Synthesis, Spectroscopic, and Electrochemical Properties of Rare Earth Double-Deckers with Tetra(*tert*-butyl)-2,3-naphthalocyaninato Ligands

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A series of rare earth(III) double-deckers RE[Nc(*t*Bu)$_4$]$_2$ [RE = La, Ce, Pr, Nd, Eu, Gd, Tb, Y, Er; Nc(*t*Bu)$_4$ = dianion of tetra(*tert*-butyl)-2,3-naphthalocyanine] (**1**–**9**) have been prepared by treating RE(acac)$_3$ · *n* H$_2$O (acac = acetylacetonate) with 6-*tert*-butylnaphthalonitrile in refluxing *n*-octanol in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). These novel sandwich-type complexes have been spectroscopically characterized. The electrochemical studies show that the first oxidation and the first reduction potentials increase with the size of the central metal ions with a relatively small separation (0.28–0.33 V), reflecting the narrow HOMO–LUMO gap.

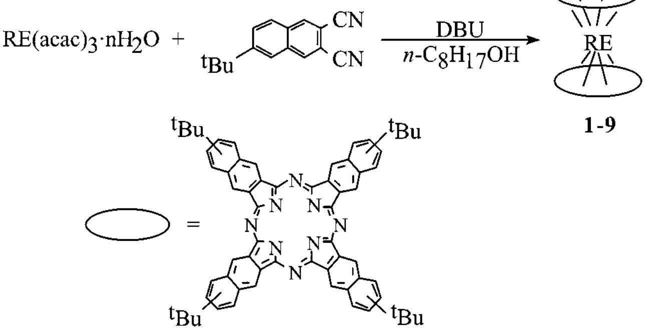
Introduction

Sandwich-type phthalocyaninato metal complexes, in which the large conjugated π systems are held in close proximity by metal ions, have found widespread applications in materials science.[1] The lutetium complex Lu(Pc)$_2$ (Pc = dianion of phthalocyanine), for example, is the first intrinsic molecular semiconductor with a conductivity of $5\cdot10^{-5}$ $\mathrm{O}^{-1}\mathrm{cm}^{-1}$ in thin films,[2] and shows promising electrochromic[3] and gas-sensing properties.[4] As the bulk characteristics of a molecular material are largely related to the properties of individual molecules, various modifications have been made on these sandwich compounds with the goal of improving their performance as advanced materials.

Long alkyl side chains[5] and crown-ether units[6] are two common functionalities added to the macrocycles to facilitate the formation of various mesophases and supramolecular structures. Another rational modification involves the replacement of the Pc ring with a naphthalocyaninato (Nc) ligand. Having more delocalized π systems, the resulting sandwich complexes should have distinct electronic and electrical properties. This has been demonstrated by L'Her et al. who show that the energy gap between the highest and lowest molecular orbitals (HOMO and LUMO) is much narrower for these Nc complexes than for the Pc counterparts.[7] Although these Nc-containing sandwich compounds appear to be promising, only a few lutetium Nc complexes have been known so far.[2,7,8] We have recently extended this series of compounds by reporting the first heteroleptic europium complexes having mixed Nc and porphyrinato ligands.[9] In this paper, we describe a new series of homoleptic Nc double-decker complexes of various rare earth metals. By changing the size of the metal center, the ring-to-ring separation can be altered, thereby providing another method of fine tuning the electronic properties of this novel class of complexes.

Results and Discussion

All the double-deckers **1−9** were prepared by base-promoted cyclization of 6-*tert*-butylnaphthalonitrile in refluxing *n*-octanol in the presence of 0.25 equiv. of RE(acac)$_3$ · *n* H$_2$O (RE = La, Ce, Pr, Nd, Eu, Gd, Tb, Y, Er) and DBU (Scheme 1). The use of additional naphthalonitrile also gave a significant amount of metal-free 2,3-naphthalocyanine H$_2$[Nc(*t*Bu)$_4$]$_2$ as a side product, as in the case of phthalocyanines,[10] which complicated the purification process. Changing the solvent to *n*-pentanol, *n*-hexanol, 1,2,4-trichlorobenzene, or 1-chloronaphthalene did not give the desired products, indicating that solvent is a critical factor for these reactions.



Scheme 1. Synthesis of rare earth double-deckers

The lutetium analog Lu[Nc(*t*Bu)$_4$](Pc) was reported previously, but only very few characterizing data were given.[11]

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As is the case in the Pc complexes,[10] these reactions afforded the protonated species REH[Nc(tBu)$_4$]$_2$ or the monoanions {RE[Nc(tBu)$_4$]$_2$}$^-$ as the initial products, which underwent oxidation in air to give the corresponding one-electron ring-oxidized complexes RE[Nc(tBu)$_4$]$_2$. The UV/Vis spectra of the dark-brown sandwich intermediates and the dark-blue/violet oxidized products were very different (see below), so the course of the reactions could be monitored by electronic absorption spectroscopy. The rate of conversion depended on the size of the metal center. Intermediates with a smaller metal center (heavy lanthanide) were more susceptible to oxidation than those with a larger metal ion (light lanthanide) which is consistent with the electrochemical data as described below. The oxidation was also found to be accelerated by the acidity of silica gel; only the ring-oxidized species **1−9** were isolated after chromatographic purification. It is worth noting that the yield of these double-deckers increases gradually with the size of the central metal ion (Table 1). This is in line with the RE(Por)$_2$ series (Por = dianion of *meso*-tetraphenylporphyrin or octaethylporphyrin),[12] but in contrast with the trend observed for RE(Pc)$_2$[13] and RE[Pc(OC$_8$H$_{17}$)$_8$]$_2$,[14] showing that bis(phthalocyaninato) complexes are easier to obtain and more stable with the smaller rare earth cations.

All these double-deckers, after being purified by column chromatography and recrystallization, were essentially pure, as shown by thin-layer chromatography. However, satisfactory analytical data could not be obtained which might be due to the presence of traces of impurities, which could not be completely removed by conventional purification methods.[15] The compounds, however, were unambiguously characterized with a range of spectroscopic methods. The matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra of all these double-deckers [except RE = Gd (**6**)] showed prominent signals attributed to the molecular ions, whose isotopic patterns were in good agreement with the respective simulated spectra (Table 1).

The electronic absorption spectra of **1−9** were recorded in CHCl$_3$/EtOH (1:1) and the data are summarized in Table 1. The spectral features resembled those of bis(phthalocyaninato) rare earth complexes (except RE = Ce),[10,16] except that all absorption bands were significantly red-shifted in the Nc series due to the extended conjugation. The spectra could thus be interpreted in a similar manner.

Figure 1 gives the UV/Vis spectra of the La, Eu, and Er double-deckers. It can be seen from this figure and Table 1, that while the B band (328−334 nm) remains relatively unshifted, both the Q band (767−799 nm) and the π-radical anion band (593−648 nm) are shifted to the red as the ionic radius of the tervalent metal cation increases from Er to La. A similar trend was also observed for the broad near-IR band (1818−2346 nm) which is characteristic of sandwich compounds having an unpaired electron in one of the rings. Similar to the Pc[17] and Por analogs,[12b,18] a linear correlation could be established between the wavenumbers of these absorptions and the RE^{III} ionic radii (Figure 2).[19] All the observation shows that as the ring-to-ring separation increases with the size of the metal ion, the π-π interactions between the Nc rings become weaker. Another interesting feature for these spectra is the intensities of the two visible bands in ca. 600−700 nm which are generally higher for sandwich compounds with a larger metal center.

Among these complexes, the Ce double-decker **2** is particularly interesting. To our knowledge, the metal center in all known Ce double-deckers including Ce(Por)$_2$,[20] Ce(Pc)$_2$,[21] and Ce(Pc)(Por)[22] is tetravalent. The presence of π-radical anion bands and the near-IR absorptions in the spectra of **2**, however, strongly suggests that the cerium center, like all the other rare earth ions, is tervalent and one of the Nc rings exists as a π-radical anion, i.e. Ce^{III}{[Nc(tBu)$_4$]$^{2-}$}{[Nc(tBu)$_4$]$^{\bullet-}$}. The electronic environment imposed by the Nc ligands seems to be unique to stabilize the Ce^{III} state and allow a facile one-electron ring-oxidation.

Upon addition of NaBH$_4$ to solutions of **1−9** in CHCl$_3$/EtOH (1:1), the absorption spectra were remarkably changed and the resulting spectra could be attributed to the monoanions {RE[Nc(tBu)$_4$]$_2$}$^-$ in which both macrocycles are dianionic. The spectral data for these anions are summarized in Table 2, and the spectra for the La, Eu, and Er double-deckers, after being treated with NaBH$_4$, are displayed in Figure 3.

It is interesting to note that while the B band (328−333 nm) is virtually unshifted upon reduction, the Q

Table 1. Reaction yields and spectral data for RE[Nc(tBu)$_4$]$_2$ (**1−9**)

Compound	Yield (%)	Mass (m/z)[a]	ν (Nc$^{\bullet-}$) (cm^{-1})	λ_{max} (nm)[b]							
La[Nc(tBu)$_4$]$_2$ (**1**)	69	2014	1314	334	437 (sh)	648	694	799	1052		2346
Ce[Nc(tBu)$_4$]$_2$ (**2**)	71	2015	1313	332	435 (sh)	640	691	790	1055		2190
Pr[Nc(tBu)$_4$]$_2$ (**3**)	63	2015	1316	331	437 (sh)	637	691	786	1057		2129
Nd[Nc(tBu)$_4$]$_2$ (**4**)	56	2019	1317	332	438 (sh)	633	690	783	1062	1681	2041
Eu[Nc(tBu)$_4$]$_2$ (**5**)	48	2027	1324	331	440 (sh)	627	689	776	1071	1674	1928
Gd[Nc(tBu)$_4$]$_2$ (**6**)	52	–[c]	1324	328	439 (sh)	596	688	774	1072	1674	1883
Tb[Nc(tBu)$_4$]$_2$ (**7**)	47	2034	1327	331	438 (sh)	622	687	772	1073	1671	1864
Y[Nc(tBu)$_4$]$_2$ (**8**)	43	1963	1329	330	443 (sh)	597	686	769	1081	1666	1822 (sh)
Er[Nc(tBu)$_4$]$_2$ (**9**)	35	2042	1329	330	448 (sh)	593	685	767	1084	1646	1818 (sh)

[a] Mass corresponding to the most abundant isotopic peak of the molecular ion. – [b] Recorded in CHCl$_3$/EtOH (1:1). – [c] The molecular ion peak could not be detected.

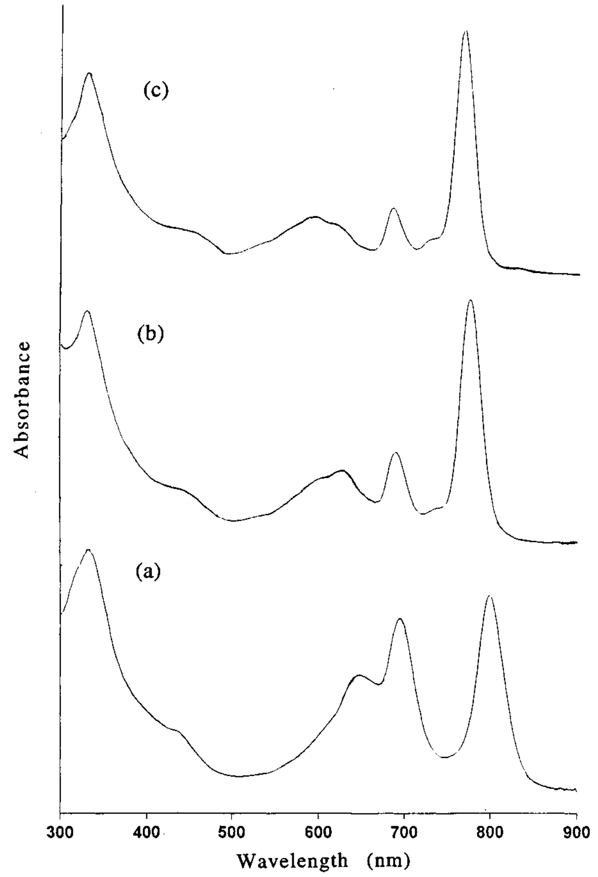

Figure 1. UV/Vis spectra of (a) La[Nc(*t*Bu)$_4$]$_2$ (**1**), (b) Eu[Nc(*t*Bu)$_4$]$_2$ (**5**), and (c) Er[Nc(*t*Bu)$_4$]$_2$ (**9**) in CHCl$_3$/EtOH (1:1)

Table 2. UV/Vis data for {RE[Nc(*t*Bu)$_4$]$_2$}$^-$ generated by adding NaBH$_4$ to **1−9** in CHCl$_3$/EtOH (1:1)

Compound	λ_{max} [nm]				
{La[Nc(*t*Bu)$_4$]$_2$}$^-$	333	400 (sh)	663	729	
{Ce[Nc(*t*Bu)$_4$]$_2$}$^-$	330	410 (sh)	658	727	782 (sh)
{Pr[Nc(*t*Bu)$_4$]$_2$}$^-$	328	417 (sh)	662	726	783 (sh)
{Nd[Nc(*t*Bu)$_4$]$_2$}$^-$	333	419 (sh)	659	725	787 (sh)
{Eu[Nc(*t*Bu)$_4$]$_2$}$^-$	332	413 (sh)	654	721	799
{Gd[Nc(*t*Bu)$_4$]$_2$}$^-$	329	418 (sh)	649 (sh)	719	802
{Tb[Nc(*t*Bu)$_4$]$_2$}$^-$	332	405 (sh)	654 (sh)	718	808
{Y[Nc(*t*Bu)$_4$]$_2$}$^-$	332	401 (sh)	657 (sh)	719	821
{Er[Nc(*t*Bu)$_4$]$_2$}$^-$	333	400 (sh)	647 (sh)	715	821

band is split for these anions (except RE = La) giving an intense and blue-shifted band at 715−729 nm together with a weak band at 782−821 nm. The energy difference between these Q bands, or the extend of splitting, increases as the metal center becomes smaller, reflecting the degree of HOMO-HOMO interactions of the two Nc rings. This fully agrees with that which is observed for the analogous Pc anions.[23]

As expected, the characteristic near-IR band was not seen for these anions, showing that the single-hole species **1−9** underwent a one-electron ring-reduction. It is also worth noting that the time for complete spectral changes again depends on the size of the metal center ranging from a few minutes (for RE = La, Ce) to more than one hour (for RE = Y, Er). This is in accord with our previous observation that the intermediates REH[Nc(*t*Bu)$_4$]$_2$ or {RE[Nc(*t*Bu)$_4$]$_2$}$^-$ with a smaller metal center are easier to undergo oxidation than those with a larger metal ion.

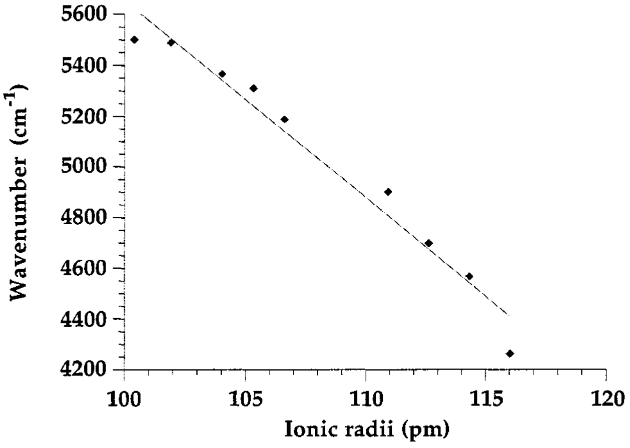

Figure 2. Plot of wavenumber of the near-IR bands of RE[Nc(*t*Bu)$_4$]$_2$ (**1−9**) as a function of the ionic radius of the RE^{III} ions[19]

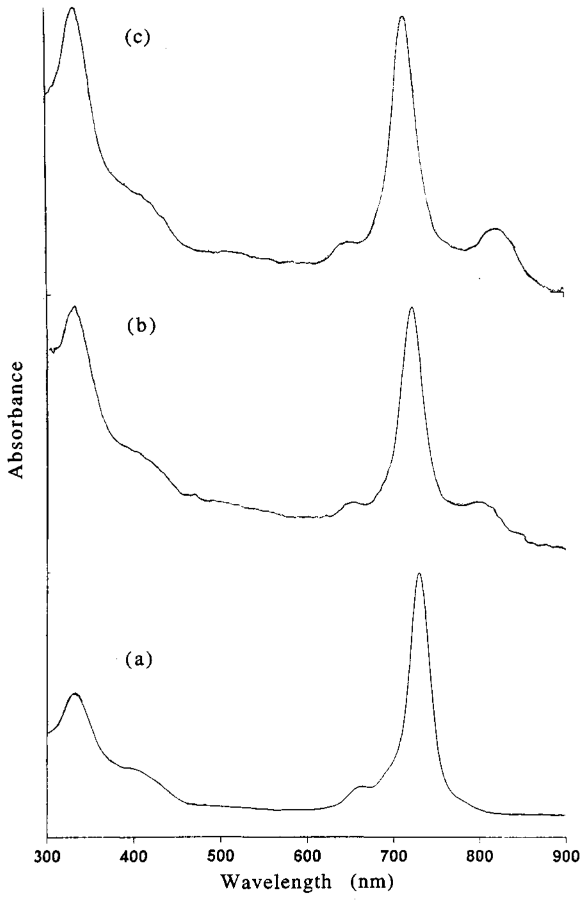

Figure 3. UV/Vis spectra of (a) La[Nc(*t*Bu)$_4$]$_2$ (**1**), (b) Eu[Nc(*t*Bu)$_4$]$_2$ (**5**), and (c) Er[Nc(*t*Bu)$_4$]$_2$ (**9**) in CHCl$_3$/EtOH (1:1) after the addition of NaBH$_4$

It is well-documented that all $RE^{III}(Pc)_2$ complexes show a strong IR band at ca. 1310 cm^{-1} which is a diagnostic band for the Pc π radical anion ($Pc^{\bullet -}$).[24] This band was also seen in this Nc series with the exact position (1313−1329 cm^{-1}) depending on the metal center (Table 1). It suggests that, due to the similar structure, the Nc π radical anion ($Nc^{\bullet -}$) also gives a marker IR band at roughly the same position as for $Pc^{\bullet -}$.

The electrochemical properties of the Nc double-deckers **1−9** in CH_2Cl_2 were studied by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The voltammograms generally displayed three quasi-reversible couples at 0.1−0.24, −(0.07−0.23), and −(1.18−1.24) V, all vs. the saturated calomel electrode (SCE), which could be assigned to the first one-electron oxidation and the first two one-electron reductions of the sandwich compounds, respectively. Additional couples could be revealed for some complexes, usually by DPV. Figure 4 gives the voltammograms of $Y[Nc(tBu)_4]_2$ (**8**) for exemplification and the results are tabulated in Table 3.

Similar to what is observed with the Pc analogs [cation][$RE(Pc)_2$] (cation = NBu_4,[25] Li[23]), the first oxidation and the first reduction potentials are linearly dependent on the ionic radius of the metal center (Figure 5), while the other redox processes are rather insensitive to the metal ions. The separation between these two potentials (0.28−0.34 V), which reflects the HOMO−LUMO gap of the complexes, is comparable with that reported for Lu(2,3-$Nc)_2$ (0.29 V) and Lu(1,2-$Nc)_2$ (0.33 V),[7] but significantly smaller than that for the Pc counterparts (ca. 0.40 V).[10]

Table 3. Electrochemical data for $RE[Nc(tBu)_4]_2$ (**1−9**)[a]

Compound	*E* (oxd.2)	*E* (oxd.1)	*E* (red.1)	*E* (red.2)	*E* (red.3)
$La[Nc(tBu)_4]_2$ (**1**)	−	0.24	−0.07	−1.20[b]	−1.59[b]
$Ce[Nc(tBu)_4]_2$ (**2**)	0.87[b,c]	0.20	−0.08	−1.18	−1.50
$Pr[Nc(tBu)_4]_2$ (**3**)	1.06[b]	0.18	−0.12	−1.19	−
$Nd[Nc(tBu)_4]_2$ (**4**)	1.10	0.17	−0.14	−1.21	−1.51
$Eu[Nc(tBu)_4]_2$ (**5**)	−	0.13	−0.21	−1.24	−
$Gd[Nc(tBu)_4]_2$ (**6**)	−	0.16	−0.15	−1.18	−1.50[b]
$Tb[Nc(tBu)_4]_2$ (**7**)	1.13[b]	0.13	−0.20	−1.19	−1.54[b]
$Y[Nc(tBu)_4]_2$ (**8**)	1.05[b]	0.07	−0.25	−1.23	−1.62[b]
$Er[Nc(tBu)_4]_2$ (**9**)	−	0.10	−0.23	−1.19	−

[a] Recorded with $[Bu_4N][ClO_4]$ as electrolyte in CH_2Cl_2 (0.1 M) at ambient temperature. Potentials were obtained by cyclic voltammetry with a scan rate of 100 mV s^{-1}, and are expressed as half-wave potentials ($E_{1/2}$) in volts relative to SCE, unless otherwise stated. − [b] By differential pulse voltammetry. − [c] May also contain the Ce^{III}/Ce^{IV} couple.

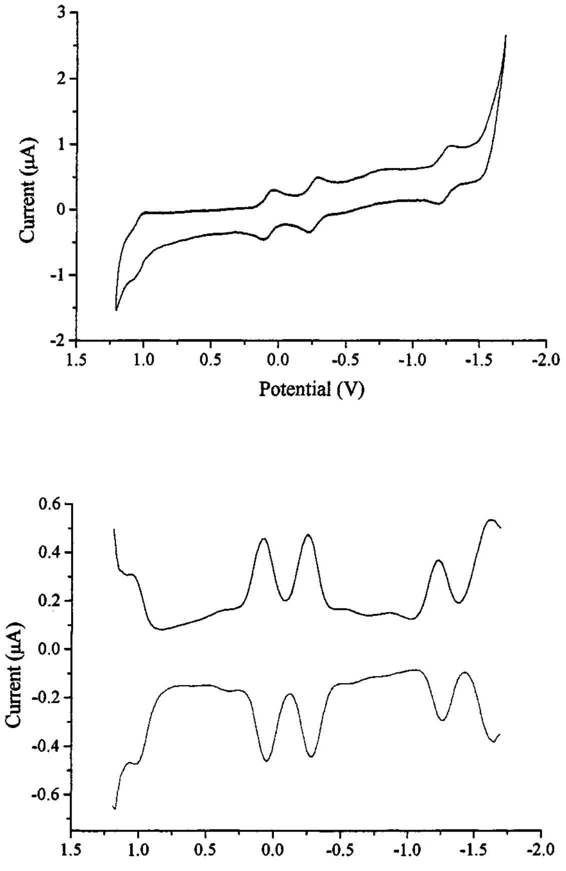

Figure 4. Cyclic voltammogram (upper) and differential pulse voltammogram (lower) of $Y[Nc(tBu)_4]_2$ (**8**) in CH_2Cl_2 containing 0.1 M $[Bu_4N][ClO_4]$ at a scan rate of 100 mV s^{-1}

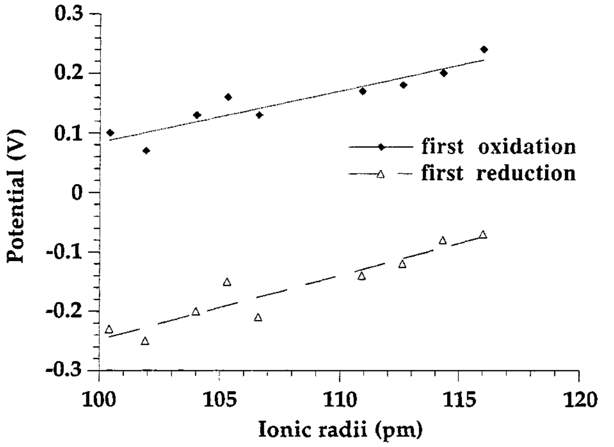

Figure 5. Redox potentials of $RE[Nc(tBu)_4]_2$ (**1−9**) as a function of the ionic radius of the RE^{III} ions[19]

The electrochemical behavior of $Ce[Nc(tBu)_4]_2$ (**2**) is of particular interest, as the Ce^{III} metal center may also undergoes an oxidation to Ce^{IV}. However, apart from the ring-based redox couples, no additional couple could be observed. As the peak to peak separation (Δ*E*) for the second oxidation of **2** was large (270 mV), as shown in its cyclic voltammogram, and the differential pulse voltammogram showed that the peak was broad and slightly split, it is likely that the Ce^{III}/Ce^{IV} couple is also embedded at this position. It has been found that the reversibility of the Ce^{III}/Ce^{IV} couple for sandwich-type compounds is usually poor, probably because the electron exchange between the electrode and the Ce center is retarded by the bulky ligands, which also participate in the electron transfer.[26] Our assignment thus seems to be in line with the previous findings.

Experimental Section

n-Octanol was distilled from sodium. The electrolyte $[Bu_4N][ClO_4]$ was recrystallized from dry acetone three times prior to use. All other reagents and solvents were of reagent grade and used as received. 6-*tert*-Butylnaphthalonitrile[27] and $RE(acac)_3 \cdot n\,H_2O$[28] were prepared by previously described methods. − UV/Vis: Hitachi U-3300. − Near-IR: Hitachi U-3100. − IR: Perkin−Elmer 1600. − MALDI-TOF-MS: Bruker BIFLEX III, α-cyano-4-hydroxycinnamic acid as matrix. − Electrochemical measurements were carried out with a BAS CV-50 W voltammetric analyzer. The cell comprised inlets for a platinum-sphere working electrode, a silver-wire counter electrode and an $Ag/AgNO_3$ (0.1 M in MeCN) reference electrode which was connected to the solution by a Luggin capillary whose tip was placed close to the working electrode.[29] Typically, a 0.1 M solution of $[Bu_4N][ClO_4]$ in CH_2Cl_2 containing the sample was purged with nitrogen for 20 min, then the voltammograms were recorded at ambient temp. Potentials were referenced to the Ag/Ag^+ couple in MeCN, which was taken as +0.31 V vs. SCE as determined for this system previously using ferrocene as an internal standard.[30]

General Procedure for the Preparation of $RE[Nc(tBu)_4]_2$ (1−9): A mixture of $RE(acac)_3 \cdot n\,H_2O$ (0.10 mmol), 6-*tert*-butylnaphthalonitrile (93 mg, 0.40 mmol), and DBU (40 mg, 0.26 mmol) in *n*-octanol (2 mL) was refluxed overnight (> 18 h) under a slow stream of nitrogen. The dark brown mixture was cooled to room temperature and the volatiles were removed under reduced pressure. The residue was purified by column chromatography on a silica gel, with $CHCl_3$ as eluent to develop a blue band containing the desired double-decker. The product obtained by this method was further purified by the same chromatographic procedure, followed by recrystallization from a mixture of $CHCl_3$ and MeOH to give a dark blue/violet powder.

Acknowledgments

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