Inorg. Chem. **2005**, *44*, 2114–2120

Inorganic Chemistry
Article

Heteroleptic Rare Earth Double-Decker Complexes with Naphthalocyaninato and Phthalocyaninato Ligands. General Synthesis, Spectroscopic, and Electrochemical Characteristics

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Received November 1, 2004

A novel one-pot procedure starting from the corresponding $M(acac)_3 \cdot nH_2O$, metal-free phthalocyanine H_2Pc', and naphthalonitrile in the presence of DBU in *n*-octanol has been developed to prepare heteroleptic (naphthalocyaninato)(phthalocyaninato) rare earth double-decker complexes. A series of six sandwich compounds with different naphthalocyaninato ligands, phthalocyaninato ligands, and central rare earth metals, namely, $Sm[Nc(tBu)_4](Pc)$ [$Nc(tBu)_4$ = 3(4),12(13),21(22),30(31)-tetra(*tert*-butyl)naphthalocyaninato; Pc = unsubstituted phthalocyaninato] (**1**), Sm(Nc)(Pc′) [Pc′ = $Pc(OC_5H_{11})_4$, $Pc(OC_8H_{17})_8$; Nc = 2,3-naphthalocyaninato; $Pc(OC_5H_{11})_4$ = 2(3),9(10),16(17),24(25)-tetrakis(3-pentyloxy)phthalocyaninato; $Pc(OC_8H_{17})_8$ = 2,3,9,10,16,17,24,25-octakis(octyloxy)phthalocyaninato] (**2**, **3**), and $M(Nc)[Pc(\alpha\text{-}OC_5H_{11})_4]$ [M = Sm, Eu, Y; $Pc(\alpha\text{-}OC_5H_{11})_4$ = 1,8,15,22-tetrakis(3-pentyloxy)phthalocyaninato] (**4**–**6**), have been isolated in good yields from this one-pot procedure demonstrating the generality of this synthetic pathway. In addition to spectroscopic analyses, the electrochemistry of these novel compounds has also been studied by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) methods.

Introduction

Phthalocyanines are an important class of pigments that have fascinated scientists for many years because of their applications in various disciplines.[1] Linear and angular annelation of benzene rings to the phthalocyanine core leads to 2,3- and 1,2-naphthalocyanine, respectively. The more extended delocalized π-electron system of naphthalocyanine, especially the 2,3 isomer, in comparison with that of phthalocyanine generates unique physical, spectroscopic, electrochemical, and photoelectrochemical properties. For instance, the red-shifted electronic absorption maxima and photoconductive properties make naphthalocyanines more suitable than phthalocyanines for potential application in photoelectrochemical cells and electrophotography.

It is also well-known that phthalocyanines can form sandwich-type complexes with a range of metal ions, including rare earths, actinides, early transition metals, and some main group metals.[2,3] The resulting bis(phthalocyaninato) metal complexes, especially the rare earth double-deckers, possess intriguing and unique electronic and optical properties which make them useful in materials science because of their possible applications in molecular electronics, molecular information storage, and nonlinear optics.[2,3] While the chemistry and properties of homoleptic bis(phthalocyaninato) rare earth complexes have been extensively studied for several decades and homoleptic bis(naphthalocyaninato)[4−7] and heteroleptic bis(phthalocyaninato) ana-

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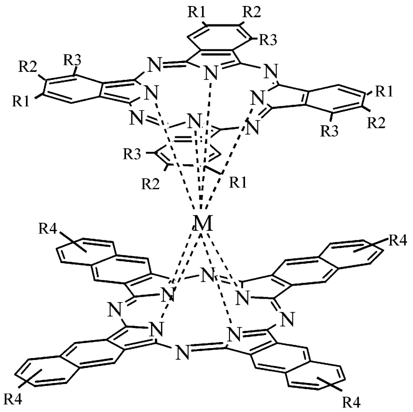
10.1021/ic048472s CCC: $30.25

logues[2,3] have also been well investigated in recent years, still little is known about the heteroleptic (naphthalocyaninato)(phthalocyaninato) rare earth analogues. Actually, a few reports deal with the naphthalocyanine-containing heteroleptic double-decker complexes, but virtually all of them are confined to the *lutetium* complexes.[8−15]

Through the continuous efforts of this group to learn more about sandwich tetrapyrrole metal compounds, we recently developed efficient methodologies for preparing heteroleptic bis(phthalocyaninato) rare earth,[16] mixed (phthalocyaninato)(porphyrinato) rare earth,[17] and mixed (naphthalocyaninato)(porphyrinato) rare earth complexes.[18] In this paper, we describe a new general pathway for heteroleptic (naphthalocyaninato)(phthalocyaninato) rare earth compounds, which involves a simple one-pot procedure, and systematically study the spectroscopic and electrochemical properties of a series of heteroleptic (naphthalocyaninato)(phthalocyaninato) rare earth complexes, namely Sm[Nc(*t*Bu)$_4$](Pc) (**1**), Sm(Nc)(Pc′) [Pc′ = Pc(OC$_5$H$_{11}$)$_4$, Pc(OC$_8$H$_{17}$)$_8$] (**2**, **3**), and M(Nc)[Pc(α-OC$_5$H$_{11}$)$_4$] (M = Sm, Eu, Y) (**4**−**6**) (Figure 1).



1: M = Sm, R_1=R_2=R_3=H, R_4=tBu

2: M = Sm, R_3=R_4=H, R_1 and R_2, one is OC_5H_{11}, then the other is H

3: M = Sm, R_3=R_4=H, R_1=R_2=OC_8H_{17}

4: M = Sm, R_1=R_2=R_4=H, R_3=OC_5H_{11}

5: M = Eu, R_1=R_2=R_4=H, R_3=OC_5H_{11}

6: M = Y, R_1=R_2=R_4=H, R_3=OC_5H_{11}

Figure 1. Schematic structure of heteroleptic (naphthalocyaninato)(phthalocyaninato) rare earth complexes M(Nc′)(Pc′) with phthalocyanine ligands.

Results and Discussion

Synthesis of M(Nc′)(Pc′). Despite the limited species of heteroleptic (naphthalocyaninato)(phthalocyaninato) lutetium complexes, Lu(Nc)(Pc) and Lu(1,2-Nc)(Pc), reported thus far, there are a number of synthetic pathways for these double-decker compounds. In the mid 1980s, Subbotin et al. claimed, without elemental analysis and mass spectrum, to have synthesized heteroleptic (naphthalocyaninato)(phthalocyaninato) lutetium Lu[Nc(tBu)$_4$](Pc) by fusion of Lu(Pc)$^+$ with naphthalonitrile; the only evidence was the appearance of two separated intense Q-bands at 654 and 776 nm.[8] This clearly conflicts with the result of the present work which shows one intense Q-band at 723 nm and a relatively weak vibronic band at 646 nm for Sm[Nc(*t*Bu)$_4$](Pc), vide infra (it is noteworthy that the Q-band of Lu[Nc(*t*Bu)$_4$](Pc) should be located at a higher energy than that of Sm[Nc(*t*Bu)$_4$](Pc) since the Q-band of neutral bis(tetrapyrrole) rare earth(III) complexes is blue-shifted along with the rare earth contraction[5,19]). Later, Simon improved this method and produced Lu(Nc)(Pc), which was characterized by mass spectroscopy, in 25% yield by reaction of Lu(Pc)(OAc) with 2,3-dicyanonaphthalene in *n*-hexanol under catalysis of DBU and ammonium molybdate.[9] The second method involves a mixed cyclization of phthalonitrile and naphthalonitrile in the presence of lutetium salt.[10] Obviously, this method is not practical because of the difficulty in separating the statistical mixtures of differently substituted bis[(na)phthalocyaninato] complexes. Well characterized, by mass, ^{1}H NMR, electronic absorption, and electrochemical techniques, heteroleptic Lu(Nc)(Pc) was obtained by the third method, i.e., the mixed condensation between Li$_2$(Pc) and Li$_2$(Nc) in the presence of Lu(OAc)$_3$·*n*H$_2$O in high-boiling point quinoline.[11] To simplify the purification by decreasing the yield of homoleptic byproducts, Ishikawa employed a stepwise procedure reacting the half-sandwich compound Lu(Pc)(OAc)(H$_2$O)$_2$ with Na$_2$(Nc) in 1-chloronaphthalene.[12,13] Interestingly, the 1,2-naphthalocyanine-containing heteroleptic compound Lu(1,2-Nc)(Pc) was also obtained recently by a similar stepwise route starting from Lu(1,2-Nc)(OAc) and Li$_2$(Pc).[14,15]

In the present work, we employed a one-pot reaction procedure using corresponding M(acac)$_3$·*n*H$_2$O, metal-free phthalocyanine H$_2$Pc′, and naphthalonitrile as starting materi-

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Table 1. Analytical and Mass Spectroscopic Data for the Heteroleptic (naphthaocyaninato)(phthalocyaninato) Rare Earth Double-Decker Complexes **1**−**6**^{a}

		analysis (%)^b			
compd	yield (%)	M$^+$ (*m/z*)^b	C	H	N
Sm[Nc(*t*Bu)$_4$](Pc) (**1**)	25	1600.5 (1600.2)	70.42 (70.92)^c	4.46 (4.47)^c	13.84 (13.77)^c
Sm(Nc)[Pc(OC$_5$H$_{11}$)$_4$] (**2**)	59	1720.6 (1720.6)	68.83 (69.82)	4.94 (4.69)	13.01 (13.03)
Sm(Nc)[Pc(OC$_8$H$_{17}$)$_8$] (**3**)	32	2401.1 (2401.2)	71.67 (71.90)	7.16 (7.04)	9.10 (9.32)
Sm(Nc)[Pc(α-OC$_5$H$_{11}$)$_4$] (**4**)	37	1720.2 (1720.6)	68.88 (69.82)	4.75 (4.69)	12.65 (13.03)
Eu(Nc)[Pc(α-OC$_5$H$_{11}$)$_4$] (**5**)	31	1721.8 (1721.6)	69.33 (69.76)	4.70 (4.68)	12.72 (13.02)
Y(Nc)[Pc(α-OC$_5$H$_{11}$)$_4$] (**6**)	34	1658.7 (1658.6)	72.14 (72.41)	4.93 (4.86)	13.15 (13.51)

[a] Calculated values given in parentheses. [b] By MALDI-TOF mass spectrometry. The value corresponds to the most abundant isotopic peak of the molecular ion (M$^+$). [c] For **1**·$^1/_4$CHCl$_3$.

Table 2. Electronic Absorption Data for Double-Deckers **1**−**6** in CHCl$_3$

compd	λ_{max}/nm (log ϵ)							
1		329 (5.31)	442 (4.64)		646 (5.21)	723 (5.38)	972 (3.99)	1667 (4.25)
2	303 (4.92)	333 (5.04)	419 (4.56)	602 (4.56)	639 (4.72)	728 (4.93)	972 (3.63)	1709 (4.01)
3	302 (5.30)	331 (5.47)	440 (4.79)	603 (4.94)	645 (5.22)	735 (5.35)	982 (4.03)	1760 (4.45)
4		323 (4.08)	435 (3.48)	610 (3.67)	656 (3.95)	753 (4.01)	994 (2.57)	1965 (2.54)
5		323 (4.12)	436 (3.50)	607 (3.68)	655 (3.95)	750 (4.09)	997 (2.62)	1917 (3.16)
6		322 (4.13)	438 (3.48)	600 (3.63)	650 (3.86)	740 (4.17)	1004 (2.75)	1753 (3.18)

als. M(Pc′)(acac), generated in situ from M(acac)$_3$·*n*H$_2$O and H$_2$Pc′ in the first step at ca. 140 °C, is considered to be the template which induces the cyclic tetramerization of dicyanonaphthalene in the presence of DBU in refluxing *n*-octanol leading to the heteroleptic double-deckers M(Nc′)(Pc′) in relatively good yield. This proposed mechanism has been verified by the formation of Sm[Nc(*t*Bu)$_4$](Pc) (**1**) starting directly from M(Pc)(acac) and the corresponding dicyanonaphthalene. Furthermore, the generality of this one-pot procedure has been well demonstrated by preparation and isolation of the other two series of heteroleptic (naphthalocyaninato)(phthalocyaninato) rare earth double-decker compounds containing different phthalocyanine ligands and rare earth metals, namely, Sm(Nc)(Pc′) [Pc′ = Pc(OC$_5$H$_{11}$)$_4$, Pc(OC$_8$H$_{17}$)$_8$] (**2**, **3**) and M(Nc)[Pc(α-OC$_5$H$_{11}$)$_4$] (M = Sm, Eu, Y) (**4**−**6**). Actually, heteroleptic complexes M(Nc)(Pc) with both unsubstituted naphthalocyaninato and unsubstituted phthalocyaninato ligands were also our target compounds for the purpose of comparative study. However, the limited solubility of these compounds, particularly after preliminary purification by column chromatography and recrystallization, retards further purification and spectroscopic studies. This observation seems to contradict the well-described result for the compound Lu(Nc)(Pc) but can be rationalized by the fact that no successive work on the other rare earth analogues, M(Nc)(Pc) (M = La−Yb except Pm), was found in the literature after the report of Lu(Nc)(Pc), and it is actually in good accord with our finding that, once isolated, unsubstituted double-deckers M(Nc)$_2$ could not be dissolved in common organic solvents.

It is worth mentioning that because of the C_{4h} symmetry of the Pc(α-OC$_5$H$_{11}$)$_4$ ring and the sandwich-like structure, the molecules of M(Nc)[Pc(α-OC$_5$H$_{11}$)$_4$] (**4**−**6**) are intrinsically chiral possessing a C_4 symmetry. However, attempts to resolve the two enantiomers of **4**−**6** by HPLC using a silica gel column coated with cellulose 2,3,6-tris(3,5-dimethylphenylcarbamate) were not successful because of the very small differences between the enantiomers.

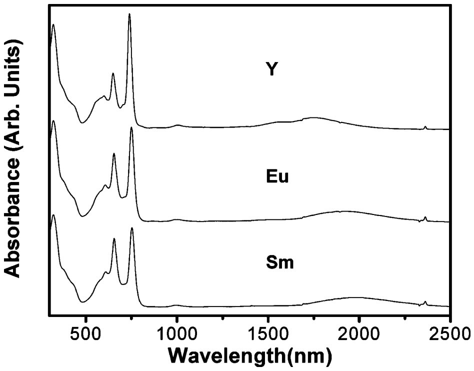

Figure 2. Electronic absorption spectra of M(Nc)[Pc(α-OC$_5$H$_{11}$)$_4$] (M = Sm, Eu, Y) (**4**−**6**) in CHCl$_3$.

Satisfactory elemental analysis results have been obtained for all of these newly prepared heteroleptic rare earth complexes after repeated column chromatography and recrystallization (Table 1). Their sandwich double-decker nature was further deduced by MALDI-TOF mass and NMR spectroscopies. The MALDI-TOF mass spectra of these compounds clearly showed intense signals for the molecular ion (M)$^+$ (Table 1). The isotopic pattern closely resembled the simulated one as exemplified by the spectrum of the heteroleptic double-decker, **5**, given in Figure S1 (see the Supporting Information).

Electronic Absorption Spectra. The electronic absorption data for all of the heteroleptic compounds were measured in CHCl$_3$ and compiled in Table 2. The electronic spectra of M(Nc′)(Pc′) complexes are very similar to those of the homoleptic analogues, namely, M(Nc′)$_2$ and M(Pc′)$_2$, and thus could be similarly assigned. Figure 2 shows the electronic absorption spectra of M(Nc)[Pc(α-OC$_5$H$_{11}$)$_4$] (M = Sm, Eu, Y) (**4**−**6**) in which the dependence of the spectral features on the metal center is clearly illustrated. All of the spectra for **4**−**6** show a typical Soret band at ca. 323 nm. The absorptions at 435−438 and 994−1004 nm are caused by electronic transitions involving the semi-occupied orbital, which has a higher Nc character. An additional characteristic near-IR band for π-radical anions at 1753−1965 nm can also

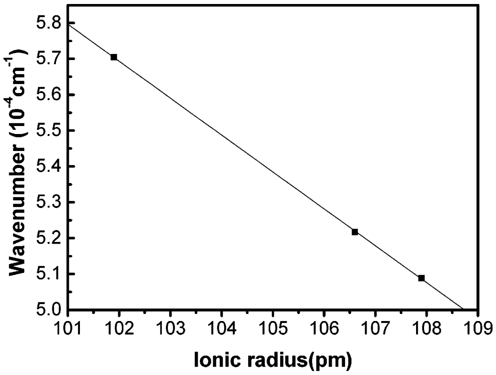

Figure 3. Plot of wavenumbers of the RRCT absorption of M(Nc)[Pc-(α-OC$_5$H$_{11}$)$_4$] (**4**−**6**) as a function of the rare earth ionic radius of M$^{\mathrm{III}}$.

be observed for the series of three tervalent rare earth double-deckers M(Nc)[Pc(α-OC$_5$H$_{11}$)$_4$]. As shown in Table 2, the positions of all the absorption bands for this series of compounds, **4**−**6**, except the Soret band at ca. 323 nm, are sensitive to the ionic radius of the metal center shifting to the red or blue depending on the nature of the transition. For instance, when the metal center becomes smaller, the absorption at 994−1004 nm shifts gradually to the red, while the characteristic π-radical anion absorption at 1753−1965 nm, assigned to the ring−ring charge transfer (RRCT) band from the dianion to the monoanion radical, is linearly blue-shifted (Figure 3).

Interestingly, the Q-band for heteroleptic bis(phthalocyaninato) rare earth analogues M(Pc)[Pc(α-OC$_5$H$_{11}$)$_4$] has been found to split giving three strong absorptions because of the lowering of the whole molecular symmetry.[20] However, in the present case for M(Nc)[Pc(α-OC$_5$H$_{11}$)$_4$] (**4**−**6**), their electronic absorption spectra resemble those of **1**−**3** and do not reflect the lowering of molecular symmetry by showing only one intense Q-band at 740−753 nm despite introduction of a Pc(α-OC$_5$H$_{11}$)$_4$ unit. This result seems to suggest the dominant role of the naphthalocyanine ligand to the Q absorption band of M(Nc)[Pc(α-OC$_5$H$_{11}$)$_4$] (**4**−**6**) compared with that of phthalocyanine. Nevertheless, the contribution from the phthalocyanine ligand can never be excluded. The fact that both the main and side Q-bands of Sm[Nc(*t*Bu)$_4$]-(Pc) (**1**) lie between the corresponding bands of the homoleptic counterparts Sm[Nc(*t*Bu)$_4$]$_2$[21] and Sm(Pc)$_2$[22] clearly reveals that the Q absorptions of heteroleptic double-decker compounds contain contributions from both the naphthalocyanine and phthalocyanine ligands because of the strong π−π interaction between the two macrocycle rings connected by the rare earth ion.

Sm(Nc)(Pc′) [Pc′ = Pc(OC$_5$H$_{11}$)$_4$, Pc(OC$_8$H$_{17}$)$_8$] (**2**, **3**) display electronic absorption features similar to those of analogous compounds **4**−**6** and **1**. Nevertheless, the attachment of more electron-donating alkoxy groups onto the peripheral positions of the phthalocyanine ligand in compound **3** than in **2** is clearly reflected by the red-shifted Q-band and RRCT band at 982 and 1760 nm for **3**, respectively, in comparison with those at 972 and 1709 nm for **2**.

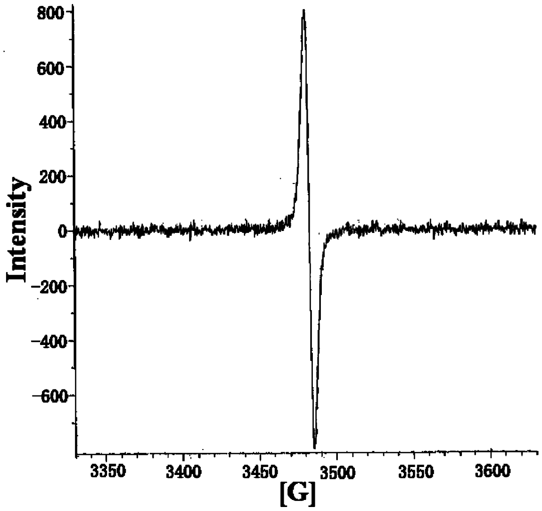

Figure 4. ESR spectrum of Y(Nc)[Pc(α-OC$_5$H$_{11}$)$_4$] (**6**) in CH$_2$Cl$_2$.

The presence of an unpaired electron in either the naphthalocyaninato or the phthalocyaninato ligand (preferentially in naphthalocyanine because of the higher energy level of the HOMO of Nc in comparison with that of Pc[21,23]) was supported by IR spectroscopy. An intense IR band at 1319−1322 cm^{-1} was observed for the whole series of M$^{\mathrm{III}}$-(Nc′)(Pc′) (**1**−**6**). This band, which is also seen in many other single-hole (na)phthalocyanine-containing double-deckers, serves as a marker for the (na)phthalocyanine radical anion.[24]

ESR Spectrum of Y(Nc)[Pc(α-OC$_5$H$_{11}$)$_4$]. As revealed by the appearance of the RRCT band in the near-IR range of the electronic absorption spectra and of the marker IR band in the IR spectra, all of the heteroleptic double-deckers, **1**−**6**, can be regarded as single-hole complexes in which an unpaired electron is present in one of the macrocyclic ligands. This was unambiguously demonstrated by the room-temperature EPR spectrum of Y$^{\mathrm{III}}$(Nc)[Pc(α-OC$_5$H$_{11}$)$_4$] (**6**) (Figure 4) which showed a characteristic signal for organic radicals at $g = 2.002$.[2−4,17b,18c] The signal exhibited a poorly resolved hyperfine structure with peak to peak separation of 4.5 G.

NMR Spectra. Because of the presence of the unpaired electron, NMR data for such single-hole complexes are difficult to obtain. However, upon addition of hydrazine hydrate as a reducing agent, well-resolved ^{1}H NMR spectra could be obtained for the reduced form of all of the

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(22) UV−Vis and near-IR spectra of Sm(Pc)$_2$ in CHCl$_3$ ($\lambda_{\max}$ (nm) (log ϵ)): 322 (5.26), 460 (4.64), 606 (4.71), 673 (5.38), 905 (3.83), 1636 (4.32).

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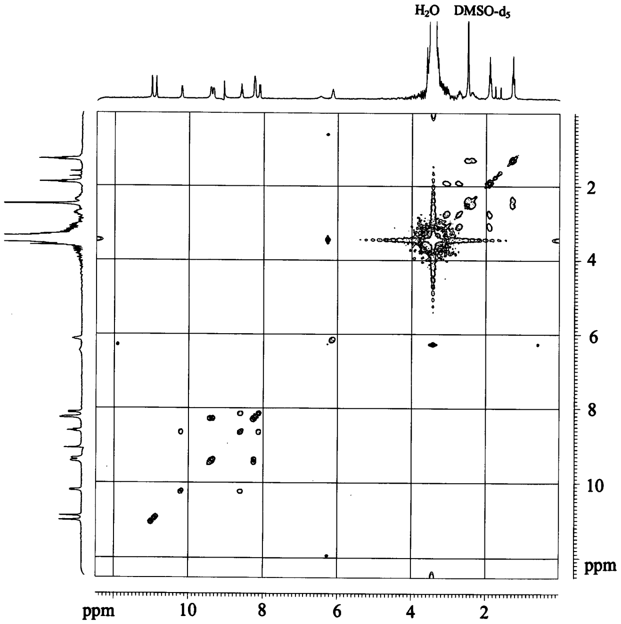

Figure 5. $^1H-^1H$ COSY spectrum of Eu(Nc)[Pc(α-OC_5H_{11})$_4$] (**5**) in $CDCl_3$/DMSO-d_6 (1:1) containing ca. 1% hydrazine hydrate.

heteroleptic double-decker complexes, **1**−**6**, in which both macrocyclic ligands become diamagnetic dianions, i.e., $[M^{III}(Nc'^{2-})(Pc'^{2-})]^-$. Figure 5 shows the $^1H-^1H$ COSY spectrum of the reduced form of **5**. The tetra-α-substituted phthalocyanine ring protons resonate at δ 10.20 (d), 8.60 (t), and 8.11 (d), as usual. Interestingly, because of the C_4 symmetry of the molecule, the α (as well as β) protons of the unsubstituted Nc are no longer equivalent in the present environment giving two singlets at δ 11.01 and 10.89 (and two multiplets in the region δ 9.33−9.45 for the β protons). The γ protons of the Nc ligand give a poorly resolved multiplet at δ 8.23−8.30. Because of the restricted rotation of the 3-pentyloxy substituent along the C(ipso)−O bond, the two methyl groups resonate as two well-resolved triplets at δ 1.90 and 1.28. The diastereotopic methylene protons give three multiplets at δ 3.03−3.13, 2.67−2.80, and 2.30−2.40. As revealed by the COSY spectrum, the remaining multiplet is embedded by the strong DMSO-d_5 signal. The methine proton gives a broad multiplet at δ 6.07−6.17. The cross-peaks arising from this proton and the methylene protons are not seen which may be caused by the neighboring strong water and DMSO-d_5 signals. The data for the other five double-deckers together with the assignments are collected in Table 3.

Electrochemical Properties. The electrochemical behavior of all of the heteroleptic double-decker complexes was investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in CH_2Cl_2. These double-decker compounds displayed up to four one-electron oxidations, labeled Oxd$_1$−Oxd$_4$, and up to five one-electron reductions (Red$_1$−Red$_5$) within the electrochemical window of CH_2Cl_2 under the present conditions. The separation between the reduction and oxidation peak potentials for each process is 65−90 mV. All of these processes are attributed to successive removal from or addition of one electron to the ligand-based orbitals. The half-wave redox potential values vs SCE are summarized in Table 4.

Table 3. ^1H NMR Data (δ) for the Reduced Form of Double-Deckers **1**−**6**[a]

	signals for the naphthalocyanine ring		
compd	$H_{\alpha/\alpha'}$	$H_{\beta/\beta'}$	$H_{\gamma/\gamma'}$
1	8.48−8.58 (m, 8 H)	8.22−8.30 (m, 8 H)	7.88 (d, J = 8.7 Hz, 4 H)
2	8.55−8.61 (m, 8 H)	8.27−8.40 (m, 8 H)	7.72−7.78 (m, 8 H)
3	8.57 (s, 8 H)	8.36−8.39 (m, 8 H)	7.68−7.71 (m, 8 H)
4	8.65 (s, 4 H) 8.63 (s, 4 H)	8.28−8.36 (m, 8 H)	7.64−7.71 (m, 12 H)[b]
5	11.01 (s, 4 H) 10.89 (s, 4 H)	9.33−9.38 (m, 4 H) 9.39−9.45 (m, 4 H)	8.23−8.30 (m, 8 H)
6	9.34 (s, 4 H) 9.31 (s, 4 H)	8.59−8.65 (m, 8 H)	7.84−7.93 (m, 12 H)[c]

	signals for the phthalocyanine ring	
compd	$H_{\alpha/\alpha'}$	$H_{\beta/\beta'}$
1	8.01−8.04 (m, 8 H)	7.74−7.77 (m, 8 H)
2	7.84 (d, J = 8.1 Hz, 4 H)	7.22−7.30 (m, 8 H)[b]
3	7.32 (s, 8 H)	−
4	−	7.55 (t, J = 7.5 Hz, 4 H) 7.12 (d, J = 7.5 Hz, 4 H)
5	10.20 (d, J = 7.5 Hz, 4 H)	8.60 (t, J = 7.5 Hz, 4 H) 8.11 (d, J = 7.5 Hz, 4 H)
6	8.36 (d, J = 7.2 Hz, 4 H)	7.47 (d, J = 7.8 Hz, 4 H)

compd	Signals for the substituents
1	1.53 (s, 36 H, *t*Bu)
2	4.26−4.38 (m, 4 H, OCH), 1.68−1.80 (m, 16 H, CH_2), 0.95−1.05 (m, 24 H, CH_3)
3	4.03−4.18 (m, 16 H, OCH_2), 1.84−1.92 (m, 16 H, CH_2), 1.52−1.60 (m, 16 H, CH_2), 1.26−1.44 (m, 64 H, CH_2), 0.88 (t, J = 6.6 Hz, 24 H, CH_3)
4	4.25−4.35 (m, 4 H, OCH), 1.27−1.55 (m, 12 H, CH_2), 1.07−1.18 (m, 4 H, CH_2), 0.68 (t, J = 6.9 Hz, 12 H, CH_3), 0.37 (t, J = 7.2 Hz, 12 H, CH_3)
5	6.07−6.17 (m, 4 H, OCH), 3.03−3.13 (m, 4 H, CH_2), 2.67−2.80 (m, 4 H, CH_2), 2.30−2.40 (m, 4 H, CH_2),[d] 1.90 (t, J = 7.2 Hz, 12 H, CH_3), 1.28 (t, J = 7.2 Hz, 12 H, CH_3)
6	4.75−4.84 (m, 4 H, OCH), 1.86−1.95 (m, 4 H, CH_2), 1.74−1.81 (m, 4 H, CH_2), 1.58−1.67 (m, 8 H, CH_2), 0.76−0.85 (m, 24 H, CH_3)

[a] Recorded in $CDCl_3$/DMSO-d_6 (1:1) with the addition of ca. 1% hydrazine hydrate on a 300 MHz spectrometer. [b] Overlapped with (one of) the phthalocyanine's $H_{\alpha/\alpha'}$ signals. [c] Overlapped with one of the phthalocyanine's $H_{\beta/\beta'}$ signals. [d] The remaining methylene proton's mulitplet is embedded by the strong signal of DMSO-d_5.

The availability of $Sm(Pc)_2$,[25] Sm[Nc(tBu)$_4$](Pc) (**1**), and Sm[Nc(tBu)$_4$]$_2$[5,21] affords a good chance to investigate the effect of the extension of the ring-conjugated system on the electrochemistry of sandwich double-deckers. Comparison of the electrochemical data for these three complexes reveals that replacement of phthalocyanine by a 2,3-naphthalocyanine ligand induces successive shifts toward the negative direction of all of the redox potentials. However, the shift induced by the introduction of the second naphthalocyanine ring is smaller when compared with that from the replacement of the first phthalocyanine ligand.

As can be seen in Table 4, the incorporation of eight electron-donating alkoxy groups onto the peripheral positions of the phthalocyanine ring of heteroleptic (naphthalocyaninato)(phthalocyaninato) double-deckers makes the compound easier to oxidize and harder to reduce than the introduction of four alkoxy groups onto the same ligand. This is well

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Table 4. Half-wave Redox Potentials for Double-Deckers **1**−**6** (V vs SCE) in CH_2Cl_2 Containing 0.1 M TBAP

compd	Oxd_4	Oxd_3	Oxd_2	Oxd_1	Red_1	Red_2	Red_3	Red_4	Red_5	$\Delta E_{1/2}$[a]	$\Delta E'_{1/2}$[b]
1			+1.28	+0.40	−0.03	−1.14	−1.50	−1.94		0.43	1.11
2				+0.33	−0.07	−1.17	−1.58	−2.00		0.40	1.10
3			+1.27	+0.29	−0.13	−1.21	−1.57	−2.01		0.42	1.08
4	+1.76	+1.27	+1.09	+0.29	−0.05	−1.26	−1.56	−1.78	−1.92	0.34	1.21
5	+1.78	+1.27	+1.09	+0.27	−0.06	−1.22	−1.52	−1.73	−1.91	0.35	1.16
6	+1.73	+1.29	+1.10	+0.22	−0.12	−1.21	−1.50	−1.72	−1.87	0.34	1.09

[a] $\Delta E_{1/2}$ is the energy for putting a second electron on the semi-occupied HOMO of the neutral double-decker radical M(Nc)[Pc(α-OC_5H_{11})$_4$] or for removing one electron of the two from the HOMO of the reduced double-decker species {M(Nc)[Pc(α-OC_5H_{11})$_4$]}$^-$: $\Delta E_{1/2} = Oxd_1 - Red_1$. [b] $\Delta E'_{1/2}$ is the potential difference between the first oxidation and first reduction processes, i.e., the HOMO−LUMO gap of {M(Nc)[Pc(α-OC_5H_{11})$_4$]}$^-$: $\Delta E'_{1/2} = Red_1 - Red_2$.

demonstrated by the lower oxidation and reduction half-wave potentials of corresponding redox processes of Sm(Nc)[Pc(OC_8H_{17})$_8$] (**3**) compared to those of Sm(Nc)[Pc(OC_5H_{11})$_4$] (**2**).

The variations of the redox potentials for the series of M(Nc)[Pc(α-OC_5H_{11})$_4$] (M = Sm, Eu, Y) (**4**−**6**) complexes along with the ionic radii of the rare earth metal centers are also listed in Table 4. As can be seen, the half-wave potentials for the first oxidation (Oxd_1) and the first reduction (Red_1) processes involving the semi-occupied orbital decrease as the size of the metal center becomes smaller, while those for the second and the third oxidations (Oxd_2 and Oxd_3) involving the second-highest occupied orbital remain almost unchanged. This is also true for the fourth oxidation which deals with the third-highest occupied orbital. These results indicate that, along with the lanthanide contraction, the semi-occupied orbital increases in energy while the energy level of the second- and third-highest occupied orbitals remains relatively constant. The increase in the energy gap between the first- and second-highest occupied orbitals is in accordance with the blue shift of the longest-wavelength near-IR band along with the lanthanide contraction. The potentials for the remaining reduction processes (Red_2, Red_3, Red_4, and Red_5) diminish along with the decrease in the ionic size of the metal center, suggesting that the energy level of the LUMO as well as the second-lowest unoccupied orbital increases slightly in the same order (Table 4).

Moreover, the potential difference between Red_1 and Red_2 ($\Delta E'_{1/2}$) of the series of M(Nc)[Pc(α-OC_5H_{11})$_4$], which represents the HOMO−LUMO gap of the reduced forms of the double-deckers, i.e., {M(Nc)[Pc(α-OC_5H_{11})$_4$]}$^-$, decreases from 1.21 V (for M = Sm) to 1.09 V (for M = Y). This reveals the increasing $\pi-\pi$ interaction between the naphthalocyanine and phthalocyanine rings along with the decreasing the ring−ring distance from the lanthanide contraction. As the first oxidation step and first reduction step deal with the HOMO and LUMO of the molecule, respectively, the energy difference between these redox processes for [{M(Nc)[Pc(α-OC_5H_{11})$_4$]}$^-$ is associated with its electrochemical molecular band gap. The value $\Delta E'_{1/2}$ thus reflects the energy necessary for the transition of an electron from HOMO to LUMO for {M(Nc)[Pc(α-OC_5H_{11})$_4$]}$^-$ and, therefore, correlates with the lowest-energy optical transition in the electronic absorption spectrum of {M(Nc)[Pc(α-OC_5H_{11})$_4$]}$^-$. Actually, the diminishing trend revealed by electrochemistry for the $\Delta E'_{1/2}$ value of heteroleptic (naphthalocyaninato)[1,8,15,22-tetrakis(3-pentyloxy)phthalocyaninato] metal complexes along with the rare earth contraction is just in line with the red shift of the lowest absorption band of {M(Nc)[Pc(α-OC_5H_{11})$_4$]}$^-$, 745 nm for M = Sm to 755 nm for M = Y, recorded in the electronic absorption spectra (Table S1).

The potential differences between Oxd_1 and Red_1 ($\Delta E_{1/2}$) for the heteroleptic samarium double-decker complexes containing the unsubstituted and peripherally octasubstituted phthalocyanine ligands **1** and **3** (0.43 and 0.42 V, respectively) are similar to those of corresponding homoleptic bis(phthalocyaninato) counterparts (0.42 and 0.41 V)[25] but larger than that for the bis(naphthalocyaninato) analogue (0.31 V).[5,21] However, the values for the heteroleptic (naphthalocyaninato)[2(3),9(10),16(17),24(25)-tetrakis(3-pentyloxy)phthalocyaninato] rare earth compounds **4**−**6** (ca. 0.34 V) are just between those observed for the corresponding M(Pc)[Pc(α-OC_5H_{11})$_4$] (ca. 0.38 V)[20b] and M[Nc(*t*Bu)$_4$]$_2$ (ca. 0.31 V).[5,21] These results suggest that these novel heteroleptic (naphthalocyaninato)(phthalocyaninato) rare earth complexes are also good molecular semiconductors.[26]

Conclusion

We have developed a general and efficient synthetic pathway for preparing a series of heteroleptic rare earth double-decker complexes with naphthalocyaninato and phthalocyaninato ligands M(Nc′)(Pc′). The compounds have been fully characterized with various spectroscopic and electrochemical methods. The sandwich nature of these double-deckers in solution has also been determined by NMR spectroscopy.

Experimental Section

General Remarks. *n*-Octanol was distilled from sodium. Dichloromethane for voltammetric studies was freshly distilled from CaH_2 under nitrogen. Column chromatography was carried out on silica gel (Merck, Kieselgel 60, 70−230 mesh) with the indicated eluents. All other reagents and solvents were used as received.

The compounds M(acac)$_3$·*n*H_2O,[27] H_2Pc' [Pc′ = Pc(OC_5H_{11})$_4$, Pc(OC_8H_{17})$_8$, Pc(α-OC_5H_{11})$_4$],[28] Sm(Pc)(acac),[29] and dicyanonaphthalenes[30] were prepared according to the published procedures.

^1H NMR spectra were recorded on a Bruker DPX 300 spectrometer (300 MHz) in $CDCl_3$/DMSO-d_6 (1:1) with the addition of ca. 1% hydrazine hydrate. Spectra were referenced internally

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using the residual solvent resonance (δ 2.49 for DMSO-d_5) relative to $SiMe_4$. The EPR spectrum was recorded in $CHCl_3$ at ambient temperature on a Bruker EMX EPR spectrometer equipped with an ER041 XG microwave bridge (X-band). The field was calibrated using 1,1-diphenyl-2-picrylhydrazyl. Electronic absorption spectra were recorded on a Hitachi U-4100 spectrophotometer. IR spectra were recorded as KBr pellets using a BIORAD FTS-165 spectrometer with 2 cm^{-1} resolution. MALDI-TOF mass spectra were taken on a Bruker BIFLEX III ultrahigh-resolution Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer with α-cyano-4-hydroxycinnamic acid as a matrix. Elemental analyses were performed by the Institute of Chemistry, Chinese Academy of Sciences.

Electrochemical measurements were carried out with a BAS CV-50W voltammetric analyzer. The cell was comprised of inlets for a glassy carbon disk working electrode 2.0 mm in diameter and a silver-wire counter electrode. The reference electrode was Ag/Ag^+, 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 internally referencing the ferrocenium/ferrocene (Fe^+/Fe) couple ($E_{1/2}(Fe^+/Fe) = 501$ mV vs SCE). Typically, a 0.1 mol dm^{-3} solution of $[Bu_4N][ClO_4]$ in CH_2Cl_2 containing 0.5 mmol of sample dm^{-3} was purged with nitrogen for 10 min, and then the voltammograms were recorded at ambient temperature. The scan rate was 20 and 10 mV s^{-1} for CV and DPV, respectively.

General Procedure for the Preparation of M(Nc′)(Pc′) (M = Sm, Eu, Y) (1−6). A mixture of H_2Pc' (0.05 mmol), $M(acac)_3 \cdot nH_2O$ (0.10 mmol), and dicyanonaphthalene (0.40 mmol) in *n*-octanol (4 mL) in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (0.05 mL) was first heated at ca. 150 °C for 2 h and then heated to reflux for 7 h under a slow stream of nitrogen. The resulting green solution was cooled to room temperature, and then the volatiles were removed under reduced pressure. The residue was chromatographed with $CHCl_3$ as the eluent to give a dark-blue fraction containing the target heteroleptic (naphthalocyaninato)(phthalocyaninato) rare earth double-decker compounds M(Nc′)(Pc′) following the first green fraction containing a small amount of bis(phthalocyaninato) rare earth side product. All compounds, **1**−**6**, were recrystallized from a mixture of $CHCl_3$ and MeOH after repeated chromatography to produce dark powders with yields of 20−61%.

It is worth mentioning that for preparation of the unsubstituted phthalocyanine-containing heteroleptic samarium double-decker **1**, Sm(Pc)(acac) (0.05 mmol), was generated from the reaction of Li_2Pc and $Sm(acac)_3 \cdot nH_2O$ in situ instead of the reaction of the insoluble metal-free phthalocyanine and $Sm(acac)_3 \cdot nH_2O$.

Acknowledgment. We thank Prof. Hung-Kay Lee for recording the EPR spectrum for **6**. Financial support from the Natural Science Foundation of China (Grants 20171028, 20325105, and 20431010), the National Ministry of Science and Technology of China (Grant 2001CB6105), the Ministry of Education of China, Shandong University for J.J., and The Chinese University of Hong Kong for D.K.P.N. is gratefully acknowledged.

Supporting Information Available: Experimental and simulated isotopic pattern for the molecular ion of $Eu(Nc)[Pc(\alpha\text{-}OC_5H_{11})_4]$ (**5**) shown in the MALDI-TOF mass spectrum and electronic absorption data for the reduced double-deckers $[M(Nc')(Pc')]^-$ in $CHCl_3$/MeOH (1:1). This material is available free of charge via the Internet at http://pubs.acs.org.

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