# Heteroleptic Rare Earth Double-Decker Complexes with Porphyrinato and 2,3-Naphthalocyaninato Ligands − Preparation, Spectroscopic Characterization, and Electrochemical Studies

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**Keywords:** Lanthanides / Actinides / Porphyrins / Phthalocyanines / Sandwich complexes

A series of RE(Nc)(TBPP) (**1**–**12**) complexes [RE = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Y, Ho, Er, Tm; Nc = 2,3-naphthalocyaninate; TBPP = *meso*-tetrakis(4-*tert*-butylphenyl)porphyrinate] and Eu[Nc($t$Bu)$_4$](TClPP) [Nc($t$Bu)$_4$ = tetra(*tert*-butyl)-2,3-naphthalocyaninate; TClPP = *meso*-tetrakis(4-chlorophenyl)porphyrinate] (**13**) have been prepared by a one-pot procedure which involves the treatment of RE(acac)$_3$·$n$H$_2$O (acac = acetylacetonate) with the corresponding metal-free porphyrins and naphthalonitriles in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in *n*-octanol. These novel double-deckers have been spectroscopically characterized. A one-electron reduction and three one-electron oxidations have been revealed by electrochemical methods. The potentials of all these processes depend linearly on the ionic radii of the central metal ions, giving a relatively large potential difference (0.50–0.57 V) between the first oxidation and the first reduction processes.

## Introduction

Tetrapyrrole derivatives such as porphyrins and phthalocyanines are able to form sandwich complexes with a range of metal ions including rare earths, actinides, group 4 transition metals, and some main group elements (e.g. Bi, In, Sn).[1] The resulting double- and triple-decker complexes possess intriguing and unique electronic and optical properties which render them useful in materials science. Bis(phthalocyaninato) rare earth complexes RE(Pc)$_2$,[2] for example, can be used in electrochromic devices,[3] field-effect transistors,[4] gas and herbicide sensors,[5] and optically addressed spatial light modulators.[6] While the chemistry and properties of both homoleptic and heteroleptic complexes with these two types of ligands have been extensively studied, little is known about the naphthalocyanine analogues which contain a more delocalized π system. It is expected that sandwich complexes containing these larger macrocyclic ligands should have distinct properties compared with the Pc counterparts owing to the narrower energy gap between the highest occupied and the lowest unoccupied molecular orbitals (HOMO and LUMO).[7,8]

A number of naphthalocyanine-containing double-[8,9] and triple-decker[8b,10] complexes have been reported, but virtually all of them are confined to lutetium complexes. Sandwich-type Nc[2] complexes of other metals have only appeared very recently.[11] It has been well documented that the electronic properties of these sandwich complexes depend on the ring-to-ring separation, which can be altered by the size of the metal center.[12] Studies of a whole series of analogous complexes with different metal centers are therefore of special importance.

We have recently developed an efficient synthetic pathway for heteroleptic sandwich complexes which involves a cyclic tetramerization of dicyanobenzenes using RE(ring)(acac) [RE = Eu, Y; ring = Pc, Por] as the template.[2,13] This method has been utilized to prepare the first hetereoleptic Nc and Por complexes Eu(Nc)(TPyP) and Eu[Nc(SC$_{12}$H$_{25}$)$_8$](TPyP).[2,14] We report herein an extension of this work which involves a simplified one-pot procedure leading to a series of (naphthalocyaninato)(porphyrinato) rare earth double-decker complexes. The spectroscopic and electrochemical properties of these novel sandwich compounds are also described herein.

## Results and Discussion

The preparation of the mixed double-deckers RE(Nc)(TBPP) (RE = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Y, Ho, Er, Tm) (**1**−**12**) was mainly based on our previously described procedure,[2,13,14] but the prior generation of the half-sandwich complexes RE(TBPP)(acac) was found to be not necessary. Thus a one-pot procedure involving the metal-free porphyrin H$_2$(TBPP), RE(acac)$_3$·$n$H$_2$O, naphthalonitrile, and DBU in *n*-octanol could also lead to the desired products (Scheme 1). Similar to the RE(Por)$_2$ [Por = TPP or OEP][2,12b,15] and RE[Nc($t$Bu)$_4$]$_2$ series,[2,11b] the yield of these mixed sandwiches decreases gradually with the size of the central metal ion (Table 1), showing that, for all these double-deckers, complexes with a smaller metal center are more difficult to obtain, probably due to

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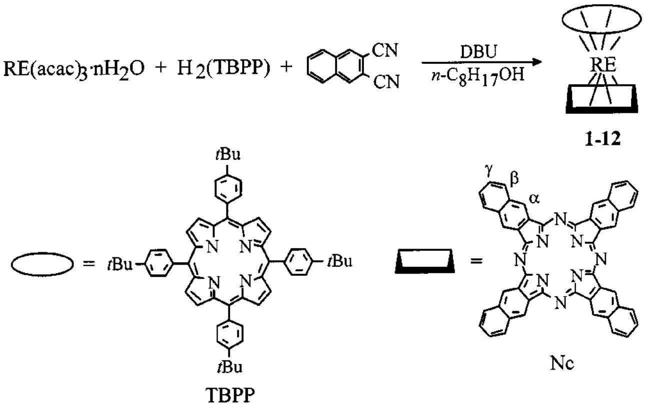
an increase in steric compression of the two macrocyclic ligands. The europium analogue Eu[Nc(*t*Bu)$_4$](TClPP) (**13**) was prepared similarly using the metal-free porphyrin H$_2$(TClPP)[2] and 6-*tert*-butylnaphthalonitrile.



Scheme 1. Synthesis of heteroleptic rare earth double-deckers

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. This might be due to the presence of traces of impurities which could not be completely removed by conventional purification methods.[16] 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 compounds showed prominent signals attributed to the molecular ions, of which the isotopic patterns were in good agreement with the respective simulated spectra (Table 1).

Figure 1 shows the absorption spectrum of Pr(Nc)(TBPP) (**2**), which is representative for the spectra of this series of compounds. The spectral features resembled those of the Pc counterparts RE$^{III}$(Pc)(Por)[12c,13b,13c,17] and the previously reported Nc complexes Eu(Nc)(TPyP) and Eu[Nc(SC$_{12}$H$_{25}$)$_8$](TPyP),[14] and thus could be assigned in a similar manner. As shown in Table 1, the Nc B band (323−329 nm) and the TBPP B band (414−424 nm ) are rather insensitive to the metal center. By analogy with the Pc analogues RE$^{III}$(Pc)(Por), the weak absorption at 479−482 nm and the near-IR band at 1025−1146 nm may arise from a hole localized on the Nc ring. The latter signal shifts gradually to the red as the size of the tervalent metal center decreases from La to Tm, which was also seen for the Pc counterparts.[12c] This observation suggests that this near-IR absorption should not be due to an intramolecular ring-to-ring charge-transfer transition as proposed previously.[14,18] For such a transition, a reverse trend should be observed because the π-π interactions between the rings will become stronger when the ring-to-ring separation decreases along the series.[12b,12c,19] This charge-transfer transition band, however, could not be detected for these complexes up to 2400 nm and the reason remains unclear at this stage. Another remarkable feature for these Nc double-deckers is the relatively intense Q bands at 549−583 and 612−635 nm, which are almost invisible in the Pc analogues.[12c,13b,13c,17] Both of these signals experience a hypsochromic shift when the size of the metal center decreases.

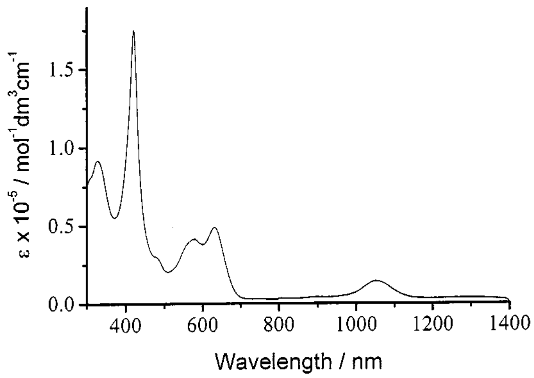


Figure 1. Electronic absorption spectrum of Pr(Nc)(TBPP) (**2**) in CHCl$_3$

The presence of Nc π radical anion (Nc$^{\cdot-}$) in these single-hole complexes was also corroborated by the strong IR marker band at 1319−1325 cm$^{-1}$ (Table 1),[11b,11c] which is also a diagnostic band for the Pc π radical anion (Pc$^{\cdot-}$).[20] Due to the presence of this unpaired electron, these complexes, like other single-hole analogues, are usually NMR

Table 1. Reaction yields and spectral data for the double-deckers **1**−**13**

| Compound | Yield (%) | Mass ($m/z$)[a] | $v$ (Nc$^{\bullet-}$) (cm$^{-1}$) | | | $\lambda_{max}$ (nm) (log ε)[b] | | | |
|---|---|---|---|---|---|---|---|---|---|
| La(Nc)(TBPP) (**1**) | 73 | 1690 | 1319 | 323 (4.95) | 424 (5.19) | 482 (4.40) | 583 (4.57) | 635 (4.67) | 1025 (4.10) |
| Pr(Nc)(TBPP) (**2**) | 76 | 1692 | 1319 | 329 (4.96) | 421 (5.24) | 480 (4.47) | 579 (4.62) | 630 (4.69) | 1053 (4.16) |
| Nd(Nc)(TBPP) (**3**) | 71 | 1694 | 1320 | 327 (4.94) | 419 (5.27) | 481 (4.46) | 574 (4.59) | 628 (4.65) | 1064 (4.10) |
| Sm(Nc)(TBPP) (**4**) | 70 | 1703 | 1320 | 325 (4.94) | 419 (5.21) | 481 (4.47) | 563 (4.59) | 622 (4.63) | 1084 (4.10) |
| Eu(Nc)(TBPP) (**5**) | 67 | 1703 | 1322 | 326 (4.91) | 417 (5.08) | 480 (4.45) | 561 (4.58) | 621 (4.60) | 1096 (4.09) |
| Gd(Nc)(TBPP) (**6**) | 63 | 1707 | 1322 | 327 (5.00) | 417 (5.17) | 481 (4.54) | 558 (4.67) | 620 (4.69) | 1104 (4.17) |
| Tb(Nc)(TBPP) (**7**) | 50 | 1708 | 1323 | 323 (4.98) | 417 (5.13) | 489 (4.52) | 555 (4.64) | 617 (4.66) | 1120 (4.14) |
| Dy(Nc)(TBPP) (**8**) | 42 | 1713 | 1323 | 327 (4.92) | 417 (5.12) | 480 (4.46) | 555 (4.69) | 616 (4.58) | 1131 (4.08) |
| Y(Nc)(TBPP) (**9**) | 43 | 1639 | 1323 | 326 (4.91) | 419 (5.11) | 479 (4.45) | 552 (4.58) | 614 (4.57) | 1131 (4.09) |
| Ho(Nc)(TBPP) (**10**) | 38 | 1715 | 1324 | 327 (4.84) | 416 (5.17) | 480 (4.38) | 553 (4.52) | 615 (4.50) | 1132 (4.00) |
| Er(Nc)(TBPP) (**11**) | 32 | 1718 | 1323 | 327 (4.90) | 414 (5.03) | 481 (4.44) | 550 (4.56) | 613 (4.55) | 1139 (4.06) |
| Tm(Nc)(TBPP) (**12**) | 29 | 1719 | 1325 | 328 (4.89) | 415 (5.01) | 482 (4.44) | 549 (4.58) | 612 (4.55) | 1146 (4.10) |
| Eu[Nc(*t*Bu)$_4$](TClPP) (**13**) | 66 | 1841 | 1327 | 334 (4.97) | 419 (5.20) | 479 (4.52) | 555 (4.52) | 642 (4.67) | 1072 (4.24) |

[a] Mass corresponding to the most abundant isotopic peak of the molecular ion. − [b] Recorded in CHCl$_3$.

Table 2. $^1$H NMR spectroscopic data for the reduced form of selected double-deckers in $CDCl_3$/[$D_6$]DMSO (1:1)

| Compound | NMR spectroscopic data[a] |
|---|---|
| La(Nc)(TBPP) (**1**)[b] | 8.91 (s, 8 H, $H_\alpha$ ), 7.97 (dd, $J$ = 3.0, 6.0 Hz, 8 H, $H_\beta$), 7.44 (s, 8 H, $H_{pyr}$), 7.26 (br s overlapping with the residue $CHCl_3$ peak, $H_\gamma$), 6.47 (br s, 4 H, $C_6H_4$), 6.17 (br s, 4 H, $C_6H_4$), 5.95 (br s, 4 H, $C_6H_4$), 5.54 (br s, 4 H, $C_6H_4$), 0.68 (s, 36 H, *t*Bu) |
| Nd(Nc)(TBPP) (**3**)[b] | 8.02 (br s, 12 H, $H_\alpha$ and $C_6H_4$), 7.73 (dd, $J$ = 3.0, 6.0 Hz, 8 H, $H_\beta$), 7.62 (s, 8 H, $H_{pyr}$), 7.43 (dd, $J$ = 3.0, 6.0 Hz, 8 H, $H_\gamma$), 7.25 (br s, 4 H, $C_6H_4$), 6.82 (br s, 4 H, $C_6H_4$), 4.59 (br s, 4 H, $C_6H_4$), 0.79 (s, 36 H, *t*Bu) |
| Sm(Nc)(TBPP) (**4**)[c] | 8.98 (s, 8 H, $H_\alpha$), 8.27 (dd, $J$ = 3.3, 5.7 Hz, 8 H, $H_\beta$), 7.47 (dd, $J$ = 3.3, 5.7 Hz, 8 H, $H_\gamma$), 7.26 (s, 8 H, $H_{pyr}$), 6.88 (br s, 4 H, $C_6H_4$), 6.68 (br s, 4 H, $C_6H_4$), 5.75 (br s, 4 H, $C_6H_4$), 5.22 (br s, 4 H, $C_6H_4$), 1.10 (s, 36 H, *t*Bu) |
| Eu(Nc)(TBPP) (**5**)[c] | 10.95 (s, 8 H, $H_\alpha$), 10.34 (br s, 4 H, $C_6H_4$), 9.36 (dd, $J$ = 3.3, 6.0 Hz, 8 H, $H_\beta$), 8.31 (dd, $J$ = 3.3, 6.0 Hz, 8 H, $H_\gamma$), 7.50 (br s, 4 H, $C_6H_4$), 7.28 (br s, 12 H, $H_{pyr}$ and $C_6H_4$), 6.30 (br s, 4 H, $C_6H_4$), 1.78 (s, 36 H, *t*Bu) |
| Eu[Nc(*t*Bu)$_4$](TClPP) (**13**)[c] | 10.79−11.17 (m, 8 H, $H_\alpha$), 10.19 (br s, 4 H, $C_6H_4$), 9.29−9.37 (m, 8 H, $H_\beta$), 8.45−8.49 (m, 4 H, $H_\gamma$), 7.34 (br s, 4 H, $C_6H_4$), 7.20−7.24 (br s, 12 H, $H_{pyr}$ and $C_6H_4$), 6.04 (br s, 4 H, $C_6H_4$), 2.10 (s, 36 H, *t*Bu) |

[a] Given as: chemical shift (δ) (multiplicity, relative intensity and assignment) where s = singlet, br s = broad signal, d = doublet, m = multiplet. − [b] Recorded in the presence of $NaBH_4$. − [c] Recorded in the presence of hydrazine hydrate.

silent. We employed the strategy developed by L'Her[8a,21] using hydrazine hydrate or $NaBH_4$ as the reducing agent to generate the monoanionic [RE$^{III}$(ring-1)(ring-2)]$^-$ or protonated RE$^{III}$H(ring-1)(ring-2) species, in which both the macrocycles become diamagnetic. We were able to obtain satisfactory $^1$H NMR spectroscopic data for the reduced form of the La, Nd, Sm, and Eu double-deckers (Table 2). The spectra for the Pr, Dy, and Tm analogues, however, were hard to interpret which could be related to the different magnetic properties of the metal ions. It is worth noting that NMR spectroscopic data for such sandwich-type complexes having a paramagnetic metal center are rare indeed.[1]

Figure 2 shows the $^1$H NMR spectra of the two Eu$^{III}$ double-deckers **5** and **13** in the presence of hydrazine hydrate. It can be seen that the Nc α protons of the reduced form of **5** resonate as a singlet at δ = 10.95 because of the symmetrical Nc ring. The corresponding signal for **13** appears as a multiplet at δ = 10.79−11.17 due to the presence of a mixture of constitutional isomers and the nonequivalence of these α protons. The assignment for the Nc β and γ protons' signals (at ca. δ = 9.3 and 8.4, respectively) for these two compounds is supported by the smaller integration observed for the latter for **13**. Similar to other sandwiches containing a TPP ligand or its derivatives,[1b,17b,22] four distinct broad signals appear for the *ortho* and *meta* aryl protons in both cases, suggesting that there is a restricted rotation about the C(*meso*)−C(aryl) bonds.

The electrochemical behavior of all the double-deckers **1−13** in $CH_2Cl_2$ was investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The voltammograms generally displayed four quasi-reversible couples assignable to the first three one-electron oxidations and the first one-electron reduction of the sandwich compounds (Table 3); all of them are ligand-based processes. Figure 3 shows the cyclic voltammogram of Sm(Nc)(TBPP) (**4**), which is typical. The second one-electron reduction process, which was commonly seen in related double-deckers, could not be revealed for these complexes under the present conditions due to a solvent breakdown. As shown in Figure 4, the potentials of all these processes are linearly dependent on the ionic radius of the metal center, with a positive gradient for the first oxidation and the first reduction processes and a negative gradient for the second and third oxidation processes. The linear correlation observed between these potentials and the ionic radii of the central metals indicates that π-π interactions are probably present in these heteroleptic double-deckers. The potential difference between the first oxidation and the first reduction

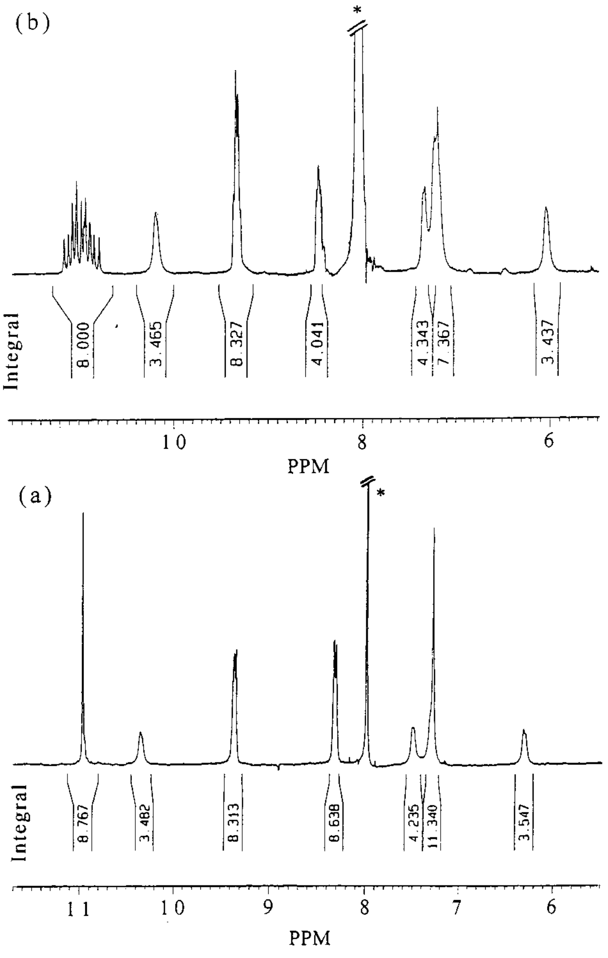


Figure 2. $^1$H NMR spectra of (a) Eu(Nc)(TBPP) (**5**) and (b) Eu[Nc(*t*Bu)$_4$](TClPP) (**13**) in the presence of a small amount of hydrazine hydrate in $CDCl_3$/[$D_6$]DMSO (1:1); * indicates the signal for hydrazine hydrate

Table 3. Electrochemical data for the double-deckers **1−13**

| Compound[a] | $E_{1/2}$ (oxd.3) | $E_{1/2}$ (oxd.2) | $E_{1/2}$ (oxd.1) | $E_{1/2}$ (red.1) |
|---|---|---|---|---|
| La(Nc)(TBPP) (**1**) | 1.32 | 1.02 | 0.55 | 0.05 |
| Pr(Nc)(TBPP) (**2**) | 1.35 | 1.04 | 0.54 | 0.02 |
| Nd(Nc)(TBPP) (**3**) | 1.38 | 1.05 | 0.54 | 0.04 |
| Sm(Nc)(TBPP) (**4**) | 1.40 | 1.08 | 0.52 | 0.00 |
| Eu(Nc)(TBPP) (**5**) | 1.38[b] | 1.04 | 0.46 | -0.06 |
| Gd(Nc)(TBPP) (**6**) | 1.41 | 1.08 | 0.49 | -0.04 |
| Tb(Nc)(TBPP) (**7**) | 1.41[b] | 1.11 | 0.48 | -0.07 |
| Dy(Nc)(TBPP) (**8**) | 1.44 | 1.09 | 0.47 | -0.06 |
| Y(Nc)(TBPP) (**9**) | 1.45 | 1.09 | 0.44 | -0.07 |
| Ho(Nc)(TBPP) (**10**) | 1.45 | 1.10 | 0.45 | -0.07 |
| Er(Nc)(TBPP) (**11**) |  | 1.12 | 0.44 | -0.10 |
| Tm(Nc)(TBPP) (**12**) | 1.47 | 1.11 | 0.42 | -0.10 |
| Eu[Nc(*t*Bu)$_4$](TClPP) (**13**) | 1.43[b] | 1.16 | 0.53 | -0.04 |

[a] Recorded with $[Bu_4N][PF_6]$ 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.

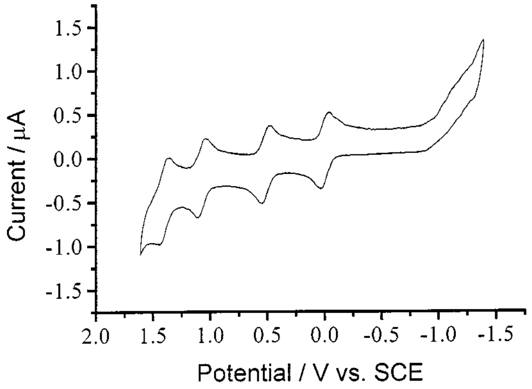


Figure 3. Cyclic voltammogram of Sm(Nc)(TBPP) (**4**) in $CH_2Cl_2$ containing 0.1 M $[Bu_4N][PF_6]$ at a scan rate of 100 mV $s^{-1}$

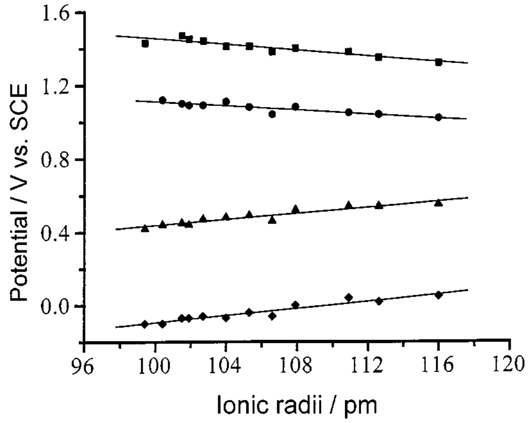


Figure 4. Redox potentials of RE(Nc)(TBPP) (**1−12**) as a function of the ionic radii of the $RE^{III}$ ions;[28] ◆ = first reduction, ▲ = first oxidation, ● = second oxidation, ■ = third oxidation

is rather insensitive to the metal center with a value ranging from 0.50 to 0.57 V. These values, which can reflect the HOMO−LUMO gap of the complexes, are slightly larger than those of the Pc counterparts $RE^{III}$(Pc)(TPP) (0.45−0.48 V)[12c] and are significantly larger than those of the bis(naphthalocyaninato) analogues (0.29−0.37 V).[8,11b,11c]

In summary, we have prepared a series of rare heteroleptic rare-earth double-decker complexes containing porphyrinato and 2,3-naphthalocyaninato ligands by a simple one-pot procedure. It is envisaged that this methodology can be extended readily to other heteroleptic sandwich systems. Having a more delocalized macrocyclic ligand, these complexes have been found to exhibit distinct spectroscopic and electrochemical properties compared with those of the Pc counterparts.

## Experimental Section

*n*-Octanol was distilled from sodium. The electrolyte $[Bu_4N][PF_6]$ was recrystallized twice from tetrahydrofuran prior to use. All other reagents and solvents were of reagent grade and used as received. Naphthalonitrile,[23] 6-*tert*-butylnaphthalonitrile,[23] $H_2$(TBPP),[24] $H_2$(TClPP),[24] and RE(acac)$_3$·$n$H$_2$O[25] 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.[26] Typically, a 0.1 M solution of $[Bu_4N][PF_6]$ 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. the saturated calomel electrode (SCE) as determined for this system previously using ferrocene as an internal standard.[27]

**General Procedure for the Preparation of RE(Nc)(TBPP) (1−12) and Eu[Nc(*t*Bu)$_4$](TClPP) (13):** A mixture of RE(acac)$_3$·$n$H$_2$O (0.10 mmol), $H_2$(TBPP) or $H_2$(TClPP) (0.05 mmol), naphthalonitrile or 6-*tert*-butylnaphthalonitrile (0.40 mmol), and DBU (50 mg, 0.33 mmol) in *n*-octanol (4 mL) was refluxed overnight (>18 h) under nitrogen to give a dark green solution. The volatiles were then removed under reduced pressure and the residue was chromatographed on a silica gel column with $CH_2Cl_2$/hexane (1:2) as eluent to remove the unchanged metal-free porphyrin as the first fraction. The column was further eluted with $CHCl_3$ to give a greenish blue band containing the desired double-decker. The crude product was further purified by the same chromatographic procedure followed by recrystallization from a mixture of $CHCl_3$ and MeOH to give a dark blue powder. The yields together with the characterizing data for these complexes are given collectively in Table 1.

## Acknowledgments

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[2] Abbreviations used for tetrapyrrole derivatives: Nc = 2,3-naphthalocyaninate, $Nc(tBu)_4$ = tetra(*tert*-butyl)-2,3-naphthalocyaninate, $Nc(SC_{12}H_{25})_8$ = 3,4,12,13,21,22,30,31-octakis(dodecylthio)-2,3-naphthalocyaninate, OEP = octaethylporphyrinate, Pc = phthalocyaninate, Por = general porphyrinate, TBPP = *meso*-tetrakis(4-*tert*-butylphenyl)porphyrinate, TClPP = *meso*-tetrakis(4-chlorophenyl)porphyrinate, TPP = *meso*-tetraphenylporphyrinate, TPyP = *meso*-tetra(4-pyridyl)-porphyrinate.

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