding to the Soret bands.

Electronic absorption and CD spectra of (*S*)-[$Y^{III}\{Pc(OBNP)_2\}(TClPP)]^-$ on the basis of TD-DFT calculations: On the basis of the experimental results described above, the change in the electronic absorption, MCD, and CD spectra of **1** and **2** is ascribed to the transformation of nonaggregated double-decker molecular conformations upon changing the solvent from DMF to $CHCl_3$. To get an insight into the relationship between the molecular conformation and the optical spectra of these double-decker compounds, TD-DFT calculations were carried out on the electronic absorption and CD spectroscopic properties of the yttrium species. Note that for economic reasons and to simplify the calculations, calculations on the spectra were actually carried on the anionic form of the yttrium double-decker [$Y^{III}\{Pc(OBNP)_2\}(TClPP)]^-$ or even [$Y^{III}\{Pc(OBNP)_2\}(Por)]^-$ (Por = porphyrinate, which is obtained from TClPP by removing the four chlorophenyl groups) instead of the protonated species [$Y^{III}H\{Pc(OBNP)_2\}(TClPP)$]. This is actually rationalized by assuming that the protonated mixed phthalocyaninato–porphyrinato rare-earth complexes have almost the same electronic absorption spectra as their anionic counterparts (Figure S8 in the Supporting Information). Figure 3

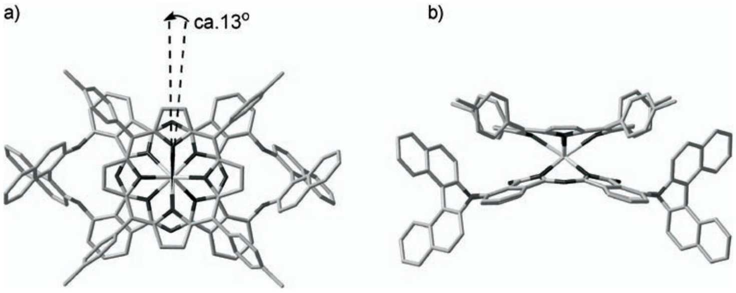

Figure 3. The top (a) and side (b) views of the optimized structure of (*S*)-$[Y^{III}\{Pc(OBNP)_2\}(TClPP)]^-$. Hydrogen atoms are omitted for clarity.

shows the optimized structure of (*S*)-$[Y^{III}\{Pc(OBNP)_2\}(TClPP)]^-$ obtained at the B3LYP/LANL2DZ level. Accordingly, the two macrocycles in this molecule are rotated from the staggered position by about 13° with a ring-to-ring separation of approximately 2.818 Å between the plane that consists of four pyrrole nitrogen atoms and another that contains four isoindole nitrogen atoms. This value is in accordance with that found experimentally for $[Y^{III}H\{Pc(\alpha\text{-}OC_5H_{11})_4\}(TClPP)]$ (2.800 Å).[10] It is worth noting that, in accordance with the experimental findings,[10] both the phthalocyanine and porphyrin ligands are revealed to bend significantly out from the double-decker molecule. This gives further support for excluding the formation of a dimer of double-decker complexes through π–π interactions between two double-decker molecules.

To further simplify the calculations, the four chlorophenyl groups were removed from the TClPP ligand in the optimized structure during TD-DFT calculations of the spectroscopic properties of the yttrium double-decker compound. By employing the same computational process as that previously used for $[Y^{III}(Pc)(Por)]^-$ (Pc = unsubstituted phthalocyaninate),[12] the electronic absorption spectrum together with the CD spectrum for (*S*)-$[Y^{III}\{Pc(OBNP)_2\}(Por)]^-$ was obtained on the basis of these calculations. Figure 4 shows the simulated absorption and CD spectra of (*S*)-$[Y^{III}\{Pc(OBNP)_2\}(Por)]^-$ and Table S1 in the Supporting Information summarizes the electronic transitions of the main absorption bands, details of which are not repeated herein due to their good agreement with those obtained for $[Y^{III}(Pc)(Por)]^-$.[12] It can be seen that the simulated electronic absorption and CD spectra of (*S*)-$[Y^{III}\{Pc(OBNP)_2\}(Por)]^-$ approximately reproduce the observed spectra of (*S*)-$[Y^{III}H\{Pc(OBNP)_2\}(TClPP)]$ in DMF. The almost degenerate LUMO (LUMO+1) or LUMO+2 (LUMO+3) orbitals for (*S*)-$[Y^{III}\{Pc(OBNP)_2\}(Por)]^-$ are responsible for the observation of the pseudo *A* term for almost all of the electronic transitions (Figure S9 in the Supporting Information). Comparison between the experimental and computational results renders it possible to assign the bands to those mainly associated with the phthalocyanine Soret, porphyrin Soret, porphyrin Q, charge-transfer (CT), and phthalocyanine Q transitions. The CD sign and relative intensity of these bands in the calculated spectra of (*S*)-$[Y^{III}\{Pc(OBNP)_2\}(Por)]^-$ are in excellent agreement with the observed CD signals for (*S*)-$[Y^{III}H\{Pc(OBNP)_2\}(TClPP)]$ in the whole spectral region, which suggests that the present double-decker system, (*S*)-$[Y^{III}H\{Pc(OBNP)_2\}(TClPP)]$, in DMF preferentially adopts a right-handed helical geometry ($\alpha = 13°$) with respect to the staggered conformation ($\alpha = 0°$).

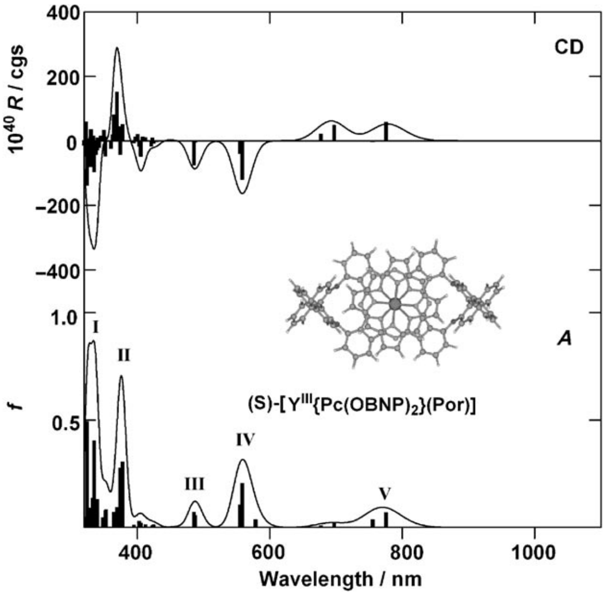

Figure 4. Simulated electronic absorption and CD spectra of (*S*)-$[Y^{III}\{Pc(OBNP)_2\}(Por)]^-$ with the rotation angle of 13°. Gaussian bands with half-bandwidths of 1000 cm^{-1} were used.

On the basis of single-crystal molecular structure investigations over a large number of bis(tetrapyrrole)–metal complexes,[2a,10,14–17] double-decker molecules with two parallel tetrapyrrole ligands connected by a large-radius metal cation can change their molecular conformation only in terms of the twist angle and ring-to-ring distance. The twist angle, θ, for bis(tetrapyrrole)–metal complexes is usually defined as the rotation angle of one macrocycle away from the eclipsed conformation of the two macrocycles. However, in the present study, the rotation angle (α) employed for the anionic mixed phthalocyaninato–porphyrinato yttrium complex is different from θ, the value of which is actually the difference between θ and an angle of 45°, that is, $\alpha = \theta - 45°$. Furthermore, it is reasonable to consider that changes in the protonated mixed-ring double-decker molecules connected by the same yttrium or europium ion in **1** and **2** should only occur in the rotation angle with the ring-to-ring distance remaining unchanged upon changing the solvent from DMF to $CHCl_3$ or vice versa. As a consequence, to understand the significant change in the CD spectra of complexes **1** and **2** upon changing the solvent from DMF to $CHCl_3$, the CD signal for the lowest-energy transition of (*S*)-$[Y^{III}\{Pc(OBNP)_2\}(Por)]^-$ together with the relative energy for this molecule was calculated by changing the rotation angle of α in the range from 13 to −2° with a ring-to-ring separation of

2.818 Å. It is worth noting that such a rotation angle range from 13 to −2° was also selected on the basis of single-crystal molecular structure investigation results,[2a] which reveal the skew angle for most bis(tetrapyrrole)–rare-earth complexes in the range between 35 and 45°, which corresponds to a range of 10 to 0° for the rotation angle of α.

As shown in Figure 5, along with the decrease in the rotation angle, the CD signal for the lowest-energy transition of (S)-[$\mathrm{Y^{III}\{Pc(OBNP)_2\}(Por)]^-}$ gradually changes its sign from positive to negative when α is less than 2°. Nevertheless, when the rotation angle becomes 0°, the intensity of the CD signal with negative sign corresponds to approximately a quarter of that for $\alpha = 13°$. This observation is in good agreement with the experimental result of (S)-[$\mathrm{Y^{III}H\{Pc(OBNP)_2\}(TClPP)}$] recorded in $CHCl_3$ (see above). As expected, the calculated relative energy (E_{rel}) of (S)-[$\mathrm{Y^{III}\{Pc(OBNP)_2\}(Por)]^-}$ increases with decreasing the twist angle α as a result of the steric repulsion between the peripheral substituents of two macrocycles. In particular, this compound appears to be unrealistic in terms of energy after the rotation angle decreases to less than −2°. On the basis of these results, the electronic absorption and CD spectra of (S)-[$\mathrm{Y^{III}\{Pc(OBNP)_2\}(Por)]^-}$ with $\alpha = 0°$ were calculated at the level of B3LYP/LANL2DZ (see Figure 6 and Table S2 in the Supporting Information). As can be found, both the calculated electronic absorption and in particular the CD properties reproduce the experimental spectra of (S)-[$\mathrm{Y^{III}H\{Pc(OBNP)_2\}(TClPP)}$] in $CHCl_3$, which suggests a fully staggered molecular structure with a rotation angle of 0° employed by the compound [$\mathrm{Y^{III}H\{Pc(OBNP)_2\}(TClPP)}$] in $CHCl_3$.

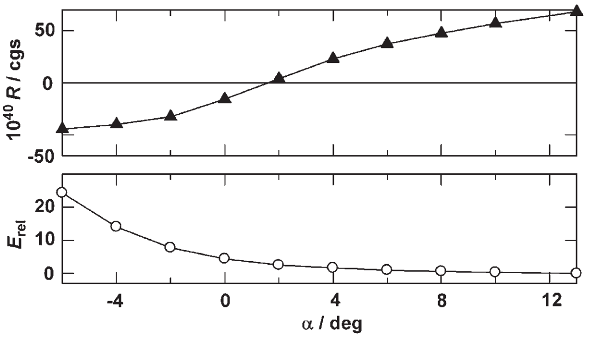

Figure 5. a) Plot of the calculated CD intensity for the lowest-energy transition. b) Plot of E_{rel} [kcal mol^{-1}] of (S)-[$\mathrm{Y^{III}\{Pc(OBNP)_2\}(Por)]^-}$ as a function of α.

At the end of this section, it must be pointed out that detailed effects of the solvent molecules on the double-decker compounds in solution is still not clear at this stage. Reproducing the interaction between solvent molecules of DMF or $CHCl_3$ and the double-decker molecule is retarded by the complexity of such systems. Efforts continue towards making progress in this direction.

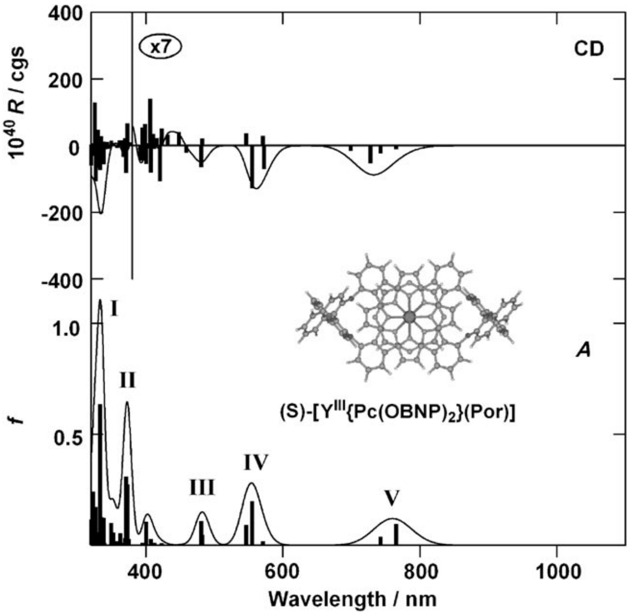

Figure 6. Simulated electronic absorption and CD spectra of (S)-[$\mathrm{Y^{III}\{Pc(OBNP)_2\}(Por)]^-}$ with a rotation angle of 0°. Gaussian bands with half-bandwidths of 1000 cm^{-1} were used.

Conclusion

In summary, we have prepared the first optically active mixed phthalocyaninato–porphyrinato rare-earth double-decker complexes **1** and **2**. Electronic absorption, MCD, and CD spectroscopic properties in different solvents reveal their solvent-dependent molecular conformations. Theoretical calculation results on their electronic absorption and, in particular, their CD spectra by using the TD-DFT method reproduce the change in the optical properties in terms of changes in the twist angle of double-decker molecules, which confirms the nonaggregated molecular conformation change of mixed phthalocyaninato–porphyrinato rare-earth double-decker complexes along with changing the solvent from DMF to $CHCl_3$. This provides a new potential of tuning the optical and electrochemical properties of sandwich-type bis(tetrapyrrole)–metal double-decker complexes in solution through changing the solvent.

Experimental Section

General: n-Octanol was distilled from sodium. Column chromatography was carried out on silica gel (Merck, Kieselgel 60, 70–230 mesh) with the eluents indicated. Optically pure (S)- and (R)-2,2′-dihydroxy-1,1′-binaphthyl and 3-nitrophthalonitrile were obtained from Aldrich. All other reagents and solvents were used as received. The compounds $\mathrm{H_2TClPP}$,[18] $\mathrm{M(acac)_3{\cdot}}n\mathrm{H_2O}$ (M = Eu,Y),[19] and optically active (S)- and (R)-$\mathrm{H_2\{Pc(OBNP)_2\}}$[9b] were prepared according to literature procedures.

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. MCD and CD measurements were carried out by using a JASCO J-725 spectrodichrometer equipped with a JASCO electromagnet that produced magnetic fields (both parallel and antiparallel) of up to 1.09 T. Its magnitude was expressed in terms of molar ellipticity per tesla $[\theta]_M/10^4\ \mathrm{deg\,mol^{-1}\,dm^3\,cm^{-1}\,T^{-1}}$. IR spectra were recorded as KBr pellets by using a BIORAD FTS-165 spectrometer with 2 $\mathrm{cm^{-1}}$ resolution.

(*S*)- or (*R*)-[YH{Pc(OBNP)$_2$}(TClPP)] (1): A mixture of [Y(acac)$_3$]·nH$_2$O (12.5 mg, 0.031 mmol) and H$_2$TClPP (21 mg, 0.028 mmol) in n-octanol (4 mL) was heated to reflux under nitrogen for approximately 1.5 h. The mixture was cooled to room temperature, then optically active (*S*)- or (*R*)-H$_2$Pc(OBNP)$_2$ (30.2 mg, 0.028 mmol) was added. The mixture was heated at reflux for a further 3 h. After being cooled to room temperature, the volatile compounds were removed under reduced pressure. The residue was chromatographed on a silica gel column by using CHCl$_3$/petroleum ether (1:1) as the eluent. A small amount of unreacted H$_2$TClPP separated first, then a green band that contained the protonated double-deckers followed by a small blue band that contain the metal-free phthalocyanine were eluted. Repeated chromatography followed by recrystallization from ethyl acetate/petroleum ether gave **1** (19 mg, 36 %). ^{1}H NMR (300 MHz, CDCl$_3$/[D$_6$]DMSO (1:1) with ca. 1 % hydrazine hydrate): $\delta = 9.01$ (d, 2H), 8.75 (d, 2H), 8.56 (d, 2H), 8.40 (d, 2H), 8.32–8.01 (m, 14H), 7.98–7.45 (m, 26H), 7.34–7.11 (m, 8H), 6.84–6.51 (m, 4H); MS: m/z: 1918.4 $[M+\mathrm{H}]^+$; elemental analysis calcd (%) for $\mathrm{C_{116}H_{61}YN_{12}O_4Cl_4{\cdot}3\,CH_3COOC_2H_5}$: C 70.46, H 3.93, N 7.70; found: C 20.91, H 4.43, N 7.29.

(*S*)- or (*R*)-[EuH{Pc(OBNP)$_2$}(TClPP)] (2): By using the procedure described above for **1** with [Eu(acac)$_3$]·nH$_2$O (14 mg, 0.031 mmol) instead of [Y(acac)$_3$]·nH$_2$O as the starting material, compound **2** was isolated after recrystallization from CHCl$_3$/MeOH (22 mg, 40 %). ^{1}H NMR data) recorded by 300 MHz, CDCl$_3$/[D$_6$]DMSO (1:1) with ca. 1 % hydrazine hydrate): $\delta = 11.77$ (m, 2H), 11.40–11.39 (m, 2H), 10.58 (d, 2H), 10.50 (m, 2H), 10.30 (m, 2H), 9.86 (m, 2H), 9.46 (d, 2H), 9.12–9.05 (m, 4H), 8.72–8.71 (m, 2H), 8.55–8.53 (m, 4H), 8.49–8.44 (m, 4H), 8.35–8.21 (m, 4H), 8.00–7.88 (m, 4H), 7.44–7.40 (m, 18H), 7.16–7.11 (m, 4H), 6.96–6.71 (m, 4H); MS: m/z: 1981.1 $[M+\mathrm{H}]^+$; elemental analysis calcd (%) for $\mathrm{C_{116}H_{61}EuN_{12}O_4Cl_4{\cdot}0.5\,CHCl_3}$: C 68.60, H 3.01, N 8.24; found: C 68.66, H 3.23, N, 7.90.

Computational details: The hybrid density functional B3LYP (Becke-Lee-Young-Parr composite of the exchange-correlation functional) method was used for both geometry optimizations and property calculations.[20] In all cases, the LANL2DZ basis set was used.[21] Geometry optimization of (*S*)-[Y$^{\mathrm{III}}${Pc(OBNP)$_2$}(TClPP)]$^-$ was carried out by imposing a C_2 symmetry restriction. One hundred excitation energies, oscillator strengths, and rotatory strengths were calculated by using the TD-DFT method at the same level as the geometry optimization. To reduce the computational cost, TD-DFT calculations were carried out on (*S*)-[Y$^{\mathrm{III}}${Pc(OBNP)$_2$}(Por)]$^-$, in which the four chlorophenyl groups were removed from the TClPP ligand in the optimized structure. Rotatory strengths are reported herein on the basis of the dipole-velocity expression. Gaussian bands with half-bandwidths of 1000 $\mathrm{cm^{-1}}$ were used to simulate the CD spectra. All calculations were carried out by using the Gaussian 03 program[22] in the IBM P690 system in Tohoku University and Shandong Province High Performance Computing Centre.

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[11] To detect whether racemization of optically active phthalocyanines in *n*-octanol at reflux occurs, unreacted metal-free phthalocyanines were recovered and purified after synthesizing the europium and yttrium mixed-ring double-decker complexes. CD spectroscopic measurement results reveal that both the CD spectra and the coefficients of CD curves for both (*S*)- or (*R*)-$H_2Pc(OBNP)_2$ do not change.

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