

From the Single- to the Triple-Decker Sandwich. Effect of Stacking on the Redox and UV–Visible Spectroscopic Properties of Lutetium(III) 1,2-Naphthalocyaninate Complexes

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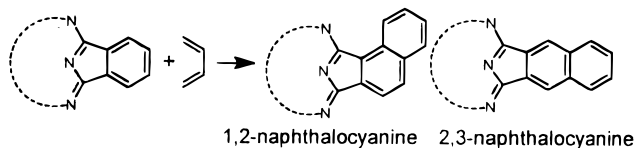
(1,2-Naphthalocyaninato)lutetium(III), bis(1,2-naphthalocyaninato)lutetium(III), and tris(1,2-naphthalocyaninato)-dilutetium(III) have been synthesized in good yields. These complexes were characterized by UV–visible, ^1H NMR, and mass spectroscopies and by electrochemical techniques. Bis(1,2-naphthalocyaninato)lutetium(III) is compared to bis(2,3-naphthalocyaninato)lutetium(III): the good correspondance between the experimental data and theoretical results obtained by others is emphasized in this work. Stacking one to three macrocyclic rings is possible in the series of the 1,2-naphthalocyanine sandwich-like complexes with lutetium(III); as shown by UV–visible spectroelectrochemistry and voltammetry, this influences greatly the π -conjugated systems, modifying spectacularly their spectroscopic and redox properties.

Introduction

In the design of molecules for applications in the field of molecular materials, one important goal is to tailor the energy level of the orbitals; the peripheral substitution of the rings is commonly used to induce modifications of the intrinsic properties of macrocycles, such as phthalocyanines, for example.¹ Research on phthalocyanine-like ligands with different conjugated π -systems led to the study of complexes of naphthalocyanines, macrocycles which have a more extended conjugation than phthalocyanine itself. From a theoretical aspect, the two naphthalocyanine rings, 2,3-Nc and 1,2-Nc, derive from the annelation of the external benzene rings of the phthalocyanine through the addition of butadiene (Scheme 1). From MO calculations for nonmetalated mono(naphthalocyanines), Brédas and co-workers have predicted very different electronic energy levels for the two structural isomers: the HOMO of 2,3-Nc would be destabilized compared to that of 1,2-Nc; consequently one should observe differences between the properties of these isomers.² These predictions have already been confirmed by the work of Hanack and co-workers on metalated mono(1,2- and 2,3-naphthalocyanines).³ Because of their unusual optical and redox properties as well as of the semiconductivity of solid phases derived from these molecules, many research groups have been interested in the lanthanide bis(phthalocyanine) family.^{1,4} However, no comparable work on the lanthanide sandwich complexes of naphthalocyanines has been reported.

The reports published on rare-earth-metal sandwich derivatives containing naphthalocyanine rings are rare; the first articles

Scheme 1. Annelation of the Isoindole Moiety of Phthalocyanine by *cis*-Butadiene



describe the unsymmetrical complex $\text{Lu}(2,3\text{-Nc})(\text{Pc})$.^{5–7} In a previous short article, the synthesis and the characterization of the symmetrical complex $\text{Lu}(2,3\text{-Nc})_2$ were described.⁷ One of the aims of the present work is the comparison of the intrinsic characteristics of 1,2-naphthalocyanine and 2,3-naphthalocyanine lutetium complexes, in order to verify if the conclusions derived from the MO calculations for nonmetalated naphthalocyanines are still valid for sandwich complexes.² Until now, no study has been published on the lutetium complex of 1,2-naphthalocyanine, $\text{Lu}(1,2\text{-Nc})_2$. This article, which details its synthesis, characterization, and electrochemical behavior, is the only report on this compound. The synthesis of $\text{Lu}(1,2\text{-Nc})_2$ allows the comparison of the sandwich complexes of the two naphthalocyanine isomers with the complex of the phthalocyanine ligand.

The conjugation can be extended in another direction than the planes of the macrocycles, perpendicularly to them, by

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stacking the rings. Since the synthesis of the complex $\text{Sn}(\text{Pc})_2$, in 1936 by Barrett et al.,⁸ much effort has been devoted stacking metal complexes of macrocyclic ligands through axial ligation and extending the length of the "wire". Extensive research has been devoted to the study of the sandwich complexes of lanthanides and related cations with porphyrins and phthalocyanines. Triple-decker sandwiches constituted by three porphyrin rings and two rare-earth-metal cations, $\text{Lu}_2(\text{Por})_3$, have been isolated and characterized,⁹ as well as porphyrin-phthalocyanine mixed complexes (1:2 and 2:1).¹⁰ However, rare are the examples of triplanar complexes of Pc rings only. Their existence was suspected^{11,12} but questionable until mass spectrometry had confirmed their formation.¹³ The synthesis and the electrochemical study of a triplanar complex with substituted phthalocyanine rings, $\text{Yb}_2(\text{obPc})_3$ (obPc = octabutoxy-substituted Pc), have been described.¹⁴ Very recently, another study was published on the unsymmetrical triple-decker complex $\text{Lu}_2(\text{Pc})_2(\text{Pc}')$, where the middle ring ($\text{Pc}' = 15\text{-crown-5-substituted Pc}$) is substituted by crown ethers.¹⁵ None of these articles fully describes the synthesis and properties. In a previous report, we briefly described the synthesis of a new triple-decker sandwich complex, $\text{Lu}_2(1,2\text{-Nc})_3$, obtained in a good yield.¹⁶ This was the first example of a triple decker with naphthalocyanine rings. This compound is of great interest because it combines two interesting characteristics: the extension of the conjugation over larger rings and also along the axis perpendicular to the planes of the three macrocyclic ligands. Consequently, the characterization of $\text{Lu}_2(1,2\text{-Nc})_3$ will be discussed. Its complete spectroelectrochemical study in solution is reported. Moreover, the comparison of $\text{Lu}(1,2\text{-Nc})(\text{OAc})$, $\text{Lu}(1,2\text{-Nc})_2$, and $\text{Lu}_2(1,2\text{-Nc})_3$ provides very valuable information on the effect of stacking on their properties. For the first time, to our knowledge, electrochemical and UV-visible spectral data have been collected for a set of compounds associating one to three identical cycles sandwiching one or two lutetium cations.

Experimental Section

(A) Materials. Phthalonitrile was a commercial product purchased from Aldrich and used after two recrystallizations in ethanol; 2,3-dicyanonaphthalene¹⁷ and 1,2-dicyanonaphthalene¹⁸ were synthesized by following published procedures.

Organic solvents were distilled before use, except 1-chloronaphthalene, which was dried over 4 Å molecular sieves and percolated through

a basic alumina column (Merck), just before use. Column chromatography was carried out on silica gel 60 (70–230 mesh) (Merck).

(B) Physical Measurements. The UV-visible spectra were recorded on an HP-8452A diode-array spectrophotometer (Hewlett-Packard). The ¹H NMR (400 MHz) spectra were obtained using a Bruker AC 400 apparatus; to improve the solubility and also reduce the compounds that are paramagnetic, hydrazine hydrate (Aldrich, 98%) was added to the deuterated solvent, $\text{DMF-}d_7$ (1% by volume). High-resolution field desorption mass spectroscopy was performed with a triple-sector VG Autospec spectrometer and electrospray instrument.

Voltammetry was carried out with a Princeton Applied Research potentiostat (Model 173) and a programmer (Model 175), on a platinum disk electrode (diameter 2 mm). The experiments were performed under purified nitrogen (O_2 and $\text{H}_2\text{O} < 5$ ppm), in an inert-atmosphere box (Jaram). A silver wire was used as a pseudoreference electrode, but all the reported potentials are referred to the ferrocene/ferrocene couple. For spectroelectrochemistry, the three-electrode cell was filled and sealed in the drybox; the thickness of the quartz cuvette was approximately 0.4 mm, the working electrode being a platinum grid. The platinum disk ultramicroelectrode (diameter 10 μm) was purchased from Tacussel. Benzotrionitrile, the solvent for the electrochemical experiments, was carefully purified as described elsewhere.¹⁹ The background electrolyte, Bu_4NPF_6 , was prepared by neutralization of tetrabutylammonium hydroxide with hexafluorophosphoric acid (Aldrich) in aqueous solution, twice recrystallized in ethanol, and dried under vacuum at 100 °C.

(C) Synthesis. 2,3-Naphthalocyanine Derivatives. $\text{Li}_2(2,3\text{-Nc})$ and $\text{Lu}(2,3\text{-Nc})_2$ were prepared according to a method described elsewhere.⁷

Lithium 1,2-Naphthalocyaninate, $\text{Li}_2(1,2\text{-Nc})$. Linstead's procedure,²⁰ slightly modified, was used for the synthesis of $\text{Li}_2(1,2\text{-Nc})$. Under N_2 , a piece of cleaned lithium metal (0.17 g, 25 mmol) is added to methanol (3 mL) and pentanol (17 mL) in a round-bottom flask. The mixture is stirred under nitrogen until lithium metal disappears. 1,2-Dicyanonaphthalene (2 g, 11 mmol) is added to the solution which rapidly turns dark green; the reaction mixture is then refluxed for 3 h under nitrogen. On cooling, and following the addition of acetic acid, $\text{H}_2(1,2\text{-Nc})$ precipitates. The dark-green powder is placed in a Soxhlet apparatus and washed successively with different solvents (acetone, methanol, CH_2Cl_2) in order to obtain pure $\text{H}_2(1,2\text{-Nc})$. Then, this compound is reacted with lithium in refluxing methanol (20 mL), under N_2 . After removal of the solvent, the mixture is placed in a Soxhlet extractor for 3 h under N_2 with acetone, to separate the lithium 1,2-naphthalocyaninate from the insoluble unreacted $\text{H}_2(1,2\text{-Nc})$ and LiOH . After evaporation of acetone, $\text{Li}_2(1,2\text{-Nc})$ is isolated as a dark-green powder. Yield: 65%. Formula: $\text{C}_{48}\text{H}_{24}\text{N}_8\text{Li}_2$. $M = 726.24$. UV-visible (acetone): λ_{max} (nm)/log $\epsilon = 673/5.28, 607/4.49$. ¹H NMR (400 MHz, in CD_3COCD_3): 7.84–7.87 ppm ($\text{H}_3, 4\text{H}, \text{m}$); 8.2–8.3 ppm ($\text{H}_2, 4\text{H}, \text{m}$); 8.38–8.44 ppm ($\text{H}_4, 4\text{H}, \text{m}$); 8.53–8.59 ppm ($\text{H}_5, 4\text{H}, \text{m}$); 9.58–9.76 ($\text{H}_6, 4\text{H}, 7\text{d}, J_{\text{H}_6-\text{H}_5} = 8.18$ Hz); 11.47–11.51 ppm ($\text{H}_1, 4\text{H}, \text{m}$).

Lutetium Acetate 1,2-Naphthalocyaninate, $\text{Lu}(1,2\text{-Nc})(\text{OAc})$. $\text{Li}_2(1,2\text{-Nc})$ (57 mg, 0.14 mmol) is added to a solution of $\text{Lu}(\text{OAc})_3$ (100 mg, 0.14 mmol) in trichlorobenzene. After 3 h of reflux, under N_2 , the solvent is removed under reduced pressure. The solid residue is dissolved in CH_2Cl_2 , and the solution is poured on top of a silica-gel column. After elution of the impurities with CH_2Cl_2 , a green band is rapidly eluted with $\text{CH}_2\text{Cl}_2/\text{MeOH}$ (9/1 v/v). After evaporation of the solvents, $\text{Lu}(1,2\text{-Nc})(\text{OAc})$ is recovered as a light-green powder. Yield: 56%. Formula: $\text{C}_{50}\text{H}_{27}\text{N}_8\text{O}_2\text{Lu}$. $M = 946.78$. UV-visible ($\text{CH}_2\text{Cl}_2/\text{MeOH}$; 9/1): λ_{max} (nm)/log $\epsilon = 682/5.01, 614/4.30, 374/4.73$. ¹H NMR (300 MHz, in $\text{DMSO-}d_6$): 7.95–8.02 ppm ($\text{H}_3, 4\text{H}, \text{m}$); 8.33–8.46 ppm ($\text{H}_2, 4\text{H}, \text{m}$); 8.49–8.58 ppm ($\text{H}_4, 4\text{H}, \text{m}$); 8.65–8.78 ppm ($\text{H}_5, 4\text{H}, \text{m}$); 9.60–9.74 ($\text{H}_6, 4\text{H}, 7\text{d}$); 11.29–11.35 ppm ($\text{H}_1, 4\text{H}, \text{m}$).

Lutetium Bis(1,2-naphthalocyaninate), $\text{Lu}(1,2\text{-Nc})_2$. Lutetium acetate (60 mg, 14 mmol) is added to a solution of lithium 1,2-naphthalocyaninate (200 mg, 27 mmol) in 15 mL of 1-chloronaphthalene (1-CNP) previously chromatographed on neutral alumina. The

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medium is stirred during 3 h at the solvent reflux, under air. After cooling, the solution is poured on a silica-gel column and eluted with CH_2Cl_2 . A green fraction comes out rapidly containing $\text{Lu}(1,2\text{-Nc})_2$ associated with 1-CNP which is removed under vacuum; $\text{Lu}(1,2\text{-Nc})_2$ is obtained as a dark-green solid. Yield: 60%. Anal. Calcd for $\text{C}_{96}\text{H}_{48}\text{N}_{16}\text{Lu}$: C, 72.04; H, 3.02; N, 14.00. Found: C, 71.75; H, 2.64; N, 13.82. Mass: $m/z = 1600$. UV-visible (CH_2Cl_2): λ_{max} (nm)/log $\epsilon = 674/5.18, 612/4.45, 516/4.41, 380/4.97, 312-314/4.97$. ^1H NMR (300 MHz, DMF-d_7 + hydrazine hydrate): 7.48–7.72 ppm (H_2 , 8H, m); 8–9.2 ppm ($\text{H}_{6,5,4,3}$, 32H, undistinguishable numerous multiplets); 10.15–10.52 ppm (H_1 , 8H, m).

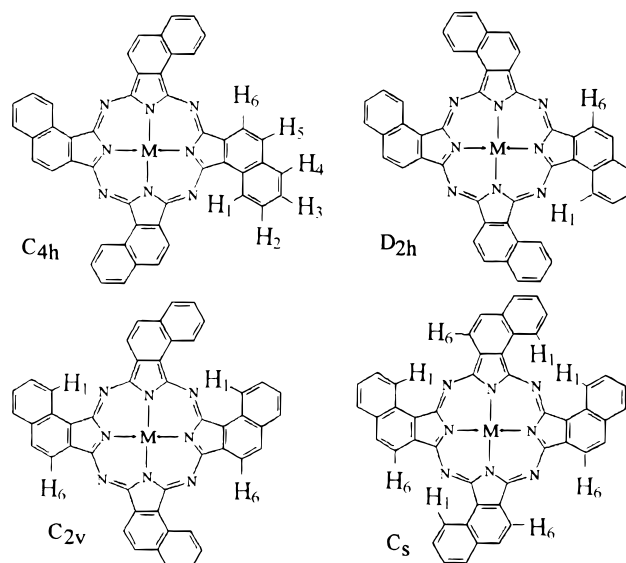
Dilutetium Tris(1,2-naphthalocyanine), $\text{Lu}_2(1,2\text{-Nc})_3$. Lutetium acetate (75 mg, 18 mmol) is added to a solution of lithium 1,2-naphthalocyanine (200 mg, 27 mmol) in 20 mL of 1-CNP, previously chromatographed on basic alumina and deaerated. Under nitrogen, the mixture is stirred overnight under reflux. The residue of the evaporation under low pressure, containing a mixture of $\text{Lu}(1,2\text{-Nc})_2$ and $\text{Lu}_2(1,2\text{-Nc})_3$, is dissolved in DMSO. Hydrazine hydrate is added to reduce $\text{Lu}(1,2\text{-Nc})_2$ selectively. This solution is poured on a silica gel column and chromatographed with CH_2Cl_2 ; the anionic reduced form of $\text{Lu}(1,2\text{-Nc})_2$ does not move under such conditions. $\text{Lu}_2(1,2\text{-Nc})_3$ is isolated and characterized. Yield: 60%. Anal. Calcd for $\text{C}_{144}\text{H}_{72}\text{N}_{24}\text{Lu}_2$: C, 69.51; H, 2.92; N, 13.51. Found: C, 69.50; H, 2.64; N, 12.92. Mass: $m/z = 2488$. UV-visible (CH_2Cl_2): λ_{max} (nm)/log $\epsilon = 676/5.15, 610/5.12, 378/5.04, 310/5.05$.

Results and Discussion

Synthesis. Rare-earth-metal sandwich complexes are prepared in our laboratory via a two-step synthesis.²¹ The first stage is the preparation of the 1,2-naphthalocyanine macrocycle through the condensation of four 1,2-dicyanonaphthalene molecules in the presence of two lithium ions; the second step, the formation of the lutetium complex, starts from the lithium salts of the macrocyclic anions. The lithium naphthalocyanine, $\text{Li}_2(1,2\text{-Nc})$, was synthesized according to the procedure described by Linstead.²⁰ However, the purification stage was modified in order to obtain a purer mono(naphthalocyanine) which was originally polluted with many impurities. $\text{H}_2(1,2\text{-Nc})$, obtained by protonation of $\text{Li}_2(1,2\text{-Nc})$, is very insoluble in common organic solvents and can be purified by washing with several solvents. Then pure $\text{Li}_2(1,2\text{-Nc})$ is back-prepared by reaction with lithium methanolate.

The condensation of four 1,2-dicyanonaphthalene molecules can give four isomers of the naphthalocyanine ring (Figure 1). One of these has been isolated in the case of the iron complex $\text{Fe}(1,2\text{-Nc})(\text{L})_2$, L = cyclohexyl isocyanide; crystallography and ^1H NMR prove that it is the isomer with the C_{4h} symmetry.^{3a} For two reasons, no attempt was made in the present work to separate the isomers: (i) the condensation of 2 equiv of the same isomer of $\text{Li}_2(1,2\text{-Nc})$ with one Lu(III) cation would lead to two isomers of $\text{Lu}(1,2\text{-Nc})_2$, except for the 1,2-naphthalocyanine with the D_{2h} symmetry; (ii) a study of the molecular orbitals of $\text{H}_2(1,2\text{-Nc})$ has shown that the electronic properties of the four isomers should be quite identical, the difference between the energy levels, as well as the HOMO–LUMO gap, being less than 0.05 eV.²² Consequently, $\text{Lu}(1,2\text{-Nc})_2$ is synthesized from the mixture of the isomers of $\text{Li}_2(1,2\text{-Nc})$, under air in 1-chloronaphthalene (1-CNP). After chromatography, $\text{Lu}(1,2\text{-Nc})_2$ is recovered as a pure green powder, as shown by elemental analysis (yield 55%). Experimental conditions are different for the synthesis of the lutetium bis(1,2- and

A) 1,2-mononaphthalocyanine isomers



B) 2,3-mononaphthalocyanine

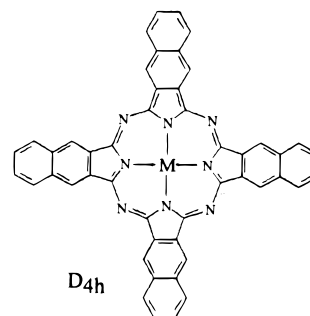


Figure 1. Molecular structures of the isomers of metallo-1,2-naphthalocyanine (A) and metallo-2,3-naphthalocyanine (B). In part A, the protons H_1 and H_6 are represented.

2,3-naphthalocyanines). $\text{Lu}(2,3\text{-Nc})_2$, which is oxidized in 1-CNP and under air, was prepared in quinoline under nitrogen.⁷

As described above, $\text{Lu}(1,2\text{-Nc})_2$ is the only product isolated from the synthesis in 1-CNP, under air; in order to study the influence of the atmosphere on the yield of the preparation, the synthesis was repeated in the same solvent, under nitrogen. Under such conditions, $\text{Lu}(1,2\text{-Nc})_2$ and the triple-decker sandwich complex $\text{Lu}_2(1,2\text{-Nc})_3$ appear together. In contrast to the porphyrin double- and triple-decker complexes of cerium, which have very different solubilities,^{9a} the latter complex cannot be purified directly by chromatography; it is eluted simultaneously with $\text{Lu}(1,2\text{-Nc})_2$, regardless of the mixture of solvents used for elution. However, when hydrazine hydrate is added to the mixture of the two compounds in solution in DMSO, only the double-decker complex is reduced to its anionic form; $\text{Lu}_2(1,2\text{-Nc})_3$ is recovered by elution with CH_2Cl_2 . After this separation, $\text{Lu}(1,2\text{-Nc})_2^-$ is eluted with a polar solvent, pure methanol, for example. Attempts to prepare $\text{Lu}_2(1,2\text{-Nc})_3$ from bis- and mono(naphthalocyanines), $\text{Lu}(1,2\text{-Nc})(\text{OAc})$ and $\text{Li}_2(1,2\text{-Nc})$ (2:1), as well as $\text{Lu}(1,2\text{-Nc})_2$ and $\text{Lu}(1,2\text{-Nc})(\text{OAc})$ (1:1), were successful. These compounds react in 1-CNP to give the expected complex, but only under N_2 ; $\text{Lu}_2(1,2\text{-Nc})_3$ is not detected when the mixtures are heated under air. The role of dioxygen during the synthesis of the two lutetium bis(naphthalocyanines) and of $\text{Lu}_2(1,2\text{-Nc})_3$ is a consequence of

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the redox properties of the different compounds. As described hereafter, $\text{Lu}(2,3\text{-Nc})_2$ ($E_{\text{O1/N}} = -0.32$ V) is much more easily oxidized than $\text{Lu}(1,2\text{-Nc})_2$ ($E_{\text{O1/N}} = 0.06$ V) and has to be synthesized under N_2 . Concerning the double- and triple-decker sandwiches of the 1,2-Nc ligand, it is also understandable, from redox considerations, that the products are different when the reaction is carried out under O_2 or N_2 . In $\text{Lu}_2(1,2\text{-Nc})_3$, all three rings are in the reduced redox state (Nc^{2-}); this very oxidizable compound must be prepared under nitrogen. For $\text{Lu}(1,2\text{-Nc})_2$, where one of the two rings is oxidized (Nc^-), the same product is obtained under N_2 or air.

NMR and Mass Spectroscopies. The ^1H NMR spectrum of $\text{Li}_2(1,2\text{-Nc}^{2-})$ is much more complex than that of $\text{Li}_2(2,3\text{-Nc})$, as all the protons have different chemical shifts that, besides, depend on the isomer considered (Figure 1). In order to assign each signal of the spectrum to the different protons of $\text{Li}_2(1,2\text{-Nc})$, a homonuclear shift correlated 2D NMR study (COSY) was performed (Figure 2). Due to the ring current of the π electrons of the macrocycle, the signals of protons H_1 and H_6 (Figure 2) are strongly shifted toward low fields; this effect is of course less important on the outermost protons. The multiplet centered at 11.49 ppm has been attributed to H_1 , those at 9.73 and 9.62 ppm correspond to H_6 . Protons H_1 and H_6 , each coupled to only one other proton, H_2 and H_5 , respectively, generate doublets. Due to the different positions of these protons on the isomers, one observes many doublets. Isomery apparently influences only weakly the chemical shift of H_1 , as it appears that its signal (11.47–11.51 ppm), constituted of intricate doublets, is rather thin. The situation is different for proton H_6 of the different isomers: the doublets are distinct in the two multiplets m1 (9.69–9.77 ppm) and m2 (9.58–9.66 ppm). In Figure 1, it is easy to distinguish two different types of H_6 protons, facing H_1 or H_6 . This is clearly illustrated by the representation of the C_s isomer; more than likely, the two distinct sets of doublets, m1 and m2, result from the existence of these two kinds of H_6 protons. Moreover, isomery modifies the chemical shift of these protons, so that, due to the symmetry patterns of the four isomers of $\text{Li}_2(1,2\text{-Nc})$, one expects eight doublets: one for each of the C_{4h} and D_{2h} isomers, as their protons are identical; two for C_{2v} . The spectrum of C_s should present four doublets, two of them having quite the same chemical shifts, as their environments are almost similar. This is effectively the number of doublets apparent in the inset in Figure 2. The hypothesis that two of the four H_6 protons of C_s must have quite identical chemical shifts leads to the conclusion that the corresponding doublets are e and f of m2. Consequently, m1 is constituted by the doublets of the H_6 protons facing H_1 . Two more doublets of C_s must be in m1: only a and d have heights comparable to those of e and f. Isomer C_{2v} must have one doublet in m1 and one in m2; from the relative intensities of the signals, these are b and h. Finally, doublet c corresponds to H_6 protons of C_{4h} and g to those of D_{2h} . As similar protons are compared, the relative intensities of the eight doublets allow a rough estimation of the proportion of each isomer in the mixture: 50, 20, 20, and 10%, respectively, for C_s , C_{4h} , C_{2v} , and D_{2h} . However, these percentages are not always the same, as verified from the different synthesis.

As a consequence of what has been said above, $\text{Lu}(1,2\text{-Nc})_2$ and $\text{Lu}_2(1,2\text{-Nc})_3$ are undoubtedly mixtures of isomers. The ^1H NMR spectrum of $\text{Lu}(1,2\text{-Nc})_2$ in $\text{DMSO}-d_6$ was obtained after reduction by hydrazine hydrate, the anionic and paramagnetic reduced form being more soluble. However its spectrum is quite useless, as all the multiplets are complex, probably because of the great number of isomers. The molecular form

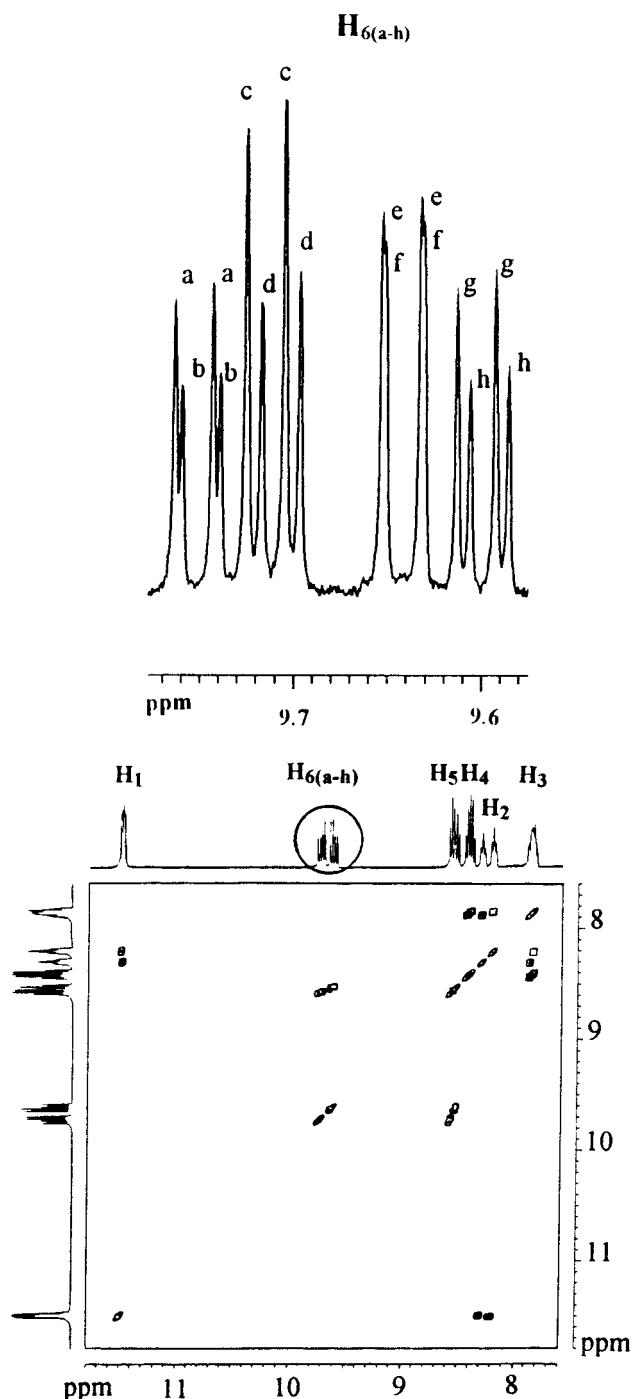


Figure 2. COSY ^1H NMR spectrum of a $\text{Li}_2(1,2\text{-Nc})$ isomer mixture (400 MHz; acetone- d_6).

of $\text{Lu}_2(1,2\text{-Nc})_3$, which is diamagnetic, could have been studied by NMR; unfortunately the spectrum is of no help because of the poor solubility of the compound in the common solvents and due to the number of isomers. The resonance frequency of the H_1 protons of $\text{Lu}(1,2\text{-Nc})_2$ is shifted upfield compared to that of $\text{Li}_2(1,2\text{-Nc})$, from 11.51 to 10.52 ppm; this has also been reported for the phthalocyanines.^{7,21,23} A similar effect is observed when $\text{Lu}(1,2\text{-Nc})_2$ is compared to $\text{Lu}_2(1,2\text{-Nc})_3$, whose H_1 protons are shifted more than those of the biplanar complex; even if the ^1H NMR spectrum of the triple-decker sandwich is not well resolved, as mentioned above, no signal is visible above 9.7 ppm. This is due to the mutual influence of the ring currents.

It would have been interesting to distinguish the protons of the central ring from those of the outer macrocycles; as was shown recently by MO calculations, the two external conjugated π -electron systems should greatly influence the protons of the central naphthalocyanine.^{15b}

Fast atom bombardement mass spectrometry has been extensively used to characterize various sandwich complexes (bisPor,²⁴ bisPc,^{5,7,21,25} and the triple decker of Pc,^{13–16} mixed Pc–Por^{9,10}). However, as has been described elsewhere, the spectra of the lutetium sandwich complexes vary drastically with the matrix used for FAB-MS.^{7,26} Thus, the positive field desorption technique (FD⁺) has been used for compounds Lu(1,2-Nc)₂ and Lu₂(1,2-Nc)₃. Their molecular ion peaks are observed respectively at $m/z = 1600$ and 2488. The exact mass measured for the molecular ion of Lu₂(1,2-Nc)₃ is 2487.502, which agrees well with the calculated value (2487.524), confirming undoubtedly the identity of the compound: C₁₄₄H₇₂N₂₇¹⁷⁵Lu₂. This result is ascertained by the perfect matching of the experimental and theoretical mass distributions. The mass spectroscopy study of Lu₂(1,2-Nc)₃ was also performed using the electrospray ionization mode (ES). This milder technique has the advantage of lowering the decomposition and recombination processes; it has been widely used for large and fragile molecules. The ES spectrum of Lu₂(1,2-Nc)₃ presents at $m/z = 2488$ the expected peak and indicates that the triple-decker complex contains less than 3% of Lu(1,2-Nc)₂ ($m/z = 1600$) (Supporting Information).

In the FD⁺ mass spectrum of Lu₂(1,2-Nc)₃, besides the molecular ion peak, M⁺ at $m/z = 2488$, other peaks are detected at $m/z = 1244$ (11%) and 830 (5%), corresponding to M²⁺ and M³⁺, respectively. In the case of Lu(1,2-Nc)₂, only the molecular ion peak ($m/z = 1600$) and a very small one corresponding to M²⁺ ($m/z = 800$; 2%) are visible in the FD⁺ spectrum. This shows that Lu₂(1,2-Nc)₃ has the tendency to accept two and three positive charges more easily than Lu(1,2-Nc)₂, because of the delocalization of the π electron over the three 1,2-naphthalocyanine rings of the triple-decker sandwich. These results are in agreement with the electrochemical data, which will be described later.

Electrochemistry. The electrochemical behavior of Lu(Pc)₂, Lu^{III}(Pc²⁻)(Pc⁻), and related compounds has been extensively investigated (* means that the species carries an unpaired electron).^{22a,27–29} Recently, the electrochemical behavior of Lu^{III}(2,3-Nc²⁻)(2,3-Nc⁻)⁷ and of phthalocyanine triple-decker¹⁴ sandwich derivatives was published, but nothing has ever been reported on the lanthanide complexes of 1,2-naphthalocyanines, except a short communication on the synthesis and characterization of the related triple decker.¹⁶

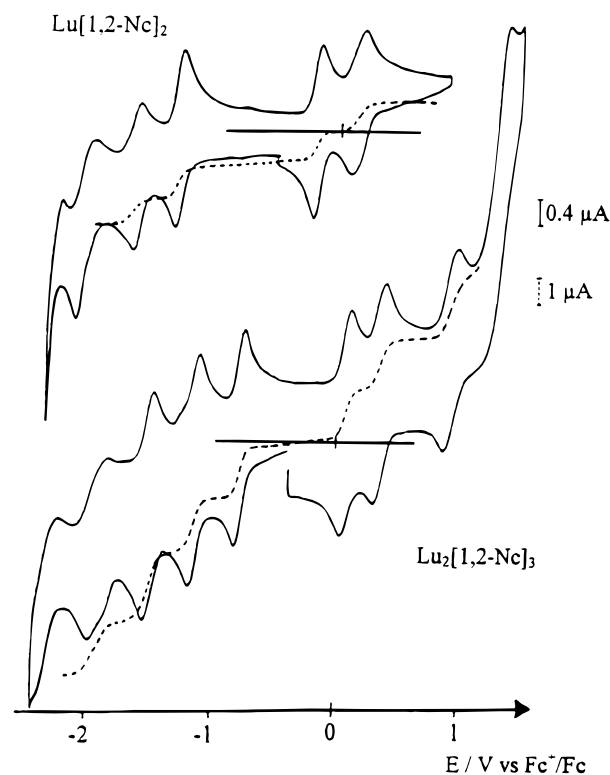


Figure 3. Voltammetry of Lu^{III}(1,2-Nc²⁻)(1,2-Nc⁻) and Lu^{III}₂(1,2-Nc²⁻)₃ in benzonitrile (Bu₄NPF₆ 0.1 M), at a platinum disk electrode (diameter: 2 mm): (—) cyclic voltammetry (scan rate 100 mV s⁻¹); (---) rotating disk electrode (500 rpm; scan rate 2 mV s⁻¹).

The different redox processes of Lu^{III}(1,2-Nc²⁻)(OAc⁻), Lu^{III}(1,2-Nc²⁻)(1,2-Nc⁻), and Lu^{III}₂(1,2-Nc²⁻)₃ were studied by cyclic and hydrodynamic voltammetry at a platinum electrode, in a glovebox; the voltammograms of the double- and triple-decker sandwiches are represented on Figure 3. The formal potentials for the electron exchanges of these complexes, in the range from -2.5 to +1.3 V, are given in Table 1. For the lutetium mono(1,2-naphthalocyaninate), Lu^{III}(1,2-Nc²⁻)(OAc⁻), only two reversible processes are detected, one in oxidation and one in reduction; the two redox states [Lu^{III}(1,2-Nc⁻)(OAc⁻)]⁺ and [Lu^{III}(1,2-Nc³⁻)(OAc⁻)]⁻ are chemically unstable. As it appears from Figure 3, the electrochemical behavior of Lu^{III}(1,2-Nc²⁻)(1,2-Nc⁻) is very similar to those of Lu(Pc)₂²⁷ and Lu(2,3-Nc)₂⁷: all the monoelectronic steps are reversible on the time scale of cyclic voltammetry. Two more oxidation steps, occurring close to the anodic limit of the domain, are not represented in Figure 3 because they are ill-defined. As the characterization of Lu₂(1,2-Nc)₃ was uncertain until the mass spectrum was obtained, one of the first experiments of the electrochemical studies was the elucidation of the redox state of the compound that had been synthesized. For that, voltammetry at a platinum ultramicroelectrode (10 μm) was performed, with and without addition of supporting electrolyte. In both experiments, the voltammograms are identical, indicating that the mass transport of the electroactive species is not influenced by the migration in the electric field; consequently, the compound reacting at the electrode is the neutral form, Lu^{III}₂(1,2-Nc²⁻)₃.³¹ Lu₂(1,2-Nc)₃ presents nine redox steps (Figure 3): four oxidations (one close to the limit of the domain) and five reductions (one at the cathodic limit). Coulometry during exhaustive electrolysis at 0.30 and 0.75 V ascertains that the

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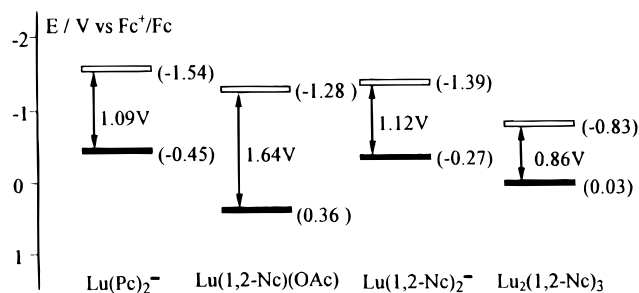
Table 1. Standard Potentials (V vs Fc⁺/Fc) for Oxidation and Reduction of the Compounds^a

| | R ₄ /R ₅ | R ₃ /R ₄ | R ₂ /R ₃ | R ₁ /R ₂ | N/R ₁ | O ₁ /N | O ₂ /O ₁ | O ₃ /O ₂ | O ₄ /O ₃ | ΔE ₁ | ΔE ₂ |
|---------------------------------------|--------------------------------|--------------------------------|--------------------------------|--------------------------------|------------------|-------------------|--------------------------------|--------------------------------|--------------------------------|-----------------|-----------------|
| Lu(Pc) ₂ | | -2.40 | -1.92 | -1.54 | -0.46 | -0.05 | 1.05 | 1.43 | | 0.41 | 1.08 |
| Lu(2,3-Nc) ₂ | | -2.26 | -1.82 | -1.52 | -0.61 | -0.32 | 0.63 | 0.77 | | 0.29 | 0.91 |
| Lu(1,2-Nc)(OAc) | | | | | -1.28 | 0.36 | | | | | 1.64 |
| Lu(1,2-Nc) ₂ | | -2.16 | -1.72 | -1.39 | -0.27 | 0.06 | ~1.2 | ~1.4 | | 0.33 | 1.12 |
| Lu ₂ (1,2-Nc) ₃ | -2.31 | -1.97 | -1.57 | -1.20 | -0.83 | 0.03 | 0.30 | 0.87 | 1.22 | | 0.86 |

^a Platinum electrode; 0.1 M Bu₄NPF₆ in benzonitrile. N = neutral; R = reduced; O = oxidized. ΔE₁ is the stability of the neutral forms of the bis(phthalocyanines) and bis(naphthalocyanines), Lu^{III}(P²⁻)(P^{•-}): ΔE₁ = E_{O₁/N} - E_{N/R₁}. ΔE₂ is the potential domain where all the macrocyclic ligands are in the P²⁻ state: ΔE₂ = E_{O₁/N} - E_{N/R₁} for Lu^{III}₂(1,2-Nc²⁻)₃ and ΔE₂ = E_{N/R₁} - E_{R₁/R₂} for the reduced double-decker complexes [Lu^{III}(P²⁻)₂]⁻. first two oxidation steps are monoelectronic and chemically reversible; as a consequence, all the redox processes are monoelectronic and reversible, at least on the time scale of cyclic voltammetry. The standard potentials are listed in Table 1, with ΔE₁ and ΔE₂ calculated from these measured potentials. ΔE₁ represents the stability of the neutral form of the bis(phthalocyanine) and bis(naphthalocyanine), Lu^{III}(P²⁻)(P^{•-}). ΔE₂ is the potential domain where the macrocyclic ligands are in the P²⁻ state.

The only redox sites on these complexes of lutetium are the ring π-systems. The bis(phthalocyanine) and bis(naphthalocyanine) derivatives have one unpaired electron on their valence orbital, thus called SOMO (singly-occupied) instead of HOMO. The potentials E_{N/O₁} in Table 1 indicate that the sequence is Lu(2,3-Nc)₂ > Lu(Pc)₂ > Lu(1,2-Nc)₂ for the oxidation of the sandwich complexes, the last compound being more difficult to oxidize; the difference between the two naphthalocyanine complexes is quite important, as the first oxidation potential of Lu^{III}(1,2-Nc²⁻)₂ is about 0.4 V higher than that of Lu^{III}(2,3-Nc²⁻)₂. E_{N/O₁} represents the energy required to remove one electron from the singly occupied HOMO of the sandwich complexes and bring it to the reference state; thus, differences in E_{N/O₁} values represent variations of the SOMO energy levels. Compared to that of Lu^{III}(Pc²⁻)₂, the SOMO of Lu^{III}(2,3-Nc²⁻)₂ is destabilized while that of Lu^{III}(1,2-Nc²⁻)₂ is stabilized. These results fully corroborate the MO calculations for this family of ligands.²

ΔE₁ = E_{O₁/N} - E_{N/R₁}, the difference between the first oxidation and the first reduction potentials of the double-decker complexes, is the stability domain of the neutral molecular form, directly related to the disproportionation constant of the molecule in solution. ΔE₁ values are different for Lu^{III}(Pc²⁻)(Pc^{•-}) (0.41 V),²⁷ Lu^{III}(1,2-Nc²⁻)(1,2-Nc^{•-}) (0.33 V), and Lu^{III}(2,3-Nc²⁻)(2,3-Nc^{•-}) (0.29 V);⁷ this is the lowest ΔE₁ value for this family of compounds and consequently means that Lu^{III}(2,3-Nc²⁻)(2,3-Nc^{•-}) disproportionates more easily than Lu^{III}(Pc²⁻)(Pc^{•-}) and Lu^{III}(1,2-Nc²⁻)(1,2-Nc^{•-}). In pure solid phases, e.g. in intrinsic semiconductors such as Lu(Pc)₂ and related compounds, charges are carried by the ions produced by the disproportionation process. It has effectively been shown that the prediction, from redox measurements, of the conductivity and of its activation is good.^{5,30} As a consequence, condensed phases prepared from Lu^{III}(1,2-Nc²⁻)(1,2-Nc^{•-}), and particularly from Lu^{III}(2,3-Nc²⁻)(2,3-Nc^{•-}), should have a better conductivity, with a lower activation energy, than Lu^{III}(Pc²⁻)(Pc^{•-}) and Li(Pc^{•-}).³² In contrast to Lu^{III}(1,2-Nc²⁻)(1,2-Nc^{•-}), the triple decker should not be an intrinsic semiconductor; nevertheless, because of the low energy gap between its oxidation and reduction, 0.86 V, the doped compound should be a good semiconductor.

**Figure 4.** Influence of the stacking on the redox properties of the 1,2-naphthalocyanine complexes of lutetium(III). The reference for the potentials is the ferrocenium/ferrocene couple.

The electrochemical data obtained for Lu^{III}(1,2-Nc²⁻)(OAc⁻), Lu^{III}(1,2-Nc²⁻)(1,2-Nc^{•-}), and Lu^{III}₂(2,3-Nc²⁻)₃ afford the opportunity to investigate the effect of the extension of the π-network along an axis perpendicular to the naphthalocyanine plane. Lu^{III}₂(1,2-Nc²⁻)₃ presents two more redox processes than Lu^{III}(1,2-Nc²⁻)(1,2-Nc^{•-}) (Figure 3). This is not really surprising because Lu^{III}₂(1,2-Nc²⁻)₃ has one more macrocyclic ring. ΔE₂ is the potential domain where the species with all the macrocycles in their P²⁻ redox state are stable. As in the neutral molecular form of the double-decker complex, one of the rings is (1,2-Nc^{•-}), the reduced species, [Lu^{III}(1,2-Nc²⁻)₂]⁻, must be considered for a comparison with the compounds Lu^{III}(1,2-Nc²⁻)(OAc⁻) and Lu^{III}₂(1,2-Nc²⁻)₃, where all the naphthalocyanine rings are in their reduced form Nc²⁻. However, it must be remembered that the HOMO of the anion [Lu^{III}(1,2-Nc²⁻)₂]⁻ should be destabilized, compared to an uncharged species; thus, ΔE₂ = E_{O₁/N} - E_{N/R₁} for Lu^{III}₂(1,2-Nc²⁻)₃ and ΔE₂ = E_{N/R₁} - E_{R₁/R₂} for the reduced double-decker complexes [Lu^{III}(P²⁻)₂]⁻. As obvious from Table 1 and Figure 4, the gap is 1.65 V for Lu(1,2-Nc)(OAc), 1.12 V for Lu(1,2-Nc)₂⁻ and only 0.86 V for Lu₂(1,2-Nc)₃. The last value is the smallest one ever reported for the series of porphyrin and phthalocyanine derivatives.^{9,10,14} The only previous electrochemical study of a phthalocyanine triple-decker sandwich was that of Yb₂(obPc)₃; for this compound, ΔE₂ = 1.0 V, a value higher than that for Lu₂(1,2-Nc)₃.¹⁴ This result makes it clear that the extension of the conjugation over the larger naphthalocyanine rings has a profound influence on the MO levels. Increasing the number of macrocycles in the stack, from 1 to 3, induces important modifications in the orbital system of these complexes. Thus, extending the possibility of delocalization of the electrons along an axial axis would lead to molecular materials with very different properties and particularly with improved electronic conductivities. However, as the electric charges are well balanced in Lu^{III}₂(2,3-Nc²⁻)₃, extending the chain further should be difficult.

UV-Visible Spectrophotometry. Since the review by Stillman and Nyokong of the absorption properties of phthalocyanines, in which the lanthanide compounds were briefly

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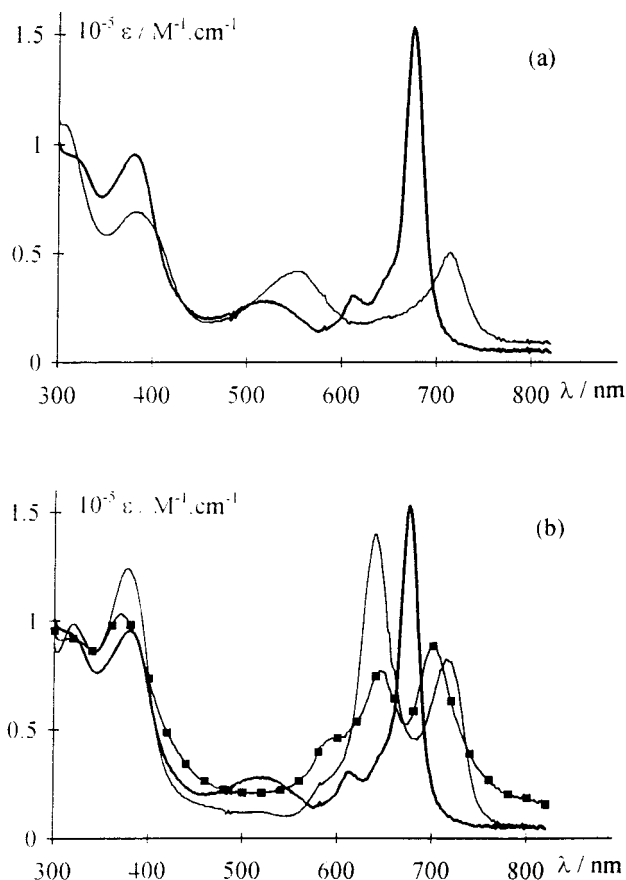


Figure 5. UV-visible spectra of Lu[1,2-Nc]₂ redox states in benzonitrile: (a) (thick curve) Lu^{III}(1,2-Nc²⁻)(1,2-Nc^{•-}), (thin curve) [Lu^{III}(1,2-Nc^{•-})(1,2-Nc^{•-})(1,2-Nc^{•-})]⁺; (b) (thick curve) Lu^{III}(1,2-Nc²⁻)(1,2-Nc^{•-}), (thin curve) [Lu^{III}(1,2-Nc²⁻)(1,2-Nc²⁻)]⁻, (—■—) [Lu^{III}(1,2-Nc³⁻)(1,2-Nc²⁻)]²⁻.

mentioned,^{1a} some articles have been specially devoted to the spectral properties of the sandwich complexes. The results concerning the bis(naphthalocyanines) of lutetium are rare, and nothing has been published on the complexes of the 1,2-Nc ligand. Ishikawa and Kaizu commented on the scarce spectroscopic data for the phthalocyanine trimers.^{15a} The UV-visible spectra of the reduced and oxidized forms of Lu(1,2-Nc)₂ and Lu₂(1,2-Nc)₃ are presented in Figures 5 and 6. The first reduced and oxidized states of these compounds are stable; however, the highly reduced and oxidized species, observable on the reverse scan of cyclic voltammetry, are very reactive and return rapidly to more stable redox states when they diffuse in solution; there is no chemical decomposition, as shown by the evolution of the spectra and by the sharp isosbestic points on the sets of spectra recorded during electrolysis. Thus, spectroelectrochemistry was the more appropriate way to observe these spectra.

Upon the first reduction, the Q band of Lu^{III}(1,2-Nc²⁻)(1,2-Nc^{•-}), at 674 nm, is replaced by two transitions at 718 and 638 nm; this changes on further reduction, three bands being visible between 600 and 750 nm (Figure 5). The B, or Soret, band is only slightly altered by reduction. Adding one electron to the neutral radical Lu^{III}(1,2-Nc²⁻)(1,2-Nc^{•-}) suppresses the band attributed to a transition from deeper levels to the singly-occupied MO (SOMO), at 509 nm. Upon oxidation of Lu^{III}(1,2-Nc²⁻)(1,2-Nc^{•-}), its Q band is replaced by a less intense transition at 710 nm and a broad band at about 550 nm (Figure 5). This behavior is very similar to what has been observed for Lu^{III}(2,3-Nc²⁻)(2,3-Nc^{•-})⁷ and Lu^{III}(Pc²⁻)(Pc^{•-}).²⁷

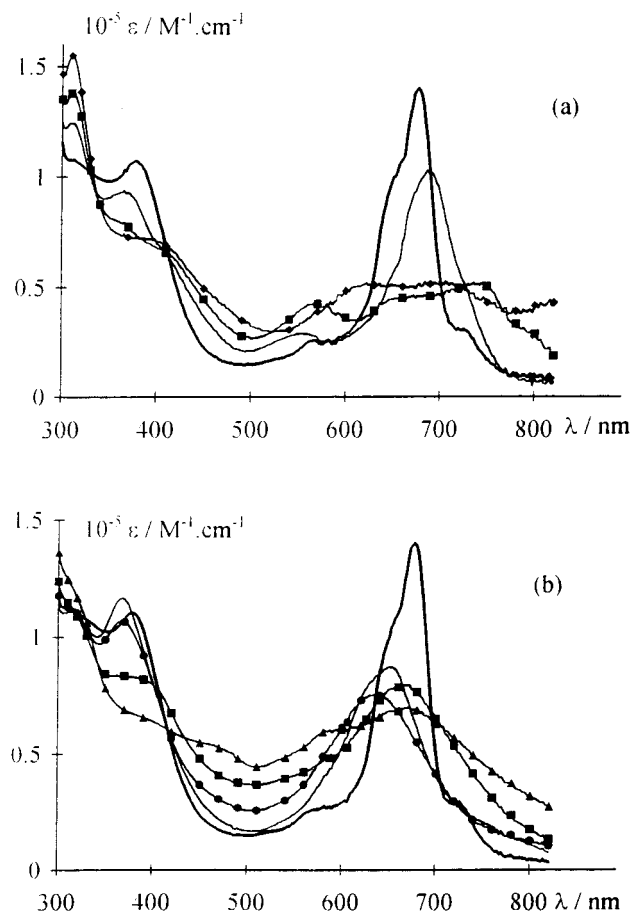


Figure 6. UV-visible spectra of Lu₂[1,2-Nc]₃ redox states in benzonitrile: (a) (thick curve) Lu^{III}₂(2,3-Nc²⁻)₃, (thin curve) [Lu^{III}₂(1,2-Nc²⁻)₂(1,2-Nc^{•-})]⁺, (—■—) [Lu^{III}₂(1,2-Nc²⁻)(1,2-Nc^{•-})₂]²⁺, (—◆—) [Lu^{III}₂(1,2-Nc^{•-})₃]³⁺; (b) (thick curve) Lu^{III}₂(1,2-Nc²⁻)₃, (thin curve) [Lu^{III}₂(1,2-Nc³⁻)(1,2-Nc²⁻)₂]⁻, (—●—) [Lu^{III}₂(1,2-Nc³⁻)₂(1,2-Nc²⁻)]²⁻, (—■—) [Lu^{III}₂(1,2-Nc³⁻)₃]³⁻, (—▲—) [Lu^{III}(1,2-Nc⁴⁻)(1,2-Nc³⁻)₂]⁴⁻.

However, compared to that of Lu^{III}(Pc²⁻)(Pc^{•-}) ($\lambda_{\max} = 658$ nm), the shift of λ_{\max} for the Q bands is modest for Lu^{III}(1,2-Nc²⁻)(1,2-Nc^{•-}) ($\lambda_{\max} = 674$ nm) and very important for Lu^{III}(2,3-Nc²⁻)(2,3-Nc^{•-}) ($\lambda_{\max} = 760$ nm). These results confirm the calculations of Bredas² and Kobayashi,^{1d} who predicted a bathochromic shift for the naphthalocyanine derivatives and a much more important one for the 2,3-naphthalocyanine complexes.

As illustrated in Figure 6, the spectrum of the triple-decker sandwich is notably different from that of Lu^{III}(1,2-Nc²⁻)(1,2-Nc^{•-}), particularly in the Q band region, where the spectrum is evidently the envelope of many transitions, with a maximum at 676 nm. When one electron is removed from the triple decker, the complex band becomes broader and less intense, with a maximum shifted to 690 nm. This oxidized form of the triple decker has some similarity to Lu^{III}(1,2-Nc²⁻)(1,2-Nc^{•-}), having an half-occupied MO level and a hole probably delocalized over the stack of the three macrocycles. Further oxidations lead to rather flat, continuous spectra from 350 to 820 nm, a more intense band at 310 nm growing at the expense of the one at 378 nm. Upon reduction, a very similar situation is observed, leading to "continuous" absorption spectra with many unresolved transitions. The broadening of the bands during the reduction of the macrocycle has been observed for Lu(Pc)₂^{27b} and for the reduced forms of M(Pc²⁻).³³

The comparison of Lu(1,2-Nc)₂ and Lu₂(1,2-Nc)₃ and the evolution of their spectra during the redox processes show that

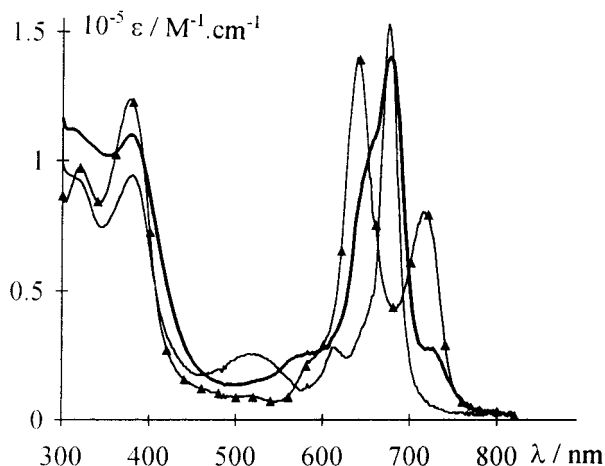


Figure 7. Comparison of (thick curve) $\text{Lu}^{\text{III}}_2(1,2\text{-Nc}^{2-})_3$, (thin curve) $\text{Lu}^{\text{III}}(1,2\text{-Nc}^{2-})(1,2\text{-Nc}^{\bullet-})$, and ($-\triangle-$) $[\text{Lu}^{\text{III}}(1,2\text{-Nc}^{2-})_2]^-$ UV-visible spectra in methylene chloride.

stacking one $[\text{Lu}^{\text{III}}(1,2\text{-Nc}^{2-})]^+$ moiety over $[\text{Lu}^{\text{III}}(1,2\text{-Nc}^{2-})_2]^-$, and thus extending the delocalization over three rings, modifies significantly the MO levels and transitions. From Figure 7, the broad Q band of the triplanar complex appears to be a combination of the transitions of $\text{Lu}^{\text{III}}(1,2\text{-Nc}^{2-})(1,2\text{-Nc}^{\bullet-})$ and of its reduced form $[\text{Lu}^{\text{III}}(1,2\text{-Nc}^{2-})_2]^-$. The spectrum of the latter consists of two bands which, in the case of $[\text{Lu}^{\text{III}}(\text{Pc}^{2-})_2]^-$, were attributed to exciton coupling and charge resonance in the excited state, respectively at lower and higher wavelengths.^{15,34}

In the case of a mixed cerium porphyrin-phthalocyanine (1:2) triple decker, the absorption spectrum of $\text{Ce}_2(\text{Por})(\text{Pc})_2$ appears to be the superimposition of the intense Soret band of $\text{Ce}^{\text{III}}(\text{Por}^{2-})(\text{Acac}^-)$ (418 nm) on the two bands of $[\text{Ce}^{\text{III}}(\text{Pc}^{2-})_2]^-$.^{10a} In their recent publication on the comparison of a phthalocyanine trimer with LuPc_2 , Ishikawa et al. have shown that the two more intense bands of $[\text{Lu}^{\text{III}}(\text{Pc}^{2-})_2]^-$ are clearly apparent in the spectrum of the trimer.^{6b} The present results are close to their observation and calculations. However, in the Q-band region, transitions are apparent below 600 nm for the trimer $\text{Lu}^{\text{III}}_2(1,2\text{-Nc}^{2-})_3$ and not visible on the spectrum reported by Ishikawa et al. for a phthalocyanine triple-decker complex. This could be explained by the calculations of these authors, who have shown that changes in the respective orientations of the three planes as well as of the interplanar distance would strongly influence the spectra, allowing some forbidden transitions.^{15b}

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Supporting Information Available: The electrospray mass spectrum of $\text{Lu}_2(1,2\text{-Nc})_3$ (1 page). Ordering information is given on any current masthead page.

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