

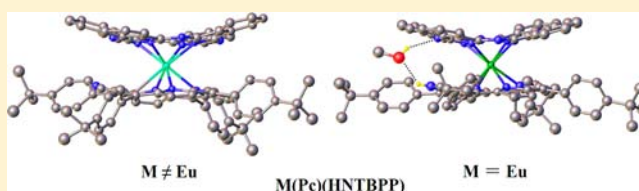
Constructing Sandwich-Type Rare Earth Double-Decker Complexes with N-Confused Porphyrinato and Phthalocyaninato Ligands

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Supporting Information

ABSTRACT: Reaction of the half-sandwich complexes $M^{III}(Pc)(acac)$ ($M = La, Eu, Y, Lu$; $Pc =$ phthalocyaninate; $acac =$ acetylacetonate) with the metal-free N-confused 5,10,15,20-tetrakis[(4-*tert*-butyl)phenyl]porphyrin (H_2NTBPP) or its N2-position methylated analogue $H(CH_3)NTBPP$ in refluxing 1,2,4-trichlorobenzene (TCB) led to the isolation of $M^{III}(Pc)(HNTBPP)$ ($M = La, Eu, Y, Lu$) or $Y^{III}(Pc)[(CH_3)NTBPP]$ in

8–15% yield. These represent the first examples of sandwich-type rare earth complexes with N-confused porphyrinato ligands. The complexes were characterized with various spectroscopic methods and elemental analysis. The molecular structures of four of these double-decker complexes were also determined by single-crystal X-ray diffraction analysis. In each of these complexes, the metal center is octa-coordinated by four isoindole nitrogen atoms of the Pc ligand, three pyrrole nitrogen atoms, and the inverted pyrrole carbon atom of the HNTBPP or $(CH_3)NTBPP$ ligand, forming a distorted coordination square antiprism. For $Eu^{III}(Pc)(HNTBPP)$, the two macrocyclic rings are further bound to a CH_3OH molecule through two hydrogen bonds formed between the hydroxyl group of CH_3OH and an aza nitrogen atom of the Pc ring or the inverted pyrrole nitrogen atom of the HNTBPP ring, respectively. The location of the acidic proton at the inverted pyrrole nitrogen atom (N2) of the protonated double-deckers was revealed by 1H NMR spectroscopy.



INTRODUCTION

Porphyrins and their non-naturally occurring analogues phthalocyanines have been intensively studied over the last few decades due to their wide range of biological relevance and industrial applications.¹ In 1994, an interesting porphyrin isomer, namely, 2-aza-21-carbaporphyrin [also known as N-confused porphyrin (NCP) or inverted porphyrin] was reported, which also has a $C_{20}N_4$ porphyrin framework, but one of the pyrrole rings is connected to the neighboring meso-carbons at the α and β' positions.² Since then, this family of compounds has received considerable attention. Because of the versatile binding modes and redox states associated with the inverted pyrrole moiety, a large number of NCP coordination compounds of various transition and main group metals have been reported.^{3–5} However, to the best of our knowledge, sandwich-type rare earth complexes with NCP ligands have not yet been reported.

It is well-known that both porphyrinato and phthalocyaninato ligands can form sandwich-type complexes with various rare earth metal ions.⁶ These complexes exhibit great potential in the fields of molecular magnets and molecular electronics.^{7,8} As a result, this class of compounds remains as a current research focus. As an extension of our works in this area, we describe herein the synthesis, spectroscopic characterization, and structures of a series of rare earth double-decker complexes with mixed phthalocyaninato and regular/methylated N-confused porphyrinato ligands in the form of $M^{III}(Pc)(HNTBPP)$ ($M = La,$

Eu, Y, Lu ; $Pc =$ phthalocyaninate; $NTBPP =$ N-confused 5,10,15,20-tetrakis[(4-*tert*-butyl)phenyl]porphyrinate} (1–4) and $Y^{III}(Pc)[(CH_3)NTBPP]$ {(CH₃)NTBPP = methylated N-confused 5,10,15,20-tetrakis[(4-*tert*-butyl)phenyl]porphyrinate} (5). These represent the first examples of sandwich-type rare earth complexes with N-confused porphyrinato ligands. Attempts were also made to reveal the location of the acidic proton attached to the inverted pyrrole nitrogen atom.

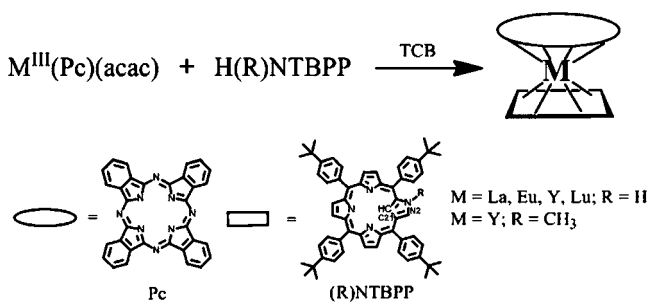
RESULTS AND DISCUSSION

Synthesis of Mixed Double-Deckers 1–5. Treatment of the half-sandwich complex $La^{III}(Pc)(acac)$ ($acac =$ acetylacetonate), generated in situ from the reaction of $La(acac)_3 \cdot nH_2O$ and Li_2Pc , with the metal-free N-confused porphyrin H_2NTBPP in refluxing 1,2,4-trichlorobenzene (TCB) for 4 h, led to the formation of mixed (phthalocyaninato)(N-confused porphyrinato) lanthanum(III) double-decker complex $La^{III}(Pc)(HNTBPP)$ (1) (Scheme 1) in 10% yield. By following the same procedure and using the isolated half-sandwich complexes $M^{III}(Pc)(acac)$ ($M = Eu, Y, Lu$) as the starting materials, the double-deckers $M^{III}(Pc)(HNTBPP)$ [$M = Eu$ (2), Y (3), Lu (4)] were also obtained. These compounds were soluble in common organic solvents such as $CHCl_3$, CH_2Cl_2 , and toluene, and could be purified readily by column chromatography. It is

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Scheme 1. Synthesis of Rare Earth(III) Double-Decker Complexes with Phthalocyaninato and Regular/Methylated N-Confused Porphyrinato Ligands



worth noting that only these protonated double-deckers were isolated as the sole product. This is in contrast to the similar reactions with 5,10,15,20-tetrakis[(4-*tert*-butyl)phenyl]porphyrin (H_2TBPP), in which the nonprotonated analogues $M^{\text{III}}(\text{Pc})(\text{TBPP})$ were obtained instead.⁹ These results clearly show that the inversion of a pyrrole ring in N-confused porphyrins can stabilize the protonated double-decker complexes.

For comparison, the methylated N-confused porphyrin $\text{H}(\text{CH}_3)\text{NTBPP}$ was also employed as the starting material. Reaction of this compound with $\text{Y}^{\text{III}}(\text{Pc})(\text{acac})$ resulted in the isolation of the mixed double-decker $\text{Y}^{\text{III}}(\text{Pc})[(\text{CH}_3)\text{NTBPP}]$ (**5**) in 8% yield (Scheme 1).

Spectroscopic Characterization. Compounds **1–5** gave satisfactory elemental analysis data, which are collected in Table 1. The MALDI-TOF mass spectra of these compounds clearly showed intense signals for the corresponding protonated molecular ion $[\text{M} + \text{H}]^+$. The isotopic pattern closely resembled the simulated one, as exemplified by the spectrum of the mixed double-decker **2** (see Figure S1 in the Supporting Information). The mass spectral data of these compounds are also listed in Table 1.

Similar to the protonated (phthalocyaninato)(porphyrinato) rare earth(III) double-decker complexes,^{10a} the mixed double-deckers $M^{\text{III}}(\text{Pc})(\text{HNTBPP})$ (**1–4**) were EPR silent, showing that they are diamagnetic in nature. However, by leaving a solid sample of these compounds for about two weeks, a very weak EPR signal at $g = 2.000$ was observed, which suggested that a small portion of these complexes was oxidized to the nonprotonated species (see the spectra of **4** given in Figure S2 in the Supporting Information as an example). Unexpectedly, an EPR signal was also observed for **5** despite that it has a methylated instead of regular N-confused porphyrin. It is likely that part of the inverted pyrrole CH bond was cleaved to give a radical anion.

Satisfactory ^1H NMR spectra were obtained for this series of compounds. This is also in contrast to the protonated (phthalocyaninato)(porphyrinato) analogues, for which satisfactory ^1H NMR spectra could not be obtained due to the tautomerization of the proton over the tetrapyrrole ligands.¹⁰ Figures 1a and S3 (Supporting Information) show the ^1H NMR spectrum of the yttrium complex **3** in CDCl_3 . The slightly broad signals at δ 9.19 and 8.08 are due to the α and β ring protons of the Pc ring, respectively. The singlets at δ 10.33 and 8.32 are assigned to the NH proton and the neighboring CH proton on the inverted pyrrole ring of HNTBPP, respectively. The correlation of these two sets of protons can be easily seen from the ^1H – ^1H COSY spectrum [Figure 1b]. The proton attached to C21 of HNTBPP resonates as a singlet at δ –3.52 due to the shielding effect of the macrocyclic ring. The signals of the β protons and some of the aryl protons appear in the region of δ 7.3–7.8. Several broad signals were observed in δ 6.3–7.2, which can be assigned to the aryl protons that are interchanged via free rotation of the aryl groups along the corresponding C(meso)–C(ipso) bonds in NTBPP. At lower temperatures, these signals were resolved into several doublets (Figure S4 in the Supporting Information) as a result of retardation of the ring rotation process. Interestingly, the signals for the aryl groups, particularly the ones next to the inverted pyrrole were too broad to be observed for the La(III) complex **1**. The signals became sharpen for the Y(III) and Lu(III) complexes **3** and **4**, particularly the latter. This observation can be ascribed to the fact that, as the size of the metal center decreases, the separation between the two macrocyclic ligands becomes smaller, which hinders the aryl group rotation to a greater extent.

The spectrum of the methylated derivative **5** was similar to that of **3** except that a new singlet at δ 4.41 appeared, which is due to the methyl group attached to the inverted pyrrole nitrogen atom, while the corresponding NH proton signal disappeared (Figure S5 in the Supporting Information). This provides a further support for the location of the signal of this proton. Nevertheless, this also gives experimental support for the location of the acid proton on the porphyrin side in the analogous protonated (phthalocyaninato)(porphyrinato) rare earth(III) double-decker compounds $\text{HM}^{\text{III}}(\text{Pc})(\text{Por})$ that was derived on the basis of theoretical investigation.¹¹ The spectra of **1** and **4** are similar to that of **3**, and the signals can be assigned similarly. The signals shown in the spectrum of the Eu(III) double-decker **2** fell into a wider region as a result of the paramagnetic nature of the metal center. The data for all these compounds are collected in Table 2.

The electronic absorption spectra of compounds **1–5** were measured in CHCl_3 (Figure 2), and the data are summarized

Table 1. Analytical and Mass Spectroscopic Data for the Mixed Double-Deckers 1–5

compound	yield (%)	$[\text{M} + \text{H}]^+ (m/z)^{a,b}$	analysis (%) ^a		
			C	H	N
$\text{La}^{\text{III}}(\text{Pc})(\text{HNTBPP})$ (1) ^c	10	1491.8 (1491.6)	73.03 (73.29)	5.09 (5.28)	11.05 (11.15)
$\text{Eu}^{\text{III}}(\text{Pc})(\text{HNTBPP})$ (2) ^d	12	1503.3 (1503.6)	72.00 (71.81)	5.40 (5.31)	10.56 (10.92)
$\text{Y}^{\text{III}}(\text{Pc})(\text{HNTBPP})$ (3) ^e	15	1441.0 (1441.6)	73.79 (73.98)	5.28 (5.60)	11.21 (11.25)
$\text{Lu}^{\text{III}}(\text{Pc})(\text{HNTBPP})$ (4) ^f	8	1527.4 (1527.6)	68.18 (68.39)	5.03 (5.43)	10.04 (10.40)
$\text{Y}^{\text{III}}(\text{Pc})[(\text{CH}_3)\text{NTBPP}]$ (5) ^c	8	1455.1 (1455.6)	75.53 (75.90)	5.60 (5.55)	11.12 (11.42)

^aCalculated values given in parentheses. ^bBy MALDI-TOF mass spectrometry. The value corresponds to the most abundant isotopic peak of the protonated molecular ion $[\text{M} + \text{H}]^+$. ^cContains 1 equiv of solvated H_2O . ^dContains 2 equiv of solvated H_2O . ^eContains 3 equiv of solvated H_2O . ^fContains 5 equiv of solvated H_2O .

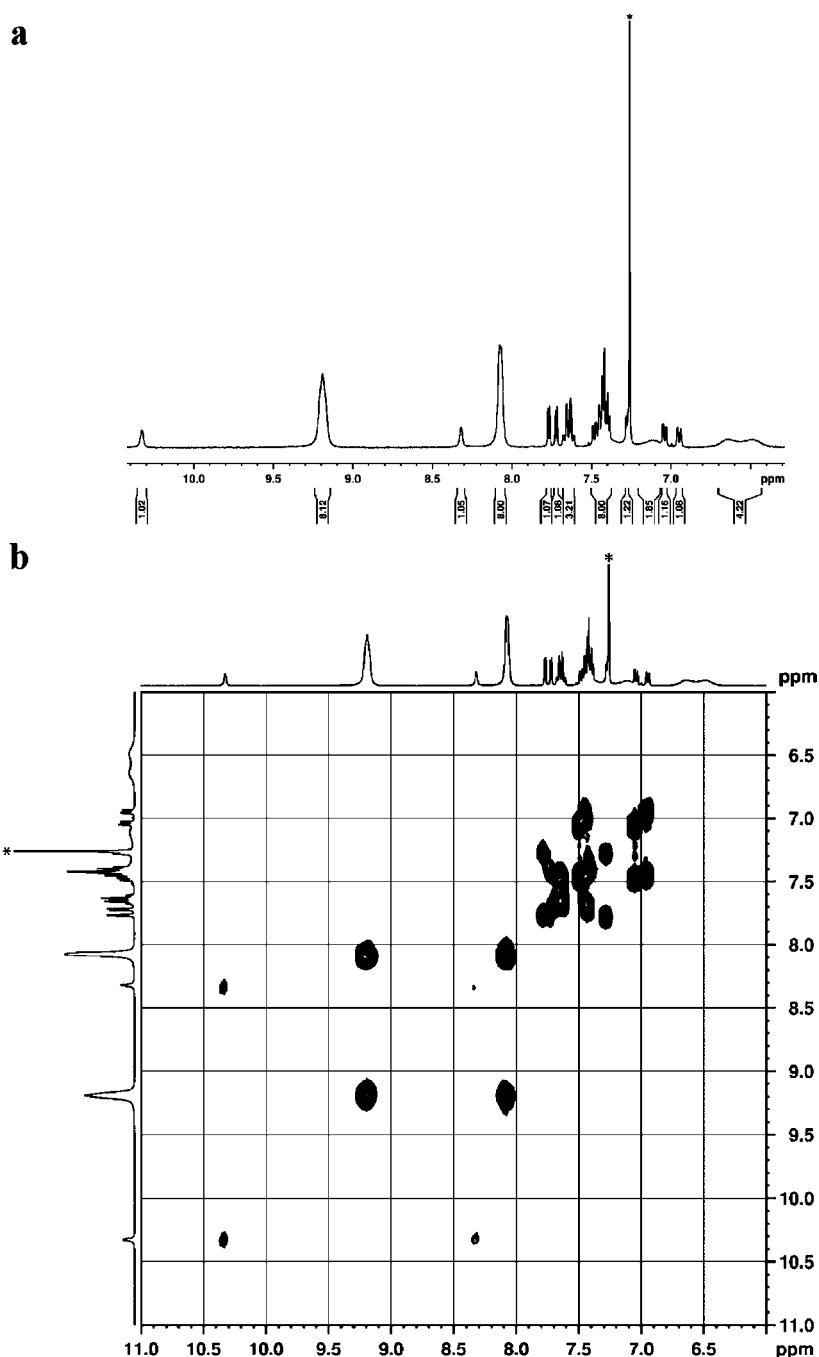


Figure 1. Part of the (a) ^1H NMR and (b) ^1H - ^1H COSY spectra of $\text{Y}^{\text{III}}(\text{Pc})(\text{HNTBPP})$ (**3**) in CDCl_3 ; the asterisk (*) indicates the signals for residual solvent and water.

in Table S1(Supporting Information). The spectra generally resembled those of double-deckers containing two dianionic ligands, such as $[\text{Ce}^{\text{IV}}(\text{Pc})(\text{TPP})]$ (TPP = 5,10,15,20-tetraphenylporphyrinate)¹² and $\text{Li}[\text{M}^{\text{III}}(\text{Pc})(\text{TPyP})]$ (M = Eu, Gd; TPyP = 5,10,15,20-tetra(4-pyridyl)porphyrinate),¹³ but the bands were slightly broadened. All the complexes gave strong bands at 335–336 and 466–471 nm, which can be attributed to the Soret bands of the phthalocyaninato and regular/methylated N-confused porphyrinato ligands, respectively, and several Q bands in the region of 533–760 nm.

The IR spectra of **1–5** showed an intense band at 1327–1331 cm^{-1} , which is a marker band for dianionic

phthalocyaninato ligands, while the $\text{Pc}^{\bullet-}$ marker band at ca. 1310–1320 cm^{-1} was not observed (Figure S6 in the Supporting Information).^{6b,14} This is in accord with the dianionic nature of the phthalocyaninato ligand in **1–5**. In addition, the IR spectra of **1–4** also showed a relatively sharp and weak band over the broad water band in the range of 3427–3433 cm^{-1} due to the N–H stretching vibration of the inverted pyrrole ring, which is absent in the IR spectrum of **5**.

Structural Studies. The molecular structures of the protonated double-deckers **2–4** and the methylated analogue **5** were determined by X-ray diffraction analyses. Single crystals of these compounds were obtained by slow diffusion of MeOH

Table 2. ^1H NMR Data (δ) for the Mixed Double-Deckers 1–5 in CDCl_3

compound	signals for NTBBP				signals for Pc	
	$\text{H}_{\alpha-c}^a$	H_β	H_{aryl}	$\text{H}_{\text{t-butyl}}$	H_α	H_β
1	10.33 (s, 1 H) 7.67 (s, 1 H) -3.56 (s, 1 H)	7.77 (d, 1 H), 7.69 (d, 1 H), 7.63 (d, 1 H), 7.52 (d, 1 H), 7.38 (d, 1 H), 7.24 (d, 1 H)	c	1.64 (s, 18 H), 1.55 (d, 18 H)	9.18 (d, 8 H)	8.04 (t, 8 H)
2	24.43 (s, 1 H) 20.34 (s, 1 H) ^b	5.25 (d, 1 H), 4.43 (d, 1 H), 3.68 (d, 1 H), 3.40 (d, 1 H), 2.98 (d, 1 H), 2.73 (d, 1 H)	14.29 (d, 1 H), 14.01 (d, 1 H), 9.59 (d, 1 H), 9.08 (d, 1 H), 10.16 (m, 2 H), 8.55 (m, 2 H) ^c	2.48 (s, 9 H), 2.44 (s, 9 H), 1.26 (d, 18 H)	10.35 (s, 8 H)	8.41 (s, 8 H)
3	10.33 (s, 1 H) 8.32 (s, 1 H) -3.52 (s, 1 H)	7.77 (d, 1 H), 7.73 (d, 1 H), 7.67–7.61 (m, 3 H), 7.49–7.38 (m, 8 H) ^{d,e}	7.05 (d, 1 H), 6.96 (d, 1 H), 7.11 (br s, 2H), 6.65–6.48 (br s, 4H), 7.67–7.61 (m, 3 H), 7.49–7.38 (m, 8 H) ^d	1.58 (s, 18 H), 1.47 (d, 18 H)	9.19 (s, 8 H)	8.08 (s, 8 H)
4	10.34 (s, 1 H) 8.37 (s, 1 H) -3.27 (s, 1 H)	7.76 (d, 1 H), 7.71 (d, 1 H), 7.63–7.53 (m, 3 H), 7.45–7.30 (m, 8 H) ^{d,e}	7.05 (d, 1 H), 6.96 (d, 1 H), 7.11 (br s, 2H), 6.65–6.48 (br s, 4H), 7.63–7.53 (m, 3 H), 7.45–7.30 (m, 8 H) ^d	1.56 (s, 18 H), 1.46 (d, 18 H)	9.20 (s, 8 H)	8.09 (s, 8 H)
5	4.41 (s, 3H) 7.82 (s, 1 H) -3.88 (s, 1H)	7.70 (d, 1 H), 7.55 (d, 1 H), 7.49 (d, 1 H), 7.46 (d, 1 H), 7.32 (d, 1 H), 7.18 (d, 1 H)	7.96 (d, 1 H), 7.59 (d, 1 H), 7.40 (d, 1 H), 6.93 (d, 1 H), 6.84 (d, 1 H), 6.73 (d, 1 H), 7.11 (br s, 2 H), 6.30–6.70 (br s, 4H) ^d	1.57 (s, 18 H), 1.47 (d, 18 H)	9.23 (s, 8 H)	8.10 (s, 8 H)

^a H_α and H_β stand for the NH [or N(CH₃) for 5] proton(s) and CH proton, respectively, on the inverted pyrrole, while H_c stands for the proton attached to 21-C in HNTBPP or (CH₃)NTBPP ligand. ^bThis signal was not observed due to the paramagnetic nature of the Eu(III) center. ^cSome of H_{aryl} signals were too broad to be observed due to the free rotation of the aryl rings along the corresponding C(meso)–C(ipso) bonds. ^dSome of the H_β and H_{aryl} proton signals were partially overlapped. ^eOne H_β proton signal was masked by the strong residual CHCl_3 signal at δ 7.26.

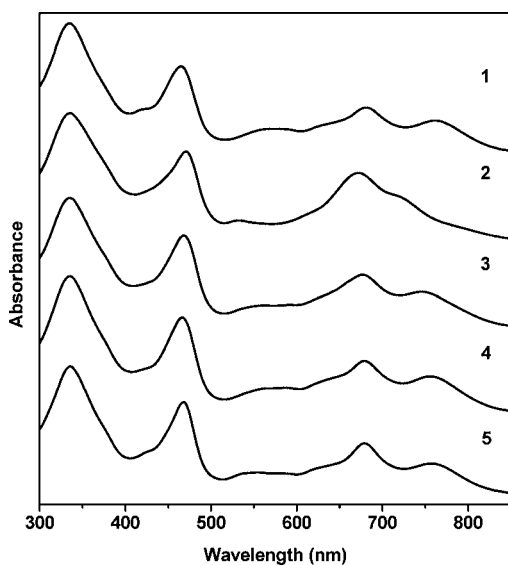


Figure 2. Electronic absorption spectra of $\text{M}^{\text{III}}(\text{Pc})(\text{HNTBPP})$ ($\text{M} = \text{La}, \text{Eu}, \text{Y}, \text{Lu}$) (1–4) and $\text{Y}^{\text{III}}(\text{Pc})[(\text{CH}_3)\text{NTBPP}]$ (5) in CHCl_3 .

into the corresponding CHCl_3 solutions. By incorporating the N-confused porphyrins, the symmetry of the complexes is lowered from D_{4h} to C_1 . They are therefore intrinsically chiral. However, attempts to resolve the two enantiomers of these double-deckers by a chiral HPLC column (ChiralPak IA) were not successful.

Compound 2 crystallizes in the monoclinic space group $P2_1/c$ with two pairs of enantiomeric double-deckers per unit cell, while 3 and 4 crystallize in the monoclinic space group $C2/c$ with four pairs of enantiomeric molecules per unit cell. The crystal structures of these double-deckers also contain some solvated CHCl_3 molecules. Figure 3 shows the molecular

structure of $\text{Y}^{\text{III}}(\text{Pc})(\text{HNTBPP})$ (3) in two different perspective views. It can be seen that the yttrium center is octa-coordinated by the four isoindole nitrogen atoms of the Pc ring and three pyrrole nitrogen atoms and the inverted pyrrole carbon atom of the NTBBP ring. The rotation angle of one ring away from the eclipsed conformation of the two rings (named as the twist angle) is 42.77° , showing that the coordination polyhedron is a slightly distorted square antiprism. The metal center lies at 1.464 and 1.334 Å to the N_3 and N_4 mean planes of NTBBP and Pc, respectively, giving a ring-to-ring separation of 2.798 Å. The N_3 and N_4 mean planes are virtually parallel with a dihedral angle of 0.74° . Similar to the structures of other mixed (phthalocyaninato)(porphyrinato) double-decker complexes reported earlier,¹⁰ the Pc ligand is significantly domed with an average dihedral angle ϕ , defined as the dihedral angle between the NC_4 mean plane of an individual isoindole ring and the N_4 mean plane of the Pc ring, of 13.83° . As expected, the overall structure of the NTBBP ligand adopts a nonplanar geometry with the inverted pyrrole ring tilted away from the metal and the remaining three pyrrole rings tilted toward the metal. The dihedral angle of the NC_4 mean plane of the inverted pyrrole ring with respect to the corresponding N_3 mean plane of N-confused porphyrin plane defined by $\text{N}(22)$ – $\text{N}(23)$ – $\text{N}(24)$ is 13.15° . The Y – $\text{C}(21)$ distance (2.823 Å) seems longer than a normal lanthanide–carbon σ -bond¹⁵ but is still much shorter than the sum of the van der Waals radii (3.92 Å),¹⁶ indicating the relatively strong bonding interaction between the Y^{III} ion and the $\text{C}(21)$ atom.

The molecular structure of the europium counterpart $\text{Eu}^{\text{III}}(\text{Pc})(\text{HNTBPP})$ (2) was different. As shown in Figure 4, the two macrocyclic ligands are further bound to a CH_3OH molecule through two hydrogen bonds formed between the hydroxyl group of CH_3OH and an aza nitrogen atom of the Pc

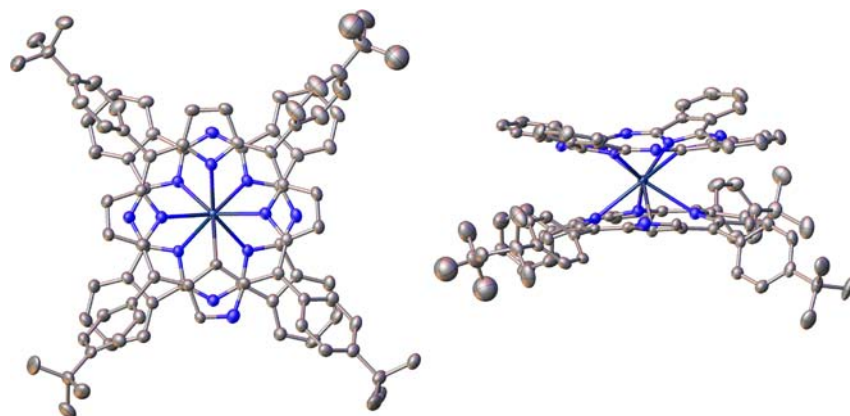


Figure 3. Molecular structure of $\text{Y}^{\text{III}}(\text{Pc})(\text{HNTBPP})$ (**3**) in top and side views with hydrogen atoms and solvent molecules omitted for clarity.

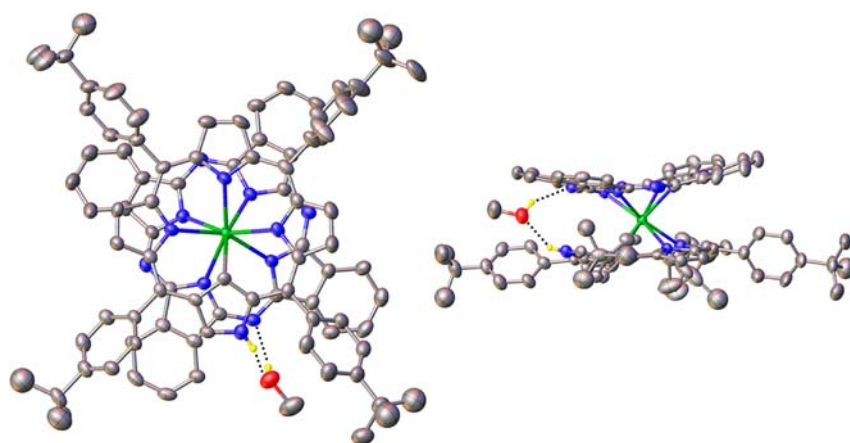


Figure 4. Molecular structure of $\text{Eu}^{\text{III}}(\text{Pc})(\text{HNTBPP}) \cdot \text{CH}_3\text{OH}$ ($2 \cdot \text{CH}_3\text{OH}$) in top and side views with selected hydrogen atoms and solvent molecules omitted for clarity.

ring and the inverted pyrrole N atom of the HNTBPP ring, respectively. It is likely that the trivalent europium ion has the most appropriate size for this secondary interaction. As a consequence, free rotation between the two tetrapyrrole ligands in this double-decker is hindered and the twist angle is reduced to 27.34° , resulting in the formation of a significantly distorted square antiprism.

The methylated N-confused porphyrin analogue **5** crystallizes in the monoclinic space group $P2_1/n$ with four pairs of enantiomeric molecules per unit cell. As expected, the molecular structure is similar to that of the protonated analogue **3** except that the proton at the inverted pyrrole nitrogen is replaced with a methyl group (Figure S7 in the Supporting Information). The crystallographic and structural data for these compounds are summarized in Tables 3 and Table S2 (Supporting Information).

Electrochemical Properties. The redox behavior of **1–5** was also studied by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in CH_2Cl_2 . As exemplified by the differential pulse voltammograms of $\text{Eu}^{\text{III}}(\text{Pc})(\text{HNTBPP})$ (**2**) (Figure 5), all the compounds exhibited two quasi-reversible one-electron oxidations and two quasi-reversible one-electron reductions, all of which can be attributed to ligand-based redox processes. The half-wave potentials are summarized in Table 4. It is worth noting that the first oxidation potentials of these complexes are in the range of 0.41–0.53 V vs saturated calomel electrode (SCE), which are significantly higher than those of

Table 3. Structural Data for the Mixed Double-Deckers 2–5

	2	3	4	5
average M–N(NTBPP) bond distance [Å]	2.530	2.512	2.501	2.499
average M–N(Pc) bond distance [Å]	2.465	2.387	2.347	2.409
M–C(21) distance [Å]	2.798	2.823	2.806	2.791
M–N ₃ (NTBPP) plane distance [Å]	1.471	1.464	1.456	1.429
M–N ₄ (Pc) plane distance [Å]	1.471	1.334	1.280	1.381
interplanar distance [Å]	2.942	2.798	2.736	2.810
dihedral angle between the N ₃ and N ₄ planes [deg]	1.12	0.74	0.83	1.34
average dihedral angle ϕ for the NTBPP ring [deg] ^a	13.42	13.70	13.86	14.36
dihedral angle ϕ between the N ₃ plane and the inverted ring [deg]	20.50	13.15	11.23	18.05
average dihedral angle ϕ for the Pc ring [deg] ^a	13.48	13.83	13.84	15.23
average twist angle [deg] ^b	27.34	42.77	43.38	43.63

^aThe average dihedral angle of the individual pyrrole or isoindole ring with respect to the corresponding N₃ or N₄ mean plane. ^bDefined as the rotation angle of one macrocycle away from the eclipsed conformation of the two macrocycles

the porphyrinato counterparts $[\text{M}(\text{Pc})(\text{TCIPP})]^-$ [$\text{TCIPP} = 5,10,15,20$ -tetrakis(4-chlorophenyl)porphyrinate] (0.12–0.31 V).¹⁷ This is in accord with the fact that the former series was isolated as the reduced protonated form $\text{M}^{\text{III}}(\text{Pc})(\text{HNTBPP})$, while the latter series was isolated as the neutral nonprotonated form $\text{M}(\text{Pc})(\text{TCIPP})$.

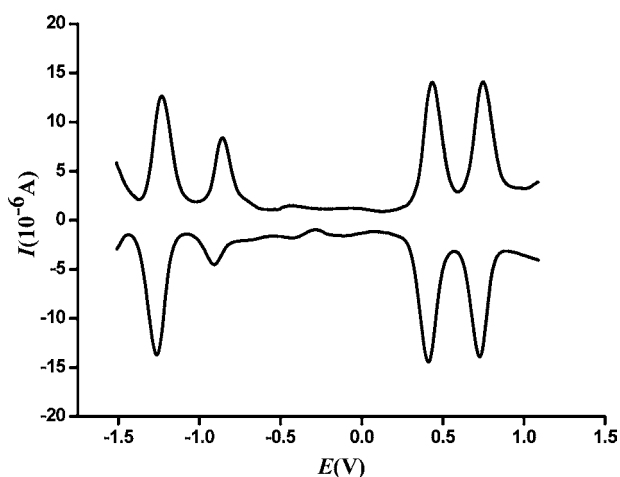


Figure 5. Differential pulse voltammograms of $\text{Eu}^{\text{III}}(\text{Pc})(\text{HNTBPP})$ (**2**) in CH_2Cl_2 containing 0.1 M $[\text{NBu}_4][\text{ClO}_4]$ at a scan rate of 10 mV s^{-1} .

Table 4. Electrochemical Data for the Mixed Double-Deckers 1–5^a

compound	Oxd ₂	Oxd ₁	Red ₁ ^b	Red ₂	$\Delta E_{1/2}^0$ ^c
1	0.83	0.53	−0.77	−1.20	1.30
2	0.74	0.43	−0.88	−1.25	1.31
3	0.75	0.41	−0.84	−1.27	1.25
4	0.78	0.44	−0.86	−1.20	1.30
5	0.80	0.43	−0.94	−1.26	1.37

^aRecorded with $[\text{Bu}_4\text{N}][\text{ClO}_4]$ as electrolyte in CH_2Cl_2 (0.1 mol dm^{-3}) at ambient temperature. Potentials were obtained by CV with a scan rate of 50 mV s^{-1} and are expressed as half-wave potentials ($E_{1/2}$) in V relative to ferrocenium/ferrocene (Fe^+/Fe) couple [$E_{1/2}(\text{Fe}^+/\text{Fe}) = 0.50 \text{ V vs SCE}$] unless otherwise stated. ^bRecorded by DPV. ^c $\Delta E_{1/2}^0$ is the potential difference between the first oxidation and the first reduction processes, i.e., the HOMO–LUMO gap of the complexes: $\Delta E_{1/2}^0 = \text{Oxd}_1 - \text{Red}_1$

CONCLUSIONS

In summary, we have designed and synthesized the first examples of rare earth(III) double-decker complexes with phthalocyaninato and regular/methylated N-confused porphyrinato ligands. By comparing their spectroscopic data, in particular ¹H NMR, the acidic proton in the protonated double-deckers has been found to localize at the inverted pyrrole nitrogen atom in the confused porphyrinato ligand. This provides the first experimental support for the location of the acid proton on the porphyrin side in the analogous protonated (phthalocyaninato)(porphyrinato) rare earth(III) double-decker compounds $\text{HM}^{\text{III}}(\text{Pc})(\text{Por})$ that was derived on the basis of theoretical investigation. By incorporating an N-confused porphyrinato ligand, the properties of the resulting double-deckers can be altered for different applications. For example, on the basis that the relaxation of magnetization of lanthanide(III) bis(tetrapyrrole) double-decker complexes is highly dependent on their molecular symmetry and structure, in particular the twist angle between the two tetrapyrrole rings,^{7a,d} this new series of double-decker compounds may function as novel single molecular magnets. Studies along this direction are underway.

EXPERIMENTAL SECTION

General. TCB and dichloromethane were freshly distilled from CaH_2 under nitrogen. Column chromatography was carried out on

silica gel columns (Merck, Kieselgel 60, 70–230 mesh) with the indicated eluents. The electrolyte $[\text{Bu}_4\text{N}][\text{ClO}_4]$ was recrystallized twice from tetrahydrofuran. All other reagents and solvents were used as received. H_2NTBPP ,¹⁸ $\text{H}(\text{CH}_3)\text{NTBPP}$,¹⁹ Li_2Pc ,²⁰ and $\text{M}(\text{acac})_3 \cdot n\text{H}_2\text{O}$ ($\text{M} = \text{La}, \text{Eu}, \text{Y}, \text{Lu}$),²¹ and $\text{M}(\text{Pc})(\text{acac})$ ($\text{M} = \text{Eu}, \text{Y}, \text{Lu}$)²² were prepared according to the published procedure.

¹H NMR spectra were recorded on a Bruker DPX 400 spectrometer in CDCl_3 . Spectra were referenced internally using the residual solvent resonance ($\delta = 7.26$) relative to SiMe_4 . Electronic absorption spectra were recorded on a Hitachi U-4100 spectrophotometer. IR spectra were recorded as KBr pellets using a Bruker Tensor 37 spectrometer with 2 cm^{-1} resolution. MALDI-TOF mass spectra were taken on a Bruker BIFLEX III ultrahigh resolution Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer with α -cyano-4-hydroxycinnamic acid as the matrix. Elemental analyses were performed on an Elementar Vavio El III elemental analyzer. Solid-state EPR spectra were recorded on a Bruker EMX EPR spectrometer.

Electrochemical measurements were carried out with a BAS CV-50W voltammetric analyzer. The cell comprised inlets for a glassy carbon disk working electrode with a diameter of 2.0 mm and a silver wire counter electrode. The reference electrode was Ag/Ag^+ (a solution of 0.01 M AgNO_3 and 0.1 M $[\text{Bu}_4\text{N}][\text{ClO}_4]$ in acetonitrile), which was connected to the solution by a Luggin capillary whose tip was placed close to the working electrode. It was corrected for junction potentials by using ferrocenium/ferrocene (Fe^+/Fe) couple [$E_{1/2}(\text{Fe}^+/\text{Fe}) = 0.50 \text{ V vs SCE}$] as an internal reference. Typically, a 0.1 M solution of $[\text{NBu}_4][\text{ClO}_4]$ in CH_2Cl_2 containing 0.5 mM of the sample was purged with nitrogen for 10 min, and then the voltammograms were recorded at ambient temperature. The scan rate was 50 and 10 mV s^{-1} for CV and DPV, respectively.

Preparation of $\text{La}^{\text{III}}(\text{Pc})(\text{HNTBPP})$ (1**).** A mixture of H_2NTBPP (42.0 mg, 0.05 mmol), $\text{La}(\text{acac})_3 \cdot n\text{H}_2\text{O}$ (25 mg, 0.05 mmol), and Li_2Pc (26 mg, 0.05 mmol) in TCB (4 mL) was heated under reflux and a nitrogen atmosphere for about 4 h. After a brief cooling, the solvent was removed under reduced pressure, and the residue was chromatographed on a silica gel column with CH_2Cl_2 as the eluent. A deep green band containing the target mixed double-decker followed by another green band containing the bis(phthalocyaninato) lanthanum(III) double-decker were developed. The column was further eluted with triethylamine and CH_2Cl_2 (1:99 v/v), giving a brown band containing the unreacted metal-free H_2NTBPP . Repeated chromatography followed by recrystallization from CHCl_3 and MeOH gave **1** as a dark green powder (7 mg, 10%).

Preparation of $\text{M}^{\text{III}}(\text{Pc})(\text{HNTBPP})$ ($\text{M} = \text{Eu}, \text{Y}, \text{Lu}$) (2–4**).** By employing the above procedure with $\text{M}(\text{Pc})(\text{acac})$ ($\text{M} = \text{Eu}, \text{Y}, \text{Lu}$) instead of Li_2Pc and $\text{M}(\text{acac})_3 \cdot n\text{H}_2\text{O}$ as the starting material, compounds **2–4** were isolated in 8–16% yield.

Preparation of $\text{Y}^{\text{III}}(\text{Pc})[(\text{CH}_3)\text{NTBPP}]$ (5**).** By utilizing the above procedure with $\text{H}(\text{CH}_3)\text{NTBPP}$ (42.8 mg, 0.05 mmol) instead of H_2NTBPP as the starting material, $\text{Y}^{\text{III}}(\text{Pc})[(\text{CH}_3)\text{NTBPP}]$ (**5**) was isolated in 10% yield.

X-ray Crystallographic Analysis of **2–5.** Single crystals suitable for X-ray diffraction analysis were grown by diffusing MeOH into the CHCl_3 solutions of these compounds. Crystal data and details of data collection and structure refinement are given in Table 4. Data were collected on an Oxford Diffraction Gemini E system with $\text{Cu}_{\text{K}\alpha}$ radiation $\lambda = 1.5418 \text{ \AA}$ at 120 K, using a ω scan mode with an increment of 1° . Preliminary unit cell parameters were obtained from 30 frames. Final unit cell parameters were obtained by global refinements of reflections obtained from integration of all the frame data. The collected frames were integrated using the preliminary cell-orientation matrix. The SMART software was used for data collecting and processing; ABSPACK for absorption correction;²³ and SHELXL for space group and structure determination, refinements, graphics, and structure reporting.²⁴ CCDC-849675–849678 contain the supplementary crystallographic data for this article. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

■ ASSOCIATED CONTENT

■ Supporting Information

Experimental and simulated isotopic pattern for the molecular ion of $\text{Eu}^{\text{III}}(\text{Pc})(\text{HNTBPP})$ (2) shown in the MALDI-TOF mass spectrum, powder EPR spectra of $\text{Lu}^{\text{III}}(\text{Pc})(\text{HNTBPP})$ (4), ^1H NMR spectra of $\text{Y}^{\text{III}}(\text{Pc})(\text{HNTBPP})$ (3) in CDCl_3 , variable-temperature ^1H NMR spectra of $\text{Y}^{\text{III}}(\text{Pc})(\text{HNTBPP})$ (3) in CDCl_3 , ^1H NMR and part of the ^1H - ^1H COSY spectra of $\text{Y}^{\text{III}}(\text{Pc})[(\text{CH}_3)\text{NTBPP}]$ (5) in CDCl_3 , IR spectra of 1–5 in the region of 400–1800 and 2600–4000 cm^{-1} , molecular structure of $\text{Y}^{\text{III}}(\text{Pc})[(\text{CH}_3)\text{NTBPP}]$ (5), electronic absorption data for the mixed double-deckers 1–5 in CHCl_3 , and crystallographic data for the mixed double-deckers 2–5 (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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