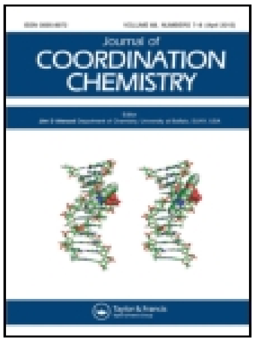

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New mixed rare earth double-decker complexes with octyloxynaphthyl-porphyrinato and phenylthio-naphthalocyaninato ligands – preparation and spectroscopic characterization

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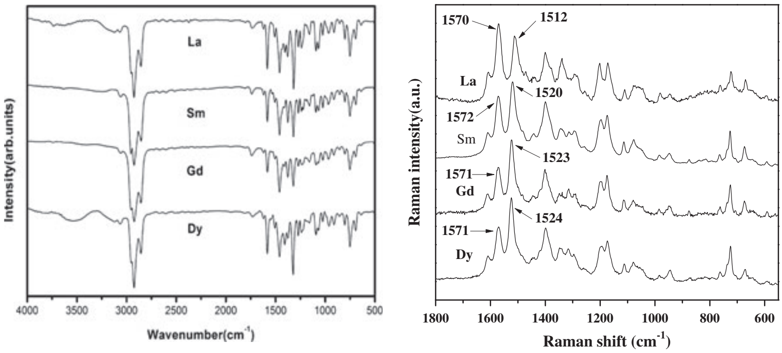

Eight new (porphyrinato)(naphthalocyaninato) rare earth(III) double-decker complexes M^{III}(TONPP)[Nc(PhS)$_8$] [M = La, Pr, Nd, Sm, Eu, Gd, Tb, and Dy; TONPP = 5,10,15,20-tetrakis(4-octyloxy-naphthyl) porphyrin; Nc(PhS)$_8$ = 3,4,12,13,21,22,30,31-octa(phenylthio)-2,3-naphthalocyanine] have been prepared and characterized by spectroscopic methods. The UV–vis absorption spectra depend on the central rare earth ionic size, suggesting that all the transitions involve molecular orbitals with contribution from both porphyrin and naphthalocyanine ligands. The IR and Raman spectra of these double-decker compounds were systemically investigated, showing that the electron hole in these mixed double-deckers is mainly localized at the naphthalocyanine ring. Their sandwich nature was also characterized by MS, EA, and ^{1}H NMR techniques.

Keywords: Porphyrin; Naphthalocyanine; Rare earth; Mixed double-decker

1. Introduction

Phthalocyanines (Pcs) are synthetic analogs of porphyrins, which present an 18 π-electron aromatic cloud delocalized over an arrangement of alternated carbon and nitrogen atoms [1–3]. 2,3-Naphthalocyanine is a phthalocyanine derivative with a more extended delocal-

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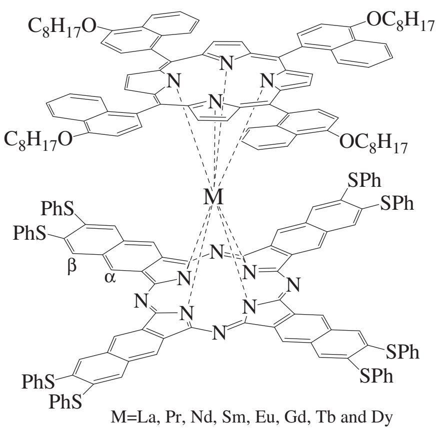
*Corresponding author. Email: fanlilu@tju.edu.cn ized system of 56 conjugated π electrons consisting of four benzoisoindole units. Double-decker tetrapyrrole complexes, in which two or three macrocyclic ligands are held by rare earth metal ions in close proximity, have been studied in recent years as prospective advanced molecular materials [4–9].

Only a few alkyl- and alkoxy-substituted homoleptic and heteroleptic sandwich-type lanthanide bis(naphthalocyanine) complexes $Ln(Nc)_2$, Ln(Nc)(Nc′) and mixed double-deckers Ln(Por)(Nc) (Ln = lanthanide; Nc′ = substituted naphthalocyanine; Por = porphyrins) have been prepared [10–16]. Much less work has been done on mixed naphthalocyanine-containing double-deckers. These compounds could possess unusual properties due to their different substituents compared with those of alkyl- and alkoxy-substituted phthalocyaninato compounds. They are very important prospective functional materials and therefore may be used as nonlinear optical materials, semiconducting materials, photoconductors, NIR-emitting materials, holographic storage, photovoltaics, electrochromism, electro-catalysis, chemical sensors, magnetic materials, photochemical hole burning, and photodynamic cancer therapy [4–9]. These properties and applications are due to their unique optical, electrical, magnetic, and other physical properties associated with more extended delocalized system and the intriguing intramolecular inter-ring π–π interactions [10–16]. In this article, a series of new complexes $M^{III}(TONPP)[Nc(PhS)_8]$ [M = La-Dy, except for Ce and Pm, TONPP = 5,10,15,20-tetrakis(4-octyloxynaphthyl)porphyrin; $Nc(PhS)_8$ = 3,4,12,13,21,22,30,31-octa(phenylthio)-2,3naphthalocyanine] were prepared and characterized, as shown in scheme 1. In addition, we give a systematic and detailed investigation of IR, Raman, and electronic absorption information.

2. Experimental

2.1. *Materials and physical measurements*

1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) was purchased from Aldrich. Toluene, hexane, $CHCl_3$, and CH_3OH were of reagent grade and used as received from Tianjin Chemical



Scheme 1. Schematic structures of mixed ring rare earth double-decker complexes $M^{III}(TONPP)[Nc(PhS)_8]$ (M = La, Pr, Nd, Sm, Eu, Gd, Tb, and Dy) with tetra(4-octyloxynaphthyl)porphyrin and (phenylthio)naphthalocyanine ligands.

Reagents without purification. Column chromatography was carried out on silica gel (Qingdao, 200–300 mesh) with the indicated eluents. *n*-Octanol was purchased from Tianjin Guangfu Fine Chemical Research Institute and distilled over sodium under argon. M $(acac)_3 \cdot nH_2O$ [17], H_2(TONPP) [18], and 6,7-bis-(thiophenyl)naphthalonitrile [19] were prepared according to the literature procedures.

The UV–vis spectra of neutral and reduced forms of M(TONPP)[Nc(PhS)$_8$] were obtained on a HP 8543 spectrophotometer. IR spectra were recorded in KBr pellets using a Bruker Alpha spectrometer. A Thermo Scientific DXR Raman microscope equipped with an Olympus microscope was used to analyze the samples. Raman spectra were recorded from 400 to 1800 cm^{-1} using a 632.8 nm diode laser with a power of 5.0–8.0 mW at the source. For these experiments, the ×10 objective was employed giving a spot size on the sample of about 5 μm. ESI mass spectra were taken on a Finnigan Lcq Max mass spectrometer. ^1H NMR spectrum was acquired in mixed solutions ($CDCl_3$: DMSO-D6 = 1 : 1) and *ca.* 5% (vol./vol.) hydrazine hydrate on a Varian 500 spectrometer.

2.2. *General procedure for the preparation of 1–8*

M(TONPP)[Nc(PhS)$_8$] were prepared by treating $M(acac)_3 \cdot H_2O$ (0.05 mmol) and H_2(TONPP) (33.17 mg, 0.025 mmol) in refluxing *n*-octanol under nitrogen for 4–6 h. After cooling to room temperature, the solution was mixed with 6,7-bis-(thiophenyl)naphthalonitrile (78.8 mg, 0.20 mmol) and DBU (25 mg, 0.165 mmol). The mixture was then refluxed for a further 16 h under nitrogen. The brown-black solution was cooled to room temperature, and *n*-octanol was removed in vacuo. The residue was separated by column chromatography with CH_2Cl_2/hexanes as the eluent. Firstly unreacted H_2Por was collected (CH_2Cl_2/hexanes = 1 : 5). We collected the second greenish blue band containing mixed double-decker complex M^{III}(TONPP)[Nc(PhS)$_8$] (CH_2Cl_2/hexane = 1 : 1). The crude product was further purified by the same chromatographic procedure followed by recrystallization with a mixture of $CHCl_3$ and CH_3OH to afford dark blue microcrystals.

2.3. *General procedure for the preparation of reduced forms 1–8*

Mixed solutions of NH_2NH_2 and MeOH were added to M^{III}(TONPP)[Nc(PhS)$_8$] (0.01 mmol) in $CHCl_3$. After stirring 30 min, M^{III}(TONPP)[Nc(PhS)$_8$] were reduced; the volume ratio of $CHCl_3$, NH_2NH_2, and MeOH is 5 : 4 : 1.

3. Results and discussion

3.1. *Synthesis of M^{III}(TONPP)[Nc(PhS)$_8$]*

Mixed (porphyrinato)(naphthalocyaninato) rare earth(III) double-decker complexes M^{III}(TONPP)[Nc(PhS)$_8$] belong to a cyclic tetrapyrrole family in which the four pyrrole or isoindole nitrogens can form complexes with a range of metal ions. With large metal centers that favor eight coordination (rare earths, actinides, Group 4 transition metals, and main group elements such as In, Sn, As, Sb, and Bi), the yield of mixed double-decker complexes M^{III}(TONPP)[Nc(PhS)$_8$] strongly depends on the ionic radius of the metal, and decreases along with the lanthanide contraction from La to Dy (except Ce), as summarized

Table 1. Elemental, analytical, and mass spectrometric data for the mixed double-decker rare earth complexes M^{III}(TONPP)[Nc(PhS)$_8$] 1–8.

Compound	M^+/MH^+ (*m/z*) Measured (Calcd)	Elemental analysis (%) C	H	N	Yield (%)
La(TONPP)[Nc(PhS)$_8$] (**1**) $LaC_{188}H_{156}N_{12}O_4S_8$	3044.17(3042.79)	74.16(74.20)	5.15(5.17)	5.50(5.53)	7.9
Pr(TONPP)[Nc(PhS)$_8$] (**2**) $PrC_{188}H_{156}N_{12}O_4S_8$	3044.75(3044.79)	74.19(74.16)	5.20(5.16)	5.55(5.52)	18.4
Nd(TONPP)[Nc(PhS)$_8$] (**3**) $NdC_{188}H_{156}N_{12}O_4S_8$	3048.84(3048.12)	74.02(74.07)	5.10(5.15)	5.49(5.51)	13.1
Sm(TONPP)[Nc(PhS)$_8$] (**4**) $SmC_{188}H_{156}N_{12}O_4S_8$	3053.89(3054.24)	73.90(73.93)	5.10(5.14)	5.44(5.50)	15.7
Eu(TONPP)[Nc(PhS)$_8$] (**5**) $EuC_{188}H_{156}N_{12}O_4S_8$	3057.63(3055.84)	73.90(73.89)	5.14(5.14)	5.51(5.50)	13.1
Gd(TONPP)[Nc(PhS)$_8$] (**6**) $GdC_{188}H_{156}N_{12}O_4S_8$	3060.05(3061.13)	73.73(73.76)	5.12(5.13)	5.43(5.49)	10.5
Tb(TONPP)[Nc(PhS)$_8$] (**7**) $TbC_{188}H_{156}N_{12}O_4S_8$	3064.35(3062.81)	73.68(73.72)	5.08(5.13)	5.40(5.48)	7.8
Dy(TONPP)[Nc(PhS)$_8$] (**8**) $DyC_{188}H_{156}N_{12}O_4S_8$	3068.36(3066.38)	73.57(73.63)	5.06(5.12)	5.35(5.38)	5.2

in table 1, which is in accord with M[Nc(tBu)$_4$]$_2$ and M(Nc)(TBPP) [Nc(tBu)$_4$ = tetra(*tert*-butyl)-2,3-naphthalocyanine; TBPP = tetra(*tert*-butyl)-porphyrin] [14, 20]. These new mixed rare earth double-deckers gave satisfactory mass spectrometric data and elemental analysis results after column chromatographic purification and recrystallization, as summarized in table 1. Their sandwich nature was further deduced from spectroscopic methods including UV–vis, IR spectra, Raman spectra, and ^{1}H NMR.

3.2. *Electronic absorption spectra of M^{III}(TONPP)[Nc(PhS)$_8$]*

The electronic absorption spectra of the eight complexes were measured in CHCl$_3$, and the data are collected in table 2. Figure 1 compares the electron absorption spectra of four complexes M^{III}(TONPP)[Nc(PhS)$_8$] (M = La, Sm, Gd, and Dy), which are similar to those of related counterparts M[Nc(SC$_{12}$H$_{25}$)$_8$](TPyP) [Nc(SC$_{12}$H$_{25}$)$_8$ = 3,4,12,13,21,22,30,31 -octa(dodecylthio)2,3-naphthalocyanine; (TPyP) = *meso*-tetra(4-pyridyl)porphyrine] [16] and M(Nc)(TBPP) [20]. As shown in figure 1 and table 2, the Nc Soret band splits into two bands at 325–338 and 352–356 nm; the former is metal-dependent, showing rare earth size

Table 2. The electronic absorption spectroscopic data for M^{III}(TONPP)[Nc(SPh)$_8$] in CHCl$_3$ (c ≈ 10^{-5} Mol L^{-1}).

Compound	λ_{max} (nm)						
La(TONPP)[Nc(SPh)$_8$] (**1**)	325	353	431	558	665	725	
Pr(TONPP)[Nc(SPh)$_8$] (**2**)	327	354	431	562	664	725	
Nd(TONPP)[Nc(SPh)$_8$] (**3**)	331	356	430	562	663	724	
Sm(TONPP)[Nc(SPh)$_8$] (**4**)	331	352	428	560	656	716	
Eu(TONPP)[Nc(SPh)$_8$] (**5**)	334	355	428	555	653	717	
Gd(TONPP)[Nc(SPh)$_8$] (**6**)	338	354	426	556	651	714	
Tb(TONPP)[Nc(SPh)$_8$] (**7**)	338	353	427	553	644	714	
Dy(TONPP)[Nc(SPh)$_8$] (**8**)		352	428	550	643	708	796

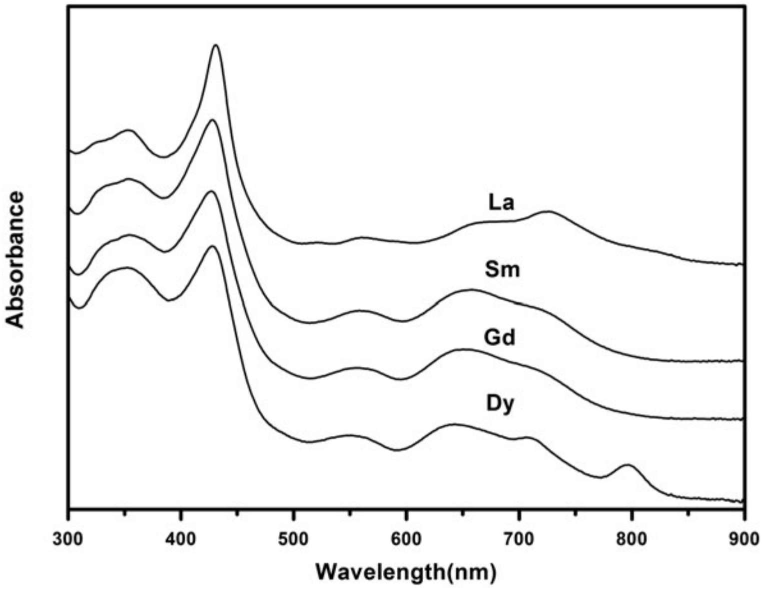


Figure 1. Electronic absorption spectra of M^{III}(TONPP)[Nc(PhS)$_8$] (M = La, Sm, Gd, and Dy) in $CHCl_3$.

effect. The splitting of the Nc Soret band is probably due to the introduction of thiophenyl on the Nc ring [12–16]. M^{III}(TONPP)[Nc(PhS)$_8$] shows strong TONPP Soret bands at 426–431 nm. It should be noted that the Nc Soret band at 352–356 nm and the TONPP Soret band at 426–431 nm were slightly sensitive to the rare earth metal. By analogy with M(Nc)(TBPP) [20], the π-radical anion ([Nc(PhS)$_8$]$^{\bullet-}$) bands at 550–562 nm as the weak absorption peak were blue-shifted with the decrease of the ionic radius of tervalent metal cation from La to Dy, clearly showing rare earth size effect, as shown in table 2. As for M(TONPP)[Nc(PhS)$_8$], the two Nc Q bands at 643–665 and 708–725 nm were also observed, which are almost invisible in the Pc analogs [21–23] due to more extended π systems of naphthalocyanine macrocyclic ring. Both of these bands shift to the blue with the decrease in size of the metal center. A weak absorption in Dy(TNOPP)[Nc(SPh)$_8$] at 796 nm was observed, which is invisible for the mixed double-deckers from La to Tb. This band may be tentatively assigned to the Nc Q absorption. It can be predicted in figure 1 that both the intensity and the wavelength of this band are moderately sensitive to the rare earth metal and gradually gain intensity, becoming an obviously distinguishable band for heavy rare earth complexes, and shifts to the higher energy. Unfortunately, heavy rare earth complexes from Ho to Lu were not obtained, probably because steric compression between porphyrin and naphthalocyanine increases along with the decrease in the metal ionic radius, showing that complexes with a smaller metal center are more difficult to obtain. When compared with the Q band of a Pc, the Q band of a Nc is red shifted and has a larger window of transparency, from 500 to 700 nm. This larger window of transparency is adjacent to the visible light region, improving the nonlinear optical properties of mixed (porphyrinato)(naphthalocyaninato) rare earth(III) double-decker complexes [1–3, 24].

For comparison, figure 2 shows electronic absorption spectra of the π-radical anion of $Tb^{III}(Pc)_2$ [21], Tb^{III}(TClPP)(Pc) [23] [TClPP = tetra(4-chloro)phenylporphyrin] and

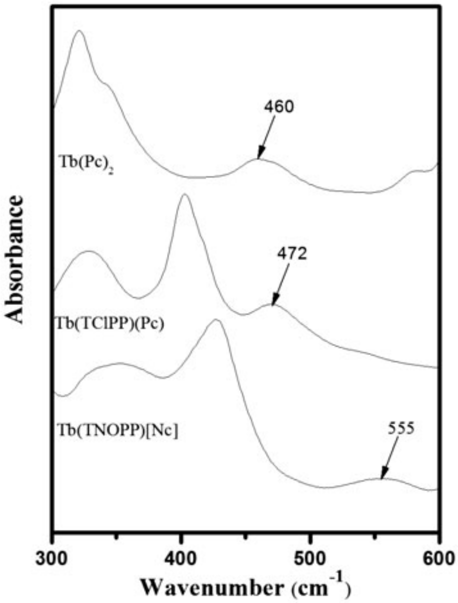


Figure 2. Electronic absorption spectra of the π-radical anion of $Tb^{III}(Pc)_2$, Tb^{III}(TClPP)(Pc), and Tb^{III}(TONPP)[$Nc(PhS)_8$] in $CHCl_3$.

Tb^{III}(TNOPP)[$Nc(PhS)_8$] in $CHCl_3$, typical for the bis(phthalocyaninato), mixed (porphyrinato)(phthalocyaninato), and mixed substituted (porphyrinato)(naphthalocyaninato) rare earth complexes, respectively. When the Pc macrocyclic ligand in bis(phthalocyaninato) compounds is replaced by a porphyrin (Por) ring, similar π-radical anion electronic absorption bands are observed [23], showing macrocycle effect due to nearly extended π-system between the porphyrin and phthalocyanine rings. However, when both Pc ligands are replaced by Nc and Por ligands, both the Soret and the π-radical anion absorption bands of mixed double-deckers M^{III}(TNOPP)[$Nc(PhS)_8$] shift to the red compared with those in the bis(phthalocyaninato) and mixed porphyrinato-phthalocyaninato derivatives, obviously showing macrocyclic ligand effect.

3.3. *Electronic absorption spectra of reduced form of M^{III}(TONPP)[$Nc(PhS)_8$]*

The presence of π-radical anion $[Nc(PhS)_8]^{\bullet-}$ in the mixed double-deckers can be verified by chemical reduction of M^{III}(TONPP)[$Nc(PhS)_8$]. Upon addition of hydrazine hydrate, absorption spectra of $\{M^{III}(TONPP)[Nc(PhS)_8]\}^-$ were remarkably changed and the resulting spectra could be attributed to $\{M^{III}(TONPP)^{2-}[Nc(PhS)_8]^{2-}\}^-$, in which both macrocycles are dianionic [20–25]. Electronic absorption spectra $M^{III}(TONPP)[Nc(PhS)_8]^-$ were measured in mixed solutions of $CHCl_3$, NH_2NH_2, and MeOH ($CHCl_3 : NH_2NH_2 : MeOH = 5 : 4 : 1$), and the data are summarized in table 3. The electronic absorption spectra of $M^{III}(TONPP)[Nc(PhS)_8]^-$ (M = La, Sm, Gd, and Dy) after being treated with hydrazine hydrate are shown in figure 3. As expected, the π-radical anion absorption bands $[Nc(PhS)_8]^{\bullet-}$ at *ca.* 550 nm were not observed, suggesting that the π-radical anion band is the most important diagnostic band for these mixed (porphyrinato)(naphthalocyaninato) rare earth complexes.

Table 3. The electronic absorption spectroscopic data for the reduced M^{III}(TONPP)[Nc(PhS)$_8$]$^-$ in $CHCl_3$ ($CHCl_3 : NH_2NH_2 : MeOH = 5 : 4 : 1$, c ≈ 10^{-5} Mol L^{-1}).

Compound	λ_{max} (nm)						
La(TONPP)[Nc(SPh)$_8$]$^-$ (**1**)	335	363	435	513	650	748	845
Pr(TONPP)[Nc(SPh)$_8$]$^-$ (**2**)	338	365	435	510	655	763	862
Nd(TONPP)[Nc(SPh)$_8$]$^-$ (**3**)	340	370	434	510	655	769	866
Sm(TONPP)[Nc(SPh)$_8$]$^-$(**4**)	342	367	434	510	665	775	873
Eu(TONPP)[Nc(SPh)$_8$]$^-$ (**5**)	342	367	433	510	676	784	880
Gd(TONPP)[Nc(SPh)$_8$]$^-$ (**6**)	342	368	433	509	677	786	880
Tb(TONPP)[Nc(SPh)$_8$]$^-$ (**7**)	343		432	508	679	793	882
Dy(TONPP)[Nc(SPh)$_8$]$^-$ (**8**)	345		432	508	687	735	884

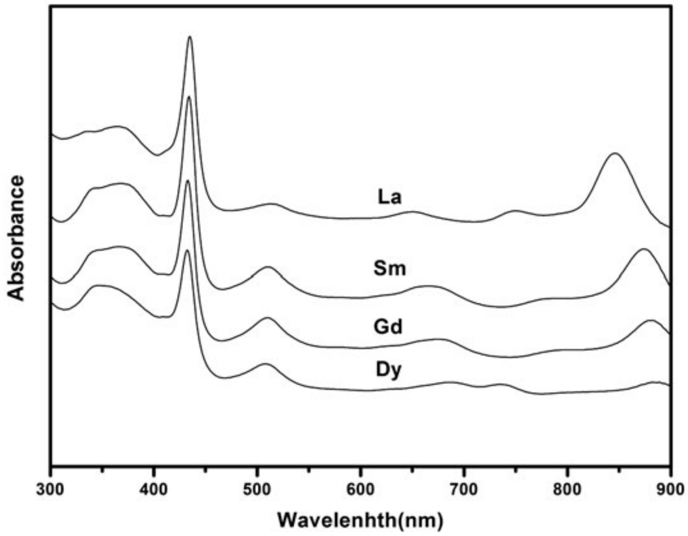


Figure 3. Electronic absorption spectra of {M^{III}(TONPP)[Nc(PhS)$_8$]}$^-$ (M = La, Sm, Gd) in $CHCl_3$/MeOH by addition of hydrazine hydrate.

The Nc Soret band slightly shifts to the red upon reduction; however, the relevant Por Soret band remains unchanged. These facts seem to suggest that the absorption spectra M^{III}(TONPP)[Nc(PhS)$_8$]$^-$ is mainly from the contribution of Nc ring, suggesting that the first reduction is naphthalocyanine-based. Figure 4 shows the plot of wavelengths of the two Q band absorptions (748–793 and 845–884 nm) of {M^{III}(TONPP)[Nc(PhS)$_8$]}$^-$ as a function of the ionic radius of M^{III}. It can be seen in table 3 and figure 4 that the two metal-dependent Q bands undergo a linear red shift with decrease in the radius of the rare earth metal ion, clearly showing rare earth size effect. These facts are indirectly supported by the characteristic features of IR and Raman spectra of the corresponding mixed double-deckers.

3.4. *IR spectra of M^{III}(TONPP)[Nc(PhS)$_8$]*

IR spectroscopy is very powerful and useful in investigating the nature of naphthalocyanine ligand in sandwich-type tetrapyrrole complexes. Vibrational (IR and Raman) characteristics

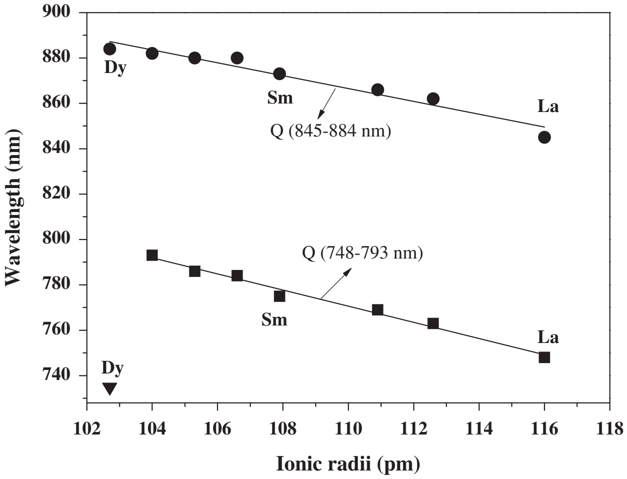


Figure 4. Plot of wavelengths of the two Q band absorptions of $\{M^{III}(TONPP)[Nc(PhS)_8]\}^-$ as a function of the ionic radius of M^{III}.

of sandwich-type tetrapyrrole complexes have been comprehensively investigated [26–30]. Before describing the IR characteristics of mixed (porphyrinato)-(naphthalocyaninato) rare earth complexes, it seems necessary to give a brief description of the porphyrin monoanion radical $por^{\bullet -}$ and naphthalocyanine π-radical anions $Nc^{\bullet -}$. In order to distinguish the redox site between the metal and porphyrin ring for metallo-porphyrins, Shimomura *et al.* developed an effective infrared spectroscopic method and assigned the band around 1520–1570 cm^{-1} and 1270–1300 cm^{-1} as the IR marker band for the porphyrin π-radicals, $OEP^{\bullet -}$ and $TPP^{\bullet -}$, respectively [31–33]. Based on their work, the bands at *ca.* 1520–1570 cm^{-1} and 1270–1300 cm^{-1} are also assigned to the diagnostic band for $TONPP^{\bullet -}$ in sandwich-type rare earth complexes. The intense marker absorption in neutral bis(naphthalocyaninato) and mixed (porphyrinato)(naphthalocyaninato) rare earth(III) complexes containing one unpaired electron has been unambiguously verified by the observation of the $Nc^{\bullet -}$ IR marker band at 1310–1325 cm^{-1} [13–15, 20, 26–30]. For $M^{III}(TONPP)[Nc(PhS)_8]$, the IR marker band at *ca.* 1270–1300 cm^{-1} was not seen for porphyrin monoanion radical $TONPP^{\bullet -}$. These facts suggest that the unpaired electron is mainly localized at the naphthalocyanine ring. Therefore, $M^{III}(TONPP)[Nc(PhS)_8]$ exist as $M^{III}(TONPP^{2-})[Nc(PhS)_8{}^{\bullet -}]$.

Characteristic IR vibrational frequencies and interpretation of the naphthalocyanine ligand in mixed double-decker rare earth complexes $M^{III}(TONPP)[Nc(PhS)_8]$ are summarized in table S1. Figure 5 shows IR spectra from 400 to 4000 cm^{-1} of $M^{III}(TONPP)[Nc(PhS)_8]$ (M = La, Sm, Gd, and Dy). All the naphthalocyanine-containing double-decker complexes show a strong marker band at 1320 cm^{-1} which is diagnostic for naphthalocyanine π-radical anions $[Nc(PhS)_8]^{\bullet -}$ [27–33]. The strong band whose frequency varies from 1316 cm^{-1} for $La(TONPP)[Nc(PhS)_8]$ to 1323 cm^{-1} for $Dy(TONPP)[Nc(PhS)_8]$ attributed to pyrrole stretching is assigned to the IR marker band of naphthalocyanine monoanion radical $[Nc(PhS)_8]^{\bullet -}$, showing dependence on the rare earth ionic size, which is linearly blue-shifted along with the lanthanide contraction (see figure 6). This observation is in line with that found in the mixed double-deckers $M[Nc(SC_{12}H_{25})_8](TPyP)$ and M(Nc)(TBPP) [16, 20]. In addition, the linear blue shift obviously reflects the extent of π–π interaction of Por and Nc rings in the mixed double-deckers. The π–π interaction and systematic variation in the

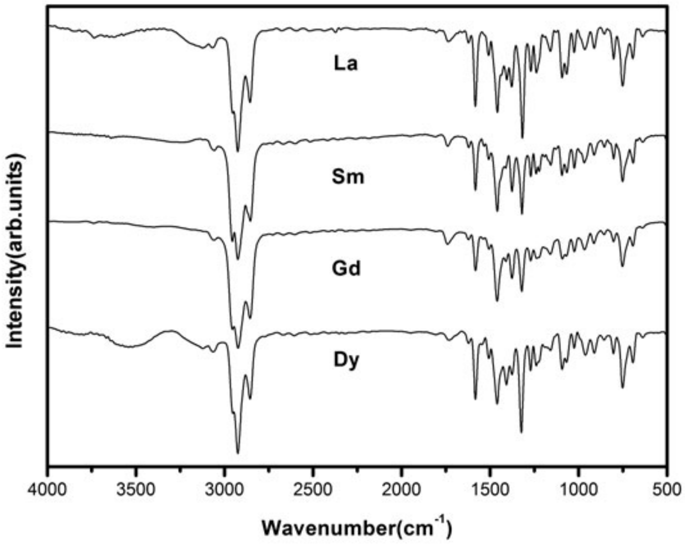


Figure 5. IR spectra of $M^{III}(TONPP)[Nc(PhS)_8]$ (M = La, Sm, Gd, and Dy).

coordination intensity of the rare earth–central nitrogen bonds are very closely related. In the mixed double-decker rare earth complexes, the large rare earth ion which locates outside the planar macrocyclic ligand is coordinated by the central nitrogens of the phthalocyanine and porphyrin ligands. Along with the decrease in the rare earth ionic radius, the central metal gets closer to the two tetrapyrrole macrocyclic rings, which favors coordination between the central rare earth ion and the isoindoline nitrogens and thus reinforces the M-N bonds, and the proximity of the two tetrapyrrole ligands becomes closer. Therefore, the π–π interaction between the naphthalocyanine and porphyrin rings becomes stronger along with lanthanide contraction. As can be seen in figure 5 and table S1, the medium bands at 751 cm^{-1} are attributed to the aromatic C-H wagging. The peaks at 1022–1026 cm^{-1} and 1220–1270 cm^{-1} as weak bands are assigned to C-H bending on the Nc ring. The absorptions at 1088–1094 cm^{-1} are assigned to C-S-C stretching. The characteristic IR absorption peaks of octyloxy substituents on the porphyrin ring mainly appear at 2800–3000 cm^{-1}. Three strong vibrations at *ca.* 2855 (symmetric), 2924 (symmetric), and 2954 (antisymmetric) cm^{-1} are attributed to the symmetric and asymmetric C-H stretching vibrations of the $–CH_2–$ and $–CH_3$ groups of the octyloxy side chains on the porphyrin ring.

The $TONPP^{\bullet -}$ IR marker band at 1270–1300 cm^{-1} was not observed for these compounds, as shown in figure 5 and table S1. This suggests that the electron hole in these mixed double-deckers is mainly localized at the naphthalocyanine ring. Good correspondence in the IR features between $M(Nc^*)_2$ and M(Por)(Nc) [11–16] provides indirect evidence that the IR spectra of $M(TONPP)[Nc(PhS)_8]$ are mainly dominated by the naphthalocyaninato-metal fragment $M[Nc(PhS)_8]$.

3.5. *Raman spectra of $M^{III}(TONPP)[Nc(PhS)_8]$*

The observed Raman spectroscopic frequencies of naphthalocyanine and partial assignments are summarized in table S2. As previously noted [34–36], Raman spectra of the mixed

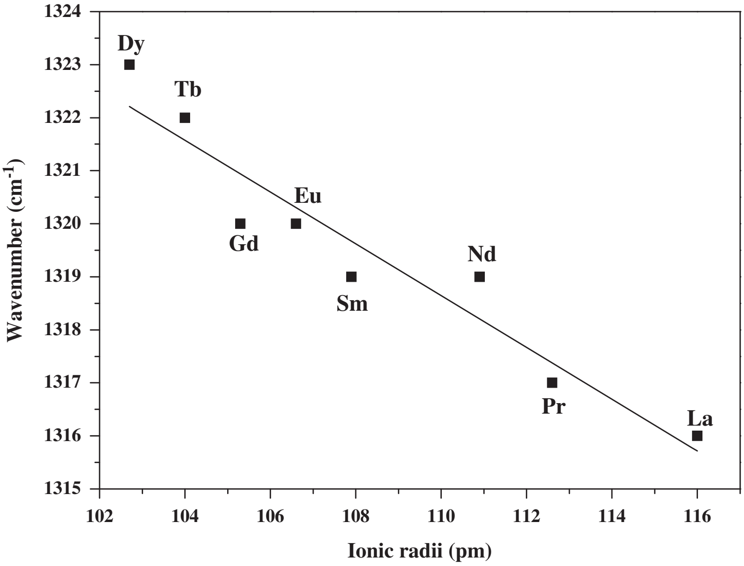


Figure 6. Plot of wave number of the pyrrole stretch of M^{III}(TONPP)[Nc(PhS)$_8$] (**1**–**8**) at *ca.* 1320 cm^{-1} as a function of the ionic radius of M^{III}.

(porphyrinato)(naphthalocyaninato) double-decker compounds of rare earth metals are dominated by the naphthalocyanine ligand when excited by laser line of 632.8 nm, mainly because the naphthalocyanine Q absorption bands located near 670 nm are in closer resonance with the laser source than are the porphyrin Q bands at *ca.* 520 nm, and the latter are only one-tenth as strong as the former. No obvious Raman absorption bands can be assigned to the (TONPP)$^{2-}$ in table S2.

Figure 7 compares Raman spectra for four tervalent rare earth compounds M(TONPP)[Nc(PhS)$_8$] (M = La, Sm, Gd, and Dy). The Raman spectra of these mixed double-deckers display similar features in the fundamental region of 500–1800 cm^{-1} due to the similar electronic and IR characteristics of M(TONPP)[Nc(PhS)$_8$]. With excitation at 632.8 nm, typical Raman marker bands of the monoanion radical [Nc(PhS)$_8$]$^{\bullet -}$ were observed at 1512–1524 cm^{-1} as very strong bands resulting from coupling of pyrrole C=C and aza C=N stretches, whose energy is linearly blue-shifted along with the decrease in the rare earth ionic radius, as shown in figure 8. In the mixed porphyrinato-naphthalocyaninato rare earth complexes, the large rare earth ion which locates between the naphthalocyanine and porphyrin is coordinated by the central N of both tetrapyrrole ligands. Along with lanthanide contraction, the central metal gets closer to the tetrapyrrole rings, which favors coordination between the central rare earth ion and the isoindoline nitrogens and thus reinforces the M–N bonds, as reflected by the blue shift observed in the experimental results. The other marker Raman bands of [Nc(PhS)$_8$]$^{\bullet -}$ due to the C=N aza stretch appear as strong peaks at 1569–1572 cm^{-1}. This observation corresponds well with that found in the double-deckers M(TBPP)(Nc) and M(OEP)(Nc) [18, 19]. From 970 to 1200 cm^{-1}, there are several bands lying at *ca.* 980, 1010, 1060, 1080, 1175, and 1120 cm^{-1} due to aromatic C–H bending. The pyrrole breathing as medium bands was observed at 1114 cm^{-1}.

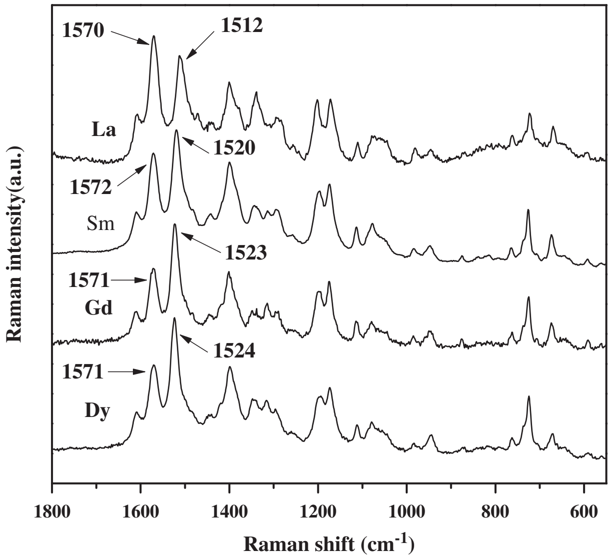


Figure 7. Raman spectra of M^{III}(TONPP)[Nc(PhS)$_8$] (M = La, Sm, Gd, and Dy) with excitation at 632.8 nm.

As can be seen in figure 7 and table S2, the introduction of octyloxynaphthyl groups onto the porphyrin ring and phenylthio groups onto the 2,3-naphthalocyanine does not induce significant changes in the resonance Raman spectra of M(TONPP)[Nc(PhS)$_8$]. This is probably due to the fact that only vibrational modes corresponding to the characteristic fingerprint vibrations of the Nc macrocycle in M(TONPP)[Nc(PhS)$_8$] are observed. The substituted group vibrations are very weak or absent under excitation with laser line of 632.8 nm.

3.6. ^{1}*H NMR spectra of* Sm^{III}*(TONPP)[Nc(PhS)*$_8$*]*

Due to the presence of the unpaired electron and the paramagnetic nature of the lanthanide ions, these mixed double-decker complexes show very weak NMR signals. However, satisfactory ^{1}H NMR spectra could be obtained for $\{Sm^{III}(TONPP)^{2-}[Nc(PhS)_8]^{2-}\}^-$, in which the $[Nc(PhS)_8]^{\bullet-}$ macrocycle was reduced into the diamagnetic dianion $[Nc(PhS)_8]^{2-}$ by hydrazine hydrate [37]. The assignments of the spectra were achieved by integration and multiplicity of the signals, and with reference to the previous results for related triple-deckers M(TBPP)(Nc) [20].

Figure S1 shows the ^{1}H NMR spectra of $\{Sm^{III}(TONPP)^{2-}[Nc(PhS)_8]^{2-}\}^-$ in the presence of hydrazine hydrate. As shown in figure S1, Nc α protons (8H) of the reduced form of Sm(TBPP)(Nc) resonate as a singlet at $\delta = 7.98$ ppm because of the symmetrical Nc ring. Nc β protons (8H) at $\delta = 6.76$ ppm as a singlet were observed. Broad signals at $\delta = 7.48$–7.82 can be assigned to phenyl groups on the Nc. The porphyrin (TONPP) pyrrole signal was observed as an 8-proton multiplet at $\delta = 8.74$ ppm. The –OCH$_2$– of octyloxy group signal was also observed as a triplet at $\delta = 3.93$ ppm. Two broad signals at $\delta = 0.94$–0.98 and 1.25–1.98 ppm can be assigned to signals of the other groups of octyloxy on the TONPP. In addition, the 24 proton signals on naphthyl group on the TONPP were observed at 7.96, 6.90, 6.45, 5.81, 5.10, and 4.88 ppm. The above assignments are observed except for the

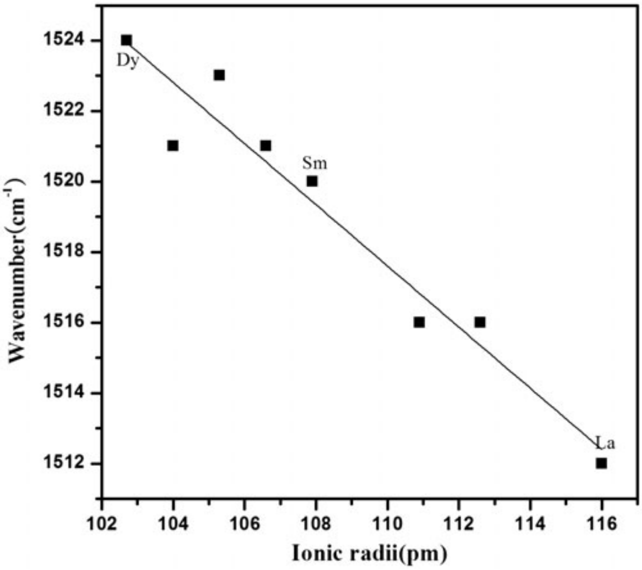


Figure 8. Plot of wave number of the coupling of pyrrole and aza stretch scattering of M(TONPP)[Nc(SPh)$_8$] at 1512–1524 cm^{-1} as a function of the ionic radius of M^{III}.

signals of $CDCl_3$/DMSO-D6/H_2O and hydrazine hydrate. The peak integral area is basically in line with the numbers of hydrogens of the reduced form of Sm(TONPP)[Nc(PhS)$_8$]. In addition, satisfactory ^{1}H NMR spectra of other complexes could not be obtained for M (TONPP)[Nc(PhS)$_8$] due to the paramagnetic nature of the rare earth ion.

4. Conclusion

Eight new mixed substituted (porphyrinato)(naphthalocyaninato) rare earth(III) sandwich complexes M(TONPP)[Nc(PhS)$_8$] have been prepared by DBU-promoted cyclization of naphthalonitrile on the M(TONPP)(acac) in refluxing *n*-octanol. The sandwich structure of these complexes has been characterized by spectroscopic methods. According to spectroscopic investigation, the electron hole in these mixed double-deckers is mainly localized at the naphthalocyanine ring. The IR and Raman spectra of M^{III}(TONPP)[Nc(PhS)$_8$] are dominated by the naphthalocyanine ring. In addition, all the compounds exhibit significant π–π interactions and the π–π interactions between the naphthalocyanine and porphyrin rings become stronger along with lanthanide contraction.

Supplemental data

Supplemental data for this article can be accessed http://dx.doi.org/10.1080/00958972.2015.1102899.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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