

Comparative Spectroscopic and Electrochemical Properties of Bis(octakis(dodecylthio)naphthalocyaninato)europium(III) and Bis(tetra-*tert*-butylnaphthalocyaninato)europium(III) Complexes

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Bis(substituted-2,3-naphthalocyaninato)europium(III) complexes: bis(octakis(dodecylthio)-2,3-naphthalocyaninato)europium(III) {Eu[2,3-Nc(SC₁₂H₂₅)₈]₂, **1**} and bis(tetra-*tert*-butyl-2,3-naphthalocyaninato)europium(III) {Eu[2,3-Nc(*t*-Bu)₄]₂, **2**} have been synthesized by cyclic tetramerization of naphthalonitriles with Eu(acac)₃·H₂O in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in refluxing *n*-octanol. These compounds were characterized by UV–visible, magnetic circular dichroism (MCD), near-IR, IR, EPR, and mass spectroscopies. The absorption and MCD spectra of **1** showed splitting of the Q band, with peaks at 700 and 784 nm, red shifted from the Q band of **2** at 763 nm. The absorption and MCD spectral band deconvolution calculations of complex **1** gave two A terms in the Q-band region. The A terms are assigned to ²A₂ → ²E₁ transitions. Cyclic voltammograms of **1** and **2** showed reversible oxidation couples at E_{1/2} = −0.28 V (for **2**) and −0.25 V (for **1**) vs ferrocenium/ferrocene (Fc⁺/Fc). The second oxidation exhibited a complicated behavior for both complexes. The reduction couples for **2** were observed at E_{1/2} = −0.61, −1.64, −1.97, and −2.42 V, and for **1** they were observed at E_{1/2} = −0.62, −1.60, −1.86, and −2.27 V vs Fc⁺/Fc. Spectral changes observed on chemical oxidation and reduction of the complexes are presented, and the behaviors of **1** and **2** are compared.

Introduction

For many years phthalocyanine derivatives have attracted attention as the result of their diverse electronic, optical, and structural properties which offer applications in the fields of nonlinear optics,² catalysis,³ liquid crystals,⁴ electrochromism,⁵ sensors,⁶ photosensitizers,⁷ molecular electronics,⁸ photovoltaic

cells,⁹ Langmuir–Blodgett films,¹⁰ and semiconductor devices.^{11,12} In many of these applications, it is important to understand the spectroscopic and electrochemical properties of phthalocyanines. The rich coordination chemistry of phthalocyanine complexes has resulted in the development of a large number of new rings or axially substituted derivatives which are tailored for specific applications. Thus, there is considerable current interest in the synthesis and elucidation of the properties of structurally modified phthalocyanines.^{13–18} In addition to

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monomeric species, many symmetrically and unsymmetrically substituted homoleptic sandwich-type lanthanide bis(phthalocyanine) complexes $\text{Ln}(\text{Pc})_2$ and $\text{Ln}_2(\text{Pc})_3$ (Ln, lanthanide; Pc, phthalocyanine dianion) have also attracted great attention for many research groups^{19–25} following the first synthesis in 1965.²⁶ On the other hand, the history of naphthalocyanine (Nc) rare earth complexes is 20 years younger. In the middle of the 80's, Luk'yanets claimed that he had prepared a mixture of isomeric substituted bis(2,3-naphthalocyaninato)lutetium and unsymmetrical heteroleptic (phthalocyaninato)(tetra-*tert*-butyl-naphthalocyaninato)lutetium compounds, which were characterized only by UV–visible absorption spectroscopy.²⁷ Lately, there has been another report on the synthesis of substituted bis(naphthalocyanines), but again only the UV–visible spectra were reported.²⁸ In 1990, Simon et al. studied the electrical properties of mixed lutetium complexes with mixed phthalocyaninato and naphthalocyaninato ligands.²⁹ More recently, L'Her and co-workers reported the detailed results on the synthesis and properties of lutetium naphthalocyaninato double- and triple-deckers $\text{Lu}(2,3\text{-Nc})_2$,³⁰ $\text{Lu}(1,2\text{-Nc})_2$,³¹ and $\text{Lu}_2(1,2\text{-Nc})_3$ ³¹ as well as the unsymmetric (2,3-naphthalocyaninato)-(phthalocyaninato)lutetium compound $\text{Lu}(\text{Pc})(2,3\text{-Nc})$.³⁰ Noteworthy is that Ishikawa et al.³² also prepared the unsymmetrical $\text{Lu}(\text{Pc})(2,3\text{-Nc})$ by a similar method employed by L'Her. Simon et al.,³³ on the other hand, prepared $\text{Lu}(\text{Pc})(2,3\text{-Nc})$ through the reaction of naphthalonitrile and $\text{Lu}(\text{Pc})(\text{OAc})$ in the presence of catalysts. Despite these studies, the sandwich Nc rare earth compounds are still less well elucidated compared with the corresponding Pc derivatives, and most importantly, metals other than lutetium have not been utilized for Nc double-deckers. Accordingly, we herein describe the synthesis, electrochemistry, and detailed spectroscopic characterization of two substituted bis(naphthalocyaninato)europium(III) complexes; i.e., bis(octakis(dodecylthio)-2,3-naphthalocyaninato)europium(III) $\{\text{Eu}[2,3\text{-Nc}(\text{SC}_{12}\text{H}_{25})_8]_2, \mathbf{1}\}$ and bis(tetra-*tert*-butyl-2,3-naphthalocyaninato)europium(III) $\{\text{Eu}[2,3\text{-Nc}(t\text{-Bu})_4]_2, \mathbf{2}\}$ have been synthesized by the cyclic tetramerization of naphthalonitrile on the template of $\text{Eu}(\text{acac})_3 \cdot \text{H}_2\text{O}$ under the catalysis of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) at high temperature. The synthesis of alkylthio-substituted mono(naphthalocyanines) has been reported by several workers,^{34–36} but this work reports for the first time the synthesis of alkylthio-substituted bis(naphthalocyanines). In addition, since absorption spectral band deconvolution has evolved as a useful tool in identifying bands in phthalocyanine spectra,^{37–39} we report on the deconvolution analysis of the spectra of $\text{Eu}[2,3\text{-Nc}(\text{SC}_{12}\text{H}_{25})_8]_2$ and use the deconvolution results to elucidate the effects of ring substituents on $\pi\text{-}\pi^*$ transition energies.

Experimental Section

Materials. Solvents for spectroscopic measurements (*N,N*-dimethylformamide (DMF), chloroform, and carbon tetrachloride) were supplied by Nacalai Tesque and used as supplied. Chloroform was also supplied by Beijing Chemical reagents. Dichlorobenzene (DCB, Nacalai Tesque, specially prepared for HPLC) was used as supplied, for electrochemical studies. Tetrabutylammonium perchlorate (TBAP) was recrystallized from absolute ethanol and used as an electrolyte for electrochemical measurements. Ferrocene used for the internal standard was recrystallized from cyclohexane. *n*-Octanol was distilled from both of anhydrous K_2CO_3 and sodium. Hydrazine hydrate (Wako), nitrosonium tetrafluoroborate (Aldrich), and DBU (Aldrich) were used as supplied. $\text{Eu}(\text{acac})_3 \cdot \text{H}_2\text{O}$ was obtained from Beijing Chemical Reagents. 2-*tert*-Butyl-6,7-dicyanonaphthalene was prepared according to published methods.⁴⁰ 2,3-Bis(dodecylthio)-6,7-dicyanonaphthalene was obtained by reacting 2,3-dibromo-6,7-dicyanonaphthalene⁴¹ with dodecanethiol in refluxing DMF in the presence of NaOH and Cu_2O .

Experimental Section

Physical Measurements. The UV–visible and near-IR spectra were recorded with a Hitachi U-3410 spectrophotometer. IR spectra (KBr pellets) were measured with a Perkin-Elmer 1600 series FT-IR spectrometer as KBr pellets. Magnetic circular dichroism (MCD) spectra

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were recorded with a JASCO J-725 spectropolarimeter in the presence of a 1.09 T magnetic field. The spectra were recorded twice, once with a parallel field and again with an antiparallel field, and their intensities were expressed by molar ellipticity per $T = [\theta]_M/10^4 \text{ deg mol}^{-1} \text{ dm}^3 \text{ cm}^{-1} \text{ T}^{-1}$. Electron paramagnetic resonance (EPR) spectra were measured at 20 K with a Bruker ESP 300E spectrometer, the temperature being controlled with an Oxford ESR 900 cold gas flow system. ^1H nuclear magnetic resonance (NMR, 400 MHz) spectra were obtained in CDCl_3 using a JEOL GSX-400 spectrometer. Mass measurements were conducted on a Perseptive Biosystem MALDI-TOF Mass Voyager DE-SI2 spectrometer using not only α -cyano-4-hydroxycinnamic acid but also 1,8-dihydroxy-9(10*H*)anthracenone (dithranol) as matrices.

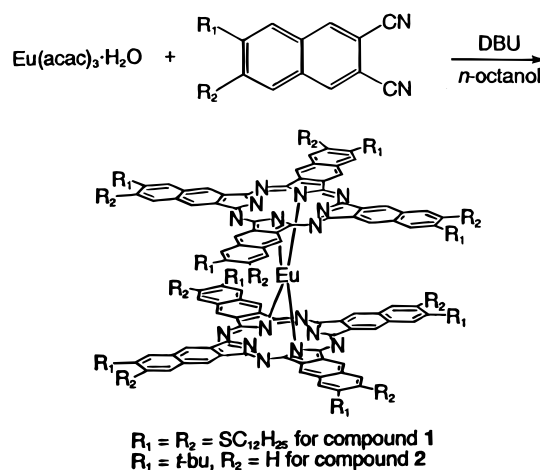
Band deconvolution of the spectral data was carried out using the program SIMPFIT⁴² developed by Stillman's group.

Cyclic voltammetry data were collected with a Hokuto Denko HA-501 potentiostat connected to a Graphtec WX 1200 XY recorder. Differential pulse voltammetry (DPV) data were recorded with a Yanaco P-1100 polarographic analyzer connected to a Watanabe WX 4401 XY recorder. Electrochemical experiments were performed under purified nitrogen gas. A glassy carbon working (area = 0.07 cm^2) and a Pt wire counter electrodes were employed. The reference electrode was Ag/AgCl corrected for junction potentials by being referenced internally to the Fc^+/Fc couple. In the solution used, i.e., in DCB containing 0.1 M TBAP, the Fc^+/Fc couple was observed at approximately 0.525 \pm 0.020 V vs Ag/AgCl.

Synthesis. (A) Bis(octakis(dodecylthio)-2,3-naphthalocyaninato)europium(III) {Eu[2,3-Nc(SC₁₂H₂₅)₈]₂, 1}. The synthesis of Eu[2,3-Nc(SC₁₂H₂₅)₈]₂ was achieved by a procedure similar to that employed for the preparation of substituted (naphthalocyaninato)lanthanide analogues Ln(Pc*)₂.¹⁹ A mixture of Eu(acac)₃·H₂O (45 mg, 0.1 mmol), 6,7-bis(dodecylthio)-2,3-dicyanonaphthalene (260 mg, 0.4 mmol), and DBU (80 mg, 0.52 mmol) in *n*-octanol (2 mL) was refluxed under nitrogen for 18 h. The resulting solution was cooled to room temperature, and then *n*-octanol was removed in vacuo. The residue was chromatographed over a silica gel column (Merck 70–230 mesh) with CHCl_3 as eluent, giving a brown-green fraction containing Eu[2,3-Nc(SC₁₂H₂₅)₈]₂ after a golden yellow unknown fraction. Repeated chromatographic purification by gel-permeation chromatography using Bio-Beads SX-1 (Bio-rad) and recrystallization from a mixture of CHCl_3 and CH_3OH afforded black liquid-crystalline solid of the double-decker. Yield: 189 mg, 79%. Anal. Calcd for C₂₈₈H₄₃₂N₁₆S₁₆Eu: C, 72.31; H, 9.10; N, 4.68. Found: C, 72.49; H, 8.92; N, 4.71. MS (*m/z*; dithranol): 4781 ($\text{M}^+ + \text{H}$). IR (KBr, cm^{-1}): 2924, 2852, 1710, 1583, 1528, 1455, 1436, 1412, 1378, 1321, 1262, 1169, 1097, 1031, 978, 900, 862, 802, 751, 722, 464.

(B) Bis(tetra-*tert*-butyl-2,3-naphthalocyaninato)europium(III) {Eu[2,3-Nc(*t*-Bu)₄]₂, 2}. A mixture of Eu(acac)₃·H₂O (0.10 mmol), DBU (40 mg, 0.26 mmol), and 6-(*tert*-butyl)naphthalonitrile (93 mg, 0.4 mmol) was refluxed in *n*-octanol (2 mL) under a slow stream of argon or nitrogen for a period longer than 18 h. The brown-black mixture was cooled to room temperature, and the volatiles were removed under reduced pressure. Then the residue was applied to a silica gel column. A golden-yellow fraction containing unknown composition was eluted with a mixture of CH_2Cl_2 /hexane (2:3 v/v). The target double-decker, Eu[2,3-Nc(*t*-Bu)₄]₂, was then developed as a black-blue band by using CHCl_3 as eluent. Furthermore, this double-decker was purified using Bio-beads SX-1 (Bio-rad) and CHCl_3 . After recrystallization from CHCl_3 – CH_3OH , pure double-decker, Eu[2,3-Nc(*t*-Bu)₄]₂, was obtained in ca. 82% yield. Anal. Calcd for C₁₂₈H₁₁₂N₁₆Eu: C, 75.87; H, 5.57; N, 11.06. Found: C, 75.43; H, 5.92; N, 10.23. MS (*m/z*; α -cyano-4-hydroxycinnamic acid): 2026 (M^+). ^1H NMR (400 MHz, DMSO-*d*₆ + hydrazine monohydrate): 11.02 (m), 9.45 (m), 8.58 (m), 7.16 (m), 2.09 (m), 1.75–0.5 (m). IR (KBr, cm^{-1}): 2958, 2924, 2854, 1615, 1461, 1417, 1392, 1365, 1324, 1258, 1206, 1174, 1154, 1099, 1022, 946, 906, 872, 811, 749, 715, 472.

Scheme 1



Results and Discussion

Synthesis. Lutetium(III) bis(naphthalocyaninato) complex, Lu(2,3-Nc)₂, is the only example of the sandwich double-decker (naphthalocyaninato)lanthanide complexes which has been fully characterized by spectroscopic methods.³⁰ It has usually been prepared by condensation of dilithium naphthalocyaninate, Li₂(2,3-Nc), with lutetium acetate in high boiling point solvents, such as quinoline or 1-chloronaphthalene.³⁰ In attempts to synthesize the substituted analogues, Ln(2,3-Nc*)₂, we tried to prepare the dilithium salt of octakis(dodecylthio)naphthalocyanine by treating 6,7-bis(dodecylthio)-2,3-dicyanonaphthalene in a refluxing mixture of methanol and pentanol. The electronic absorption spectrum of the resulting brown solution showed the characteristic band of metal naphthalocyaninate, but the isolation of the corresponding dilithium salt from a large amount of impurities could not be achieved by the procedure of L'Her,^{30,31} probably due to its increased instability and solubility in hexane by introduction of long side chains onto the naphthalene ring. The dilithium salt generated in situ after evaporating the solvent was then treated with Eu(acac)₃·H₂O in refluxing 1,2,4-trichlorobenzene (TCB), *n*-octanol, or 1-chloronaphthalene. These reactions gave a significant amount of the metal free naphthalocyanine H₂[2,3-Nc(SC₁₂H₂₅)₈] with no indication of the double-decker complex.

The substituted bis(naphthalocyaninato)europium(III) complexes, Eu[2,3-Nc(SC₁₂H₂₅)₈]₂ and Eu[2,3-Nc(*t*-Bu)₄]₂, can however be readily prepared in relatively high yield by treating the corresponding naphthalonitrile with Eu(acac)₃·H₂O and DBU in a high boiling point alcohol, *n*-octanol (Scheme 1). The UV-vis spectrum of the reaction mixture showed two bands at ca. 719 and 763 nm for Eu[2,3-Nc(*t*-Bu)₄]₂, in the Q absorption region of naphthalocyanine, of which the former peak decreased in intensity and blue-shifted to 679 nm and the latter peak gained intensity during further purification and exposure to air. For the dodecylthio-substituted naphthalocyaninato double-decker, the electronic absorption spectra were complicated, and this will be discussed in detail below. The target double-decker compound could easily be separated from the reaction mixture by column chromatography and gel-permeation chromatography. It is worth pointing out that the lower boiling point amyl alcohol failed to give the double-decker naphthalocyaninato complex. It seems that the reaction temperature is one of most critical parameters in determining the formation of the double-decker complexes.

Satisfactory elemental analysis results could not be achieved

until passing through gel-permeation chromatography columns for these substituted mixed double-decker complexes.

NMR and Mass Spectroscopy. The mass spectra of these two compounds were measured by MALDI-TOF technique using first α -cyano-4-hydroxycinnamic acid as a matrix. Figure S1 (see Supporting Information) shows the molecular ion region of the two complexes. For complex **2**, the molecular ion peak was observed at $m/z = 2026$ and the isotopic distribution can be clearly resolved. However, for complex **1**, the molecular ion peak was not obtained using the same matrix. For this reason, the matrix was changed to dithranol and the laser power was increased than that for **2**. Though the spectra were not so clear as for **2**, a cluster of peaks appeared between 4780 and 4786 including the desired $m/z = 4780$, indicating that **1** was obtained.

The bis(phthalocyaninato)lanthanide(III) and bis(naphthalocyaninato)lutetium(III) are usually NMR silent due to the paramagnetism derived from the unpaired electron delocalized over both of the macrocyclic rings. This problem has been overcome by L'Her et al.³⁰ by reducing the paramagnetic neutral double-deckers into the diamagnetic monoanionic species with hydrazine hydrate. By addition of hydrazine hydrate into a DMSO- d_6 solution of complex **2**, its ^1H NMR spectrum was obtained. The existence of isomers made the characterization of each peak difficult, but the integral ratio of alkyl protons to aromatic protons was theoretically 9 to 5. On the other hand, the spectrum of **1** could not be measured because we could not find any solvent which dissolves both **1** and hydrazine hydrate to the extent needed for NMR measurements.

Electrochemistry. L'Her et al.^{30,31} reported on the redox properties of the bis(naphthalocyanine) complexes (2,3- Nc^{2-})- Lu^{III} (2,3- Nc^-) and (1,2- Nc^{2-})- Lu^{III} (1,2- Nc^-) and of the lutetium complexes containing both naphthalocyanine and phthalocyanine moieties. The redox properties of the triple-decker complexes, $\text{Lu}^{\text{III}}_2(1,2\text{-Nc}^{2-})_3$, have also been reported.^{31,43} The redox processes in **1** and **2** were studied by cyclic voltammetry and differential pulse voltammetry in dichlorobenzene (DCB) containing tetrabutylammonium perchlorate (TBAP), Figure 1. The redox potential values are listed in Table 1. The cyclic voltammograms of **1** and **2** are similar to those of the (Nc^{2-}) Lu^{III} (Nc^-) complex^{30,31} and are typical of (Pc^{2-}) Ln^{III} (Pc^-)⁴⁴ complexes, except for two redox couples (II_O and III_O) of alkylthio-substituted **1**. Redox couples are observed at -0.28 V (I_O) and -0.61 V (I_R) for **2**, Figure 1a, and at -0.25 V (I_O) and -0.62 V (I_R) for **1**, Figure 1b. The similarity in the redox behavior of the sandwich complexes is useful for their characterization. For both **1** and **2**, I_O and I_R showed reversible to quasi-reversible behavior: $i_a/i_c = 1$; i proportional to $\nu^{1/2}$ (for scan rates ranging from 20 to 200 mV/s). For **2**, the anodic to cathodic peak separation (ΔE) was 80 mV for both I_O and I_R , and for **1**, ΔE was 90 mV for I_O and 80 mV for I_R . In comparison with the analogous bis(naphthalocyaninato)lutetium complexes,^{30,31} I_O corresponds to the (Nc^-) Eu^{III} (Nc^-)/(Nc^{2-})- Eu^{III} (Nc^-) couple and I_R to (Nc^-) Eu^{III} (Nc^{2-})/(Nc^{2-}) Eu^{III} (Nc^{2-}).

An important parameter in the electrochemistry of bis(phthalocyanine) and bis(naphthalocyanine) complexes is the difference between the first oxidation and the first reduction potentials (ΔE°). This value gives information on the disproportionation and hence the conductivity of the complexes. Table 1 lists ΔE° values for **1** and **2** to be 0.37 and 0.33 V, respectively. The ΔE° value for lutetium bis(naphthalocyanine)

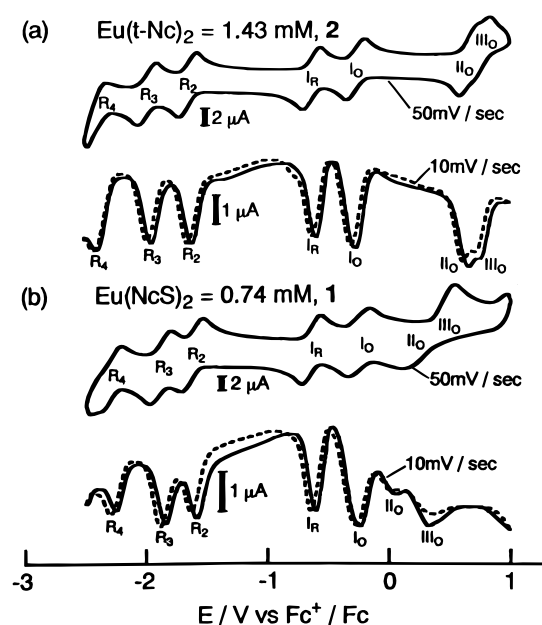


Figure 1. Cyclic (CV) and differential pulse (DPV) voltammograms of (a) $\text{Eu}[2,3\text{-Nc}(t\text{-Bu})_4]_2$ and (b) $\text{Eu}[2,3\text{-Nc}(\text{SC}_{12}\text{H}_{25})_8]_2$ in dichlorobenzene containing 0.1 M TBAP. In the differential pulse studies, the solid and dotted lines indicate anodic and cathodic scans, respectively. Numbers indicate the scan rates in mV s^{-1} . See text for the description of the couples: I_O , II_O , and I_R . [$\text{Eu}[2,3\text{-Nc}(t\text{-Bu})_4]_2$] = 1.43 mM, and [$\text{Eu}[2,3\text{-Nc}(\text{SC}_{12}\text{H}_{25})_8]_2$] = 0.74 mM.

complexes ranged from 0.29 to 0.33 V³¹ and was 0.41 V for lutetium bis(phthalocyanine).³⁰ The ΔE° value for substituted bis(phthalocyaninato)europium(III) was near 0.4 and showed very little variation with the length of the alkyl chain.^{26b} The ΔE° values for both **1** and **2** are thus in the range reported for similar complexes. It is however surprising that ΔE° for **1** is larger than that for **2**, although thiol-substituted naphthalocyanines are expected to show good conductivity.⁴⁵

The second oxidation of **2** showed behavior similar to that reported before for lutetium bis(naphthalocyanine).³¹ Overlapping redox couples (II_O and III_O) were observed near 0.65 and 0.74 V vs Fc^+/Fc . For **1**, the second and third oxidations were irreversible with two current peaks at 0.03 and 0.34 V (judged from the DPV curve). In the cyclic voltammogram of **1**, an oxidation peak whose current may correspond to a two-electron process appeared at ca. 0.5 V, but its rereduction peak was observed at ca. 0.2 V. The separation of these peaks became larger at higher scan rate, indicating that the electron-transfer rate in these processes is low.

Up to four ring-based one-electron reductions have been observed in bis(naphthalocyanine) complexes.³¹ We observed three more reduction couples, R_2 , R_3 , and R_4 , at -1.60 , -1.86 , and -2.27 V for **1** and -1.64 , -1.97 , and -2.42 V for **2**, respectively, assigned to (Nc^{2-}) Eu^{III} (Nc^{2-})/(Nc^{2-}) Eu^{III} (Nc^{3-}), (Nc^{2-}) Eu^{III} (Nc^{3-})/(Nc^{3-}) Eu^{III} (Nc^{3-}) and (Nc^{3-}) Eu^{III} (Nc^{3-})/(Nc^{3-}) Eu^{III} (Nc^{4-}). Furthermore, as can be judged from the values in Table 1, the potential differences among reductions or oxidations are slightly smaller for **1** than for **2**, implying qualitatively that the energy levels of molecular orbitals (MOs) are more condensed for the former. Thus, though the ΔE° value alone of **1** is larger than that of **2**, the energy separation of MOs appears to be generally smaller for **1**.

IR Spectra. The IR spectra of the sandwich phthalocyanine complexes are characteristic and may be used in differentiating between the neutral ($\text{Pc}^- \text{Ln}^{\text{III}} \text{Pc}^{2-}$) and the reduced ($\text{Pc}^{2-} \text{Ln}^{\text{III}} \text{Pc}^{2-}$) species. However, the IR data for bis(naphthalocyaninato)lan-

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Table 1. Electrochemical Data for Eu[2,3-Nc(*t*-Bu)₄]₂ and Eu[2,3-Nc(SC₁₂H₂₅)₈]₂ in Dichlorobenzene Containing 0.1 M TBAP

couple	$E_{1/2}/V$ (vs Fc ⁺ /Fc)		assgnts
	Eu[2,3-Nc(<i>t</i> -Bu) ₄] ₂ , 2	Eu[2,3-Nc(SC ₁₂ H ₂₅) ₈] ₂ , 1	
III _O	0.74	0.34	
II _O	0.65	0.03	
I _O	-0.28	-0.25	(Nc ⁻)Eu ^{III} (Nc ⁻)/(Nc ⁻)Eu ^{III} (Nc ²⁻)
I _R	-0.61	-0.62	(Nc ²⁻)Eu ^{III} (Nc ²⁻)/(Nc ²⁻)Eu ^{III} (Nc ⁻)
R ₂	-1.64	-1.60	(Nc ²⁻)Eu ^{III} (Nc ²⁻)/(Nc ²⁻)Eu ^{III} (Nc ³⁻)
R ₃	-1.97	-1.86	(Nc ²⁻)Eu ^{III} (Nc ³⁻)/(Nc ³⁻)Eu ^{III} (Nc ³⁻)
R ₄	-2.42	-2.27	(Nc ³⁻)Eu ^{III} (Nc ³⁻)/(Nc ³⁻)Eu ^{III} (Nc ⁴⁻)
ΔE^a	0.33	0.37	

^a ΔE between the first oxidation and reduction potentials.

thanides are still scarce; only those of Lu(2,3-Nc)₂ and Lu(2,3-Nc)(Pc) are mentioned by L'Her.³⁰ In analogy with the IR spectra of Lu(2,3-Nc)₂ and Ln(Pc)₂,^{21,26e} the strong absorbance for both these Eu compounds at around 1320 cm⁻¹ is attributed to the marker IR band for naphthalocyanine monoanion radical, Nc⁻. The weak band at about 750 cm⁻¹ is assigned to the -CH vibration of the naphthalene. A strong band derived from the naphthalocyanine isoindole stretch appears at about 1461 cm⁻¹. In the substituted double-decker, three peaks ranging from medium to strong appear in the region from 2852 to 2954 cm⁻¹ due to the C-H stretching vibrations of CH₂ and/or CH₃ groups in naphthalocyanine side chains.

UV-Visible and MCD Spectroscopy. The absorption spectra of naphthalocyanines are shifted to longer wavelengths when compared to those of the phthalocyanines, due to the extension of the conjugated system.^{46,47} The UV-visible and MCD spectra of **1** and **2** are shown in Figure 2. Complex **2** showed a similar electronic absorption spectrum to its lutetium analogue, Lu(2,3-Nc)₂, rather than Lu(1,2-Nc)₂. An intense Q-band is observed in CCl₄ at 763 nm, and the Soret band at 332 nm. Also shown in Figure 2 are the near-IR spectra of complexes **1** and **2**. The low-energy bands, observed for **1** at 1881, 1669, and 1069 nm and at 1849, 1636, and 1060 for **2**, are typical⁴⁸ of the Pc⁻Ln^{III}Pc²⁻ complexes. The near-IR bands have been assigned to charge-transfer from the Pc²⁻ to the cation radical moiety, Pc⁻.^{48b,c} The absorption band near 900 nm, in particular, is often used as diagnosis for the presence of the oxidized phthalocyanine ring in bis(phthalocyanine) complexes.^{48d} This absorption band is shifted to longer wavelengths for the bis(naphthalocyanine) complexes, as expected, and is observed at 1069 nm for **1** and 1060 nm for **2**. Absorption bands near 450 nm are also associated with transitions involving the Pc⁻ or Nc⁻ rings in sandwich complexes. This band is observed at 442 nm in **2**, though not clearly observable in **1**.

The Q-band absorption spectra of **1** are not typical of the spectra of the neutral Nc⁻Ln^{III}Nc²⁻ or Pc⁻Ln^{III}Pc²⁻. There is a significant splitting in the Q-band (peaks at 700 and 784 nm), Figure 2, which is normally associated with the reduced [Nc²⁻Lu^{III}Nc²⁻]⁻ or [Pc²⁻Ln^{III}Pc²⁻]⁻ complexes. However, the presence of the absorption band at 1069 nm and the electro-

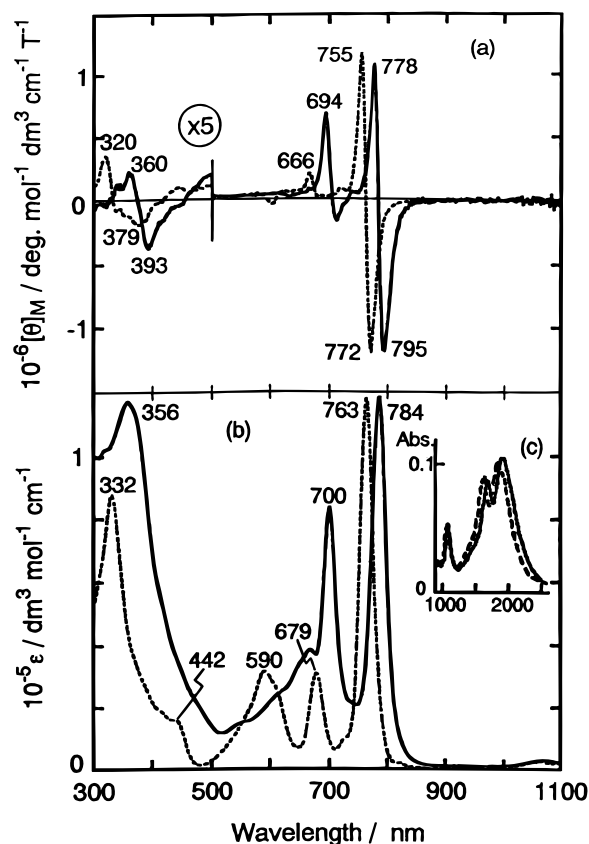


Figure 2. MCD (a), UV-visible (b), and near-IR (c) absorption spectra of Eu[2,3-Nc(*t*-Bu)₄]₂ (broken lines) and Eu[2,3-Nc(SC₁₂H₂₅)₈]₂ (solid lines) in CCl₄.

chemical studies discussed above confirm the presence of the oxidized Nc⁻ ring. The shape of the Q-band is different from the Q-band spectra observed in instances of aggregation in soluble metallophthalocyanines.^{39,49} A split in the Q-band was also observed for alkylthio-substituted monomeric metallophthalocyanines⁵⁰ and was attributed to intermolecular interactions involving the alkylthio groups. This kind of intermolecular interaction may also explain the splitting in the Q-band observed for **1** but not **2**. The absorption spectra of **1** are shifted to longer wavelengths when compared to those of **2**, due to the introduction of electron-donating dodecylthio groups onto the Nc ring. This results in the elevation of HOMO as well as other occupied molecular orbitals, resulting in decreased energy necessary for the transfer of an electron from HOMO or other occupied molecular orbitals to the LUMO or higher energy unoccupied

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molecular orbitals of the double-decker. The intramolecular ring-to-ring charge-transfer absorption bands in the near-IR region are also red shifted for **1** compared to **2**. There generally is a bathochromic shift in the Q-band on ring substitution of phthalocyanines with alkyl groups,^{34,51} and alkylthio substitution shifts the Q-band to even longer wavelengths.^{50,52,53} These are consistent with the discussion in Electrochemistry.

The MCD spectrum of **2** is remarkably similar to those of MgPc and other MPc complexes with D_{4h} symmetry,⁵⁴ with an intense Faraday A term in the Q-band region and a weaker A term in the Soret region. The MCD spectrum of **1** was different from those of the symmetrical metallophthalocyanines in that there is splitting of the absorption bands in the Q-band region. It is also different from that of H₂Pc in that the MCD spectrum clearly shows the presence of A terms. A symmetrical and relatively intense A term is observed for **1** at 784 nm. Another weaker and unsymmetrical A term is observed corresponding to the second component of the Q-band at 700 nm. At least one A term is evident in the Soret region MCD spectrum of **1**. The Soret region may, however, be complicated by the fact that the second HOMO is naphthalene-centered in naphthalocyanine complexes.^{47a}

Figures S2 (see Supporting Information) and 3 show the results of chemical reduction and oxidation, respectively, of **1** and **2**. Chemical reduction was carried out in DMF (for **2**) and a mixture of DMF and dichlorobenzene (for **1**) using hydrazine. Chemical oxidation was carried out in CCl₄ using nitrosium tetrafluoroborate. For both complexes, reduction (Figure S2) occurred isospectically and in two steps, resulting in spectral changes that are associated³¹ with the reduction of Nc⁻Eu^{III}Nc²⁻ to [Nc²⁻Eu^{III}Nc²⁻]⁻, Figure S2a, and the subsequent reduction of [Nc²⁻Eu^{III}Nc²⁻]⁻ to [Nc²⁻Eu^{III}Nc³⁻]²⁻, Figure S2b. The second stage reduction for **2** however occurred very slowly and did not go to completion. Hence, in Figure S2a, we show the first stage reduction for **2**, and Figure S2b shows the second stage reduction of **1** which gave a complete transformation. The reductions were reversible in that the chemical reoxidation after either the first or the second reduction step fully regenerated the starting material as judged by the UV–visible spectral changes. For both complexes, the first stage of oxidation gave spectral changes characteristic^{30,31} of the formation of the [Nc⁻Eu^{III}Nc⁻]⁺ species, Figure 3ai,bi. For **2**, the final spectra following the second oxidation step were similar to the reported³⁰ spectra for [Nc⁰Lu^{III}Nc⁻]²⁺, Figure 3aii. The spectral changes for the second oxidation step of **1** were quite different from those observed for **2**. The spectral changes showed diffuse isosbestic points suggesting probably a coupled chemical reaction or aggregation, Figure 3bii. The new spectra formed could not be identified with any of the reported oxidation forms of the bis(naphthalocyanine) or bis(phthalocyanine) complexes. Also, it is unlikely that the spectral changes are due to oxidation based on the naphthalene unit, since the changes were not observed for **2**. Spectral changes similar to those shown in Figure 3bii were also observed on chemical oxidation of the monomeric Eu^{III}[2,3-Nc(SC₆H₁₃)₈](acac) complex,⁵⁵ showing that the second oxidation is most likely ascribed to the Nc ligand containing thioether groups. In connection with this, Ellis et al. reported on the analysis of an n–π* transition band seen

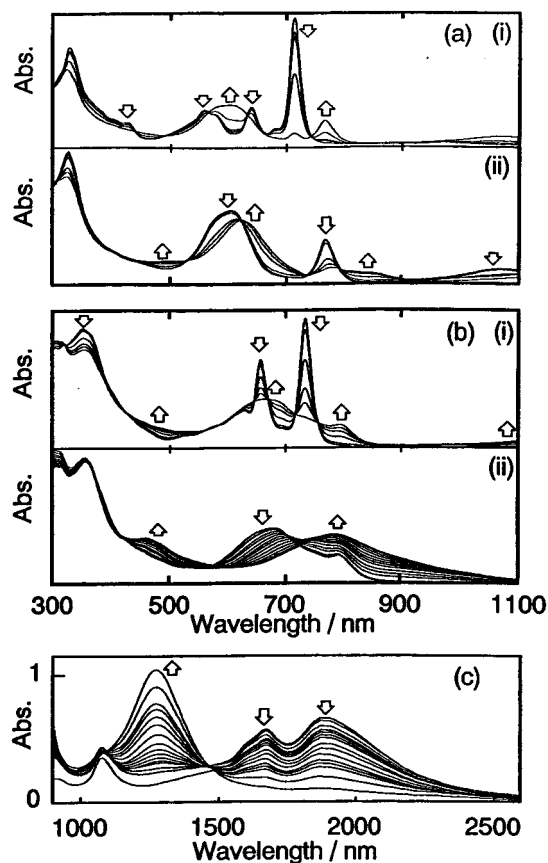


Figure 3. Absorption spectral changes observed during oxidation (using nitrosium tetrafluoroborate) of (a) Eu[2,3-Nc(*t*-Bu)₄]₂ and (b) Eu[2,3-Nc(SC₁₂H₂₅)₈]₂ in CCl₄, (i) the first oxidation step and (ii) the second oxidation step, and (c) the changes observed in the near-IR region during oxidation of Eu[2,3-Nc(SC₁₂H₂₅)₈]₂ in CCl₄.

commonly to the red of the Soret band of thioether- or ether-substituted tetraazaporphyrins (TAPs) and Pcs.⁵⁶ They concluded that this band is a charge-transfer band from S or O to the π system of the Pc or TAP core. Thus, in the second oxidation of compound **1** also, the nonbonding electrons of S are considered to be somehow participating, particularly since this n–π* band lies between the Q and Soret bands which can be explained by two HOMOs and LUMOs (four orbitals).

Spectral changes following chemical oxidation in the near-IR region are shown in Figure 3c for complex **1**. The absorption bands at 1881 and 1669 nm decrease in intensity, and a new band is formed at 1268 nm. There is not much change in the absorption band at 1069 nm, implying that this band is a feature of all ring-based oxidations in bis(naphthalocyanine) complexes. The MCD spectra of the bands in this region would indeed be useful.

EPR Spectra. The EPR spectra of **1** and **2** in toluene at 20 K are shown in Figure S3 (see Supporting Information). The EPR spectrum of **1** shows a small inflection, but that of **2** shows clear splitting (ca. 62–64 G). Temperature-dependent inflections have been observed in the EPR spectra of Ln(OEP)₂ (OEP, octaethylporphyrin).⁵⁷ The EPR spectra of both **1** and **2** are relatively broad with peak-to-peak distances of 82 G for **1** and

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Table 2. Band-Fitting Parameters for Eu[2,3-Nc(SC₁₂H₂₅)₈]₂ in CCl₄^a

	type	ν/cm^{-1}	ν/nm	E	Γ/cm^{-1}	D_0	$\langle\epsilon\rangle_0$	$\langle\epsilon_M\rangle_n$	A_1 or B_0	$B_0(A_1)/D_0$
1	B	11 833	845	2 408	1380	0.92	299.0	-1242.8	-8.1	-8.80
2	B	12 629	792	26 811	678	4.69	1536.4	-28240	-185.2	-39.49
3	A	12 755	784	85 014	359	7.80	2547.1	7418207	48644.2	6236.4
4	B	12 948	772	38 423	487	4.71	1538.3	1692.3	11.1	2.36
5	B	13 552	738	23 011	599	3.32	1083.1	3093.2	20.3	6.11
6	B	13 999	714	25 675	409	2.44	797.9	-2433.2	-16.0	-6.56
7	A	14 305	699	83 592	396	7.54	2462.9	2630034	17246.2	2287.3
8	B	14 554	687	15 522	343	1.19	389.1	-624.5	-4.1	-3.45
9	B	14 864	673	30 934	615	4.17	1363.6	3380.5	22.2	5.32
10	B	15 375	650	29 726	804	5.07	1654.8	1588.5	10.4	2.05
11	B	16 012	625	13 932	924	2.62	855.7	660.4	4.3	1.64
12	B	16 500	606	15 651	1189	3.68	1200.8	2731.8	17.9	4.86
13	B	17 275	579	12 512	1241	2.93	956.7	1705.1	11.2	3.82
14	B	18 245	548	12 925	1260	2.91	950.8	1907.9	12.5	4.30
15	B	19 590	510	13 130	1644	3.59	1173.1	2847.6	18.7	5.21

^a ν , calculated band center energy in cm^{-1} ; E , extinction coefficient of the band center in $\text{cm}^{-1} \text{mol}^{-1} \text{L}$; Γ , bandwidth in cm^{-1} ; D_0 , dipole strength in Debye (D) units: $D_0 = \langle\epsilon\rangle_0/326.6$; $\langle\epsilon\rangle_0$, the zeroth moment of the absorption band intensity. $\langle\epsilon_M\rangle_n$: zeroth moment for B terms ($n = 0$); first moment for A terms ($n = 1$); A_1 and B_0 , Faraday terms, $A_1 = \langle\epsilon_M\rangle_1/152.5$ and $B_0 = \langle\epsilon_M\rangle_0/152.5$.

129 G for **2**. The increase in the EPR line width with decrease in temperature in $[\text{Pc}^{2-}\text{Ln}^{\text{III}}\text{Pc}^{2-}]^-$ was attributed to intercluster interactions between unpaired electrons on adjacent molecules.⁵⁸

Values of g were near 2.0 and hence were near the organic radical value for both complexes, with $g = 2.02(1)$ and $2.09(2)$ for complexes **1** and **2**, respectively. Because of the strong coupling of the naphthalocyanine radical electron with the lanthanide f electrons, deviations of g from the free electron value were said to be significant in lanthanide bis(phthalocyanine) complexes.⁵⁸ Eu^{III} has both electronic and nuclear contributions to the EPR spectra, and some fine structure from Eu^{III} ion was observed in the EPR spectra of Eu^{III}(OEP)₂.⁵⁹ The EPR spectra of both **1** and **2** do not show the fine structure expected for Eu^{III}. The g value for **2** is larger than for **1**, reflecting the differences in the ligand field effects of the alkylthio and tertiary butyl substituents.

Band Deconvolution. The program SIMPFIT⁴² has been used extensively for band assignments of neutral, oxidized, and reduced metal phthalocyanines and porphyrins.^{37–39,54,57b,60} The program uses least-squares and Simplex iteration routines and it also uses MCD data in conjunction with the absorption spectral data to obtain the best fit. Thus the MCD and absorption fits use the same number of bands and similar bandwidths. We fitted only the MCD and absorption spectra in the Q-band region since the Soret region is expected to be complicated by absorptions centered on the naphthalene unit. Table 2 summarizes the fitting parameters for complex **1** (those of complex **2** were not included in this table, since the isomers in complex **2** may lower the quality of the fitting). The bandwidths given in Table 2 are from the absorption spectral fits. Compared with the spectral fits normally obtained in the Q-band region of phthalocyanine complexes, the fits observed in Figure 4 appear very complicated. The deconvolution calculations required 15 bands to obtain satisfactory fits for both MCD and absorption spectra. A reasonable fit could only be obtained by fitting two A terms at 12 755 (784 nm) and 14 305 cm^{-1} (699 nm). As can be judged from the residuals, the fit around ca. 700 nm is better than that around 784 nm. Attempts to use two oppositely signed B terms for the bands at either 12 755 or 14 305 cm^{-1} gave unacceptable fits. There is generally a progressive broadening of bands with increase in energy in accordance with the observations of Hochstrasser and Marzocco⁶¹ and Mack and Stillman.⁶⁰ The

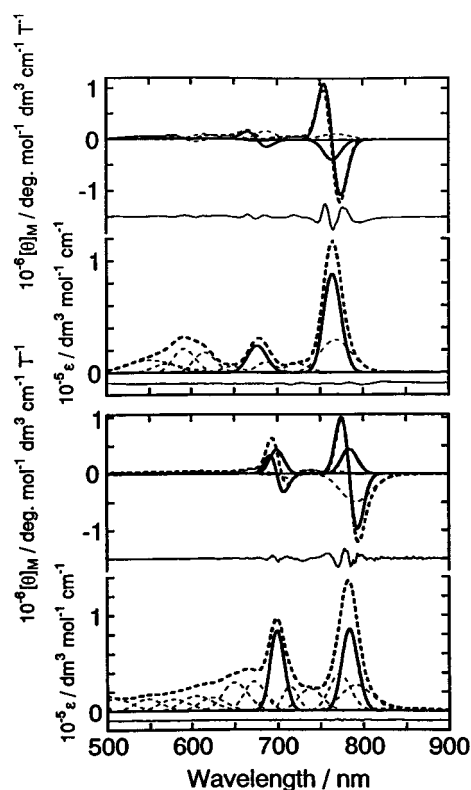


Figure 4. Deconvolution analysis of the Q-band region of Eu[2,3-Nc(*t*-Bu)₄]₂ (top) and Eu[2,3-Nc(SC₁₂H₂₅)₈]₂ (bottom). Bold dotted lines are simulation data, and thinner solid lines represent the residuals. Two bold solid lines in each absorption spectrum indicate the degenerate transitions. Experimental data overlap almost completely with the simulation data and, therefore, are omitted for clarity.

spectral fits for **1** showed more B terms, of higher relative intensity, in the vicinity of the Q-bands when compared to other MPc complexes. Generally MPc complexes with charge-transfer bands lying near the Q-band show Faraday B terms of large intensity in the Q-band region. It is thus likely that the Faraday B terms observed in the Q-band region following spectral deconvolution of **1** are a result of charge-transfer transitions.

Molecular orbital calculations have been performed by several researchers on Lu(Pc)₂.^{49b,62,63} According to Ishikawa,^{49b} a single

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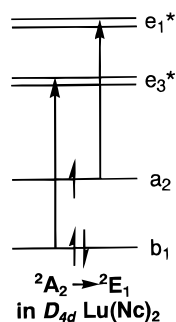


Figure 5. Molecular orbital diagram of $\text{Lu}(\text{Nc})_2$, assuming D_{4d} symmetry. Solid arrows show x/y -polarized transitions from the 2A_2 ground state to the 2E_1 excited state.

A term is observed in the Q-band MCD spectra of $\text{Lu}(\text{Pc})_2$ and $\text{Lu}(\text{Nc})_2$ in solution and there was no evidence for overlapping transitions in this region. On the other hand, Orti et al.⁶³ predicted four excitations in the Q-band region of the $\text{Lu}(\text{Pc})_2$ complex, which were degenerate, giving two transitions at 13 793 (725 nm) and 16 293 cm^{-1} (614 nm). From matrix isolated data and band deconvolution, VanCott et al.⁶² obtained three A terms in the Q-band region, at close proximity to each other at 15 564, 15 612, and 15 525 cm^{-1} . These bands were assigned to ${}^2A_2 \rightarrow {}^2E_1$ transitions arising from the HOMO-1(b_1)→LUMO(e_3) and HOMO(a_2)→LUMO+1(e_1) transitions in D_{4d} symmetry (Figure 5). VanCott et al. suggested that their matrix isolated data were due to two excitations with the third being due to spin pairing effects, thus being in agreement with Orti et al.⁶³ The assignments of the absorption bands for $\text{Lu}(\text{Nc})_2$ are similar to those of $\text{Lu}(\text{Pc})_2$;^{49b} however, the nomenclature used by Ishikawa^{49b} differs from that used by VanCott et al.⁶² in that the ${}^2A_2 \rightarrow {}^2E_1$ transition was assigned to the near-IR band (~900 nm) by the former and to the Q-band envelope of transitions by the latter.

Band deconvolution calculations for **1** gave two A terms in the Q-band region in support of the observation of at least two A terms from matrix isolated data for $\text{Lu}(\text{Pc})_2$.⁶² Orti et al. predicted transitions in the Q-band region at 725 and 614 nm.⁶³ Band deconvolution calculations for **1** give the two A terms at 784 and 699 nm. As discussed above, the shift to longer wavelengths is expected both from the extension of the phthalocyanine to the naphthalocyanine ring and by the presence of alkylthio ring substituents. The observation of a split in the Q-band for complex **1** and not for $\text{Lu}(\text{Nc})_2$ in solution^{49b} is a consequence of the enhancement of the splitting of the Q-band by alkylthio substituents. Using the nomenclature of VanCott et al.,⁶² we assign the A terms for complex **1** to ${}^2A_2 \rightarrow {}^2E_1$ transitions of the Q_{00} band.

In conclusion, we have characterized substituted bis(naphthalocyaninato)europium(III) complexes using UV–visible, MCD, EPR, and mass spectra and using electrochemistry. We have shown in this work that substitution of the naphthalocya-

nine ring with *tert*-butyl groups gives MCD and UV–visible spectra that are similar to that of the bis(naphthalocyaninato)lutetium complex, though shifted to longer wavelengths. Substitution with alkylthio groups results in considerable splitting of the Q-band which may be attributed to intermolecular interactions involving the alkylthio substituents. Band deconvolution of MCD and absorption spectra of $\text{Eu}[2,3\text{-Nc}(\text{SC}_{12}\text{H}_{25})_8]_2$ gave evidence of the presence of two A terms in the Q-band region which are assigned to the ${}^2A_2 \rightarrow {}^2E_1$ transitions resulting from the splitting of the Q_{00} band. The EPR spectra confirmed the presence of an unpaired electron in both $\text{Eu}[2,3\text{-Nc}(\text{SC}_{12}\text{H}_{25})_8]_2$ and $\text{Eu}[2,3\text{-Nc}(t\text{-Bu})_4]_2$. However, the g value is clearly affected by the naphthalocyanine ring substituents, with the *tert*-butyl-substituted complex giving larger g value and larger peak to peak distance. Cyclic and differential pulse voltammetry of the *tert*-butyl- and alkylthio-substituted bis(naphthalocyaninato)europium(III) are similar, although the potential differences in reduction or oxidation processes in the latter are slightly smaller than those in the former. Chemical reduction of both complexes ($\text{Eu}[2,3\text{-Nc}(\text{SC}_{12}\text{H}_{25})_8]_2$ and $\text{Eu}[2,3\text{-Nc}(t\text{-Bu})_4]_2$) resulted in spectral changes typical of consecutive one-electron reduction of the ring and formed $[(\text{Nc}^{2-})\text{Eu}^{\text{III}}(\text{Nc}^{2-})]^-$, $[(\text{Nc}^{2-})\text{Eu}^{\text{III}}(\text{Nc}^{3-})]^{2-}$, and $[(\text{Nc}^{3-})\text{Eu}^{\text{III}}(\text{Nc}^{3-})]^{3-}$. Voltammetry revealed a complicated redox behavior for the second oxidation of $\text{Eu}[2,3\text{-Nc}(\text{SC}_{12}\text{H}_{25})_8]_2$, with an irreversible oxidation being observed on the cyclic voltammetry time scale. Chemical oxidation of $\text{Eu}[2,3\text{-Nc}(t\text{-Bu})_4]_2$ gave spectral changes associated with the consecutive formation of $[(\text{Nc}^-)\text{Eu}^{\text{III}}(\text{Nc}^-)]^+$, $[(\text{Nc}^-)\text{Eu}^{\text{III}}(\text{Nc}^0)]^{2+}$, and $[(\text{Nc}^0)\text{Eu}^{\text{III}}(\text{Nc}^0)]^{3+}$. For $\text{Eu}[2,3\text{-Nc}(\text{SC}_{12}\text{H}_{25})_8]_2$, only the first stage chemical oxidation gave spectral changes that are typical of naphthalocyanine based processes with the formation of $[(\text{Nc}^-)\text{Eu}^{\text{III}}(\text{Nc}^-)]^+$. Judging from the similarity of redox potentials to those of $\text{Eu}[2,3\text{-Nc}(t\text{-Bu})_4]_2$ (Table 1), subsequent oxidations may also be Nc ring-centered, although the reason for irreversibility is unknown.

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Supporting Information Available: Figures S1–S3, showing mass spectra of $\text{Eu}[2,3\text{-Nc}(\text{SC}_{12}\text{H}_{25})_8]_2$, **1**, and $\text{Eu}[2,3\text{-Nc}(t\text{-Bu})_4]_2$, **2** with theoretical plots, absorption spectral changes observed during oxidation of compounds **1** and **2** in CCl_4 , and EPR spectra of **1** and **2** in toluene at 20 K. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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