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A_3B-Type Phthalocyanine-Based Homoleptic Lanthanide(III) Double-Decker π-Radical Complexes Bearing Functional Hydroxy Groups: Synthetic Approach, Spectral Properties and Electrochemical Study

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The sandwich lanthanide(III) complexes $^{BnO,Bu}Pc_2Ln$ ($^{BnO,Bu}Pc$ = 2-benzyloxy-9,10,16,17,23,24-hexa-*n*-butylphthalocyaninate; Ln = Eu, Lu) (**1a**, **1b**) were obtained from $[Ln(acac)_3]\cdot nH_2O$ and $^{BnO,Bu}PcH_2$ by heating these compounds in *n*-hexadecanol, and then treating the reaction solution with H_2SO_4 to yield the corresponding neutral double-decker complexes $^{HO,Bu}Pc_2Ln$ ($^{HO,Bu}Pc$ = 9,10,16,17,23,24-hexa-*n*-butyl-2-hydroxyphthalocyaninate) (**2a**, **2b**), which are promising structural building blocks and stable phenolic hydroxy group containing π-radical species. A combination of UV/Vis/NIR, NMR spectroscopy, MALDI-TOF mass spectrometry, cyclic voltammetry and spectroelectrochemistry provided unambiguous characterization of the newly prepared bis(phthalocyanines), and also allowed their stability and behavior in solution to be investigated.

Introduction

Since their synthesis for the first time more than 40 years ago[1] sandwich-type phthalocyanines of rare-earth elements (REE) have become an important class of tetrapyrrolic coordinating compounds, include several different types of structures,[2] and have a wide range of applications.[3] Introduction of functional groups on the periphery of these molecules allows them to be coupled with different surfaces including carbon nanotubes[4] and also makes them promising building blocks for the creation of nanoscale structures that are useful in multibit information storage,[5] gas sensing,[6] nonlinear optics[7] and other advanced areas.

Controlling the number and location of functional groups on the phthalocyanine–REE complexes requires the synthesis of asymmetrically substituted derivatives, in particular, complexes with A_3B-type ligands. To the best of our knowledge, there have been no well-characterized homoleptic REE–phthalocyanine sandwich complexes containing functionalized A_3B ligands reported to date, although a few examples of heteroleptic complexes are known.[8] The synthetic procedures available for such compounds are based on the template complexation either of two different phthalonitriles with a lanthanide salt[8a] or of phthalonitriles with the corresponding monophthalocyanines.[8b–8d] Alternatively, the procedures involve direct interaction of a half-sandwich REE compound, formed in situ, with lithium phthalocyaninate,[8e] which usually give mixtures of products in comparatively low yields that are hard to separate.

In our recent work[9] we have reported the development of effective synthetic pathways to A_3B phthalocyanines and their selective transformation to covalently bridged clamshell-type complexes. The accessibility of these clamshell-type compounds allowed us to demonstrate the possibility of obtaining novel sandwich-type structures through complexation with Lu salt.[10]

In this paper we describe the development of an optimal synthetic route to bis(phthalocyanines) bearing functional OH groups, which can then be used as structural building blocks. Moreover, the physicochemical and redox properties of these compounds are of great interest since these molecules represent stable π-radical species that contain phenolic OH groups as peripheral substituents.

Results and Discussion

Synthesis of Homoleptic Double-Decker Complexes 1 and 2

Treatment of the metal-free phthalocyanine $^{HO,Bu}PcH_2$ with benzyl chloride in dimethylformamide in the presence of sodium hydride at room temperature gave the protected ligand $^{BnO,Bu}PcH_2$ (Scheme 1) within 30 min.

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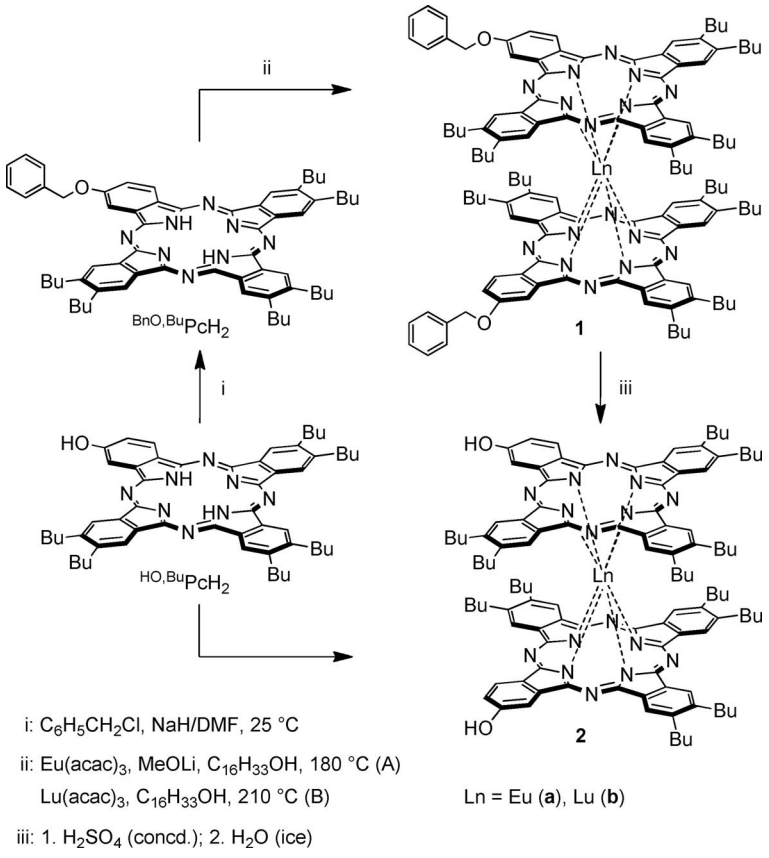

Scheme 1. Synthesis of double-decker complexes.

The reaction of $^{BnO,Bu}PcH_2$ with $Ln(acac)_3{\cdot}nH_2O$ (Ln = Eu, Lu) in *n*-hexadecanol, a method that is similar to a procedure developed earlier in our group[11] for the synthesis of lanthanide(III) complexes based on symmetrical 2,3,9,10,16,17,23,24-octabutylphthalocyanine ($^{Bu}PcH_2$), led to the selective formation of double-decker complexes **1a** and **1b**. An important feature of the synthesis technique reported herein concerns the synthesis of europium complex **1a**, which was prepared by heating the starting reagents at 180 °C in the presence of lithium methoxide (Scheme 1, pathway A) instead of DBU that was required for the synthetic procedure reported in ref.[11] This allowed the reaction time to be decreased from 2–3 h to 20 min, while also generating a higher yield of the target compound. These advantages that result from the use of lithium methoxide in the synthetic procedure instead of DBU may derive from the noncoordinating nature of the lithium methoxide: the tendency of DBU to form coordinating bonds with the lanthanide ion of the intermediate half-sandwich mono(phthalocyanine) compound[12] should create steric hindrance at the metal centre that prevents further complexation. In addition, reduction of the reaction time appears to be an essential factor that influences the product yield because of the thermal lability of the benzyloxy substituents in compounds **1**. It is noteworthy that when the reaction was carried out without basic additives the process selectivity substantially decreases due to the formation of the corresponding triple-decker mixture. In contrast, complexation of $^{BnO,Bu}PcH_2$ with a lutetium salt at 210 °C (Scheme 1, pathway B) selectively yielded the double-decker complex **1b**. An increase in the reaction temperature favors the formation of triple-decker complexes, as observed in the case of compound **1a**. Treatment of complexes **1a** and **1b** with concentrated sulfuric acid followed by pouring into ice and precipitation gave the target bis(phthalocyanine) complexes **2a** and **2b**. Complex **2b** was produced in a quantitative yield, whereas in the case of **2a** $^{HO,Bu}PcH_2$ was also observed in the product mixture, reflecting the lower stability of **2a** with respect to **2b**. Thus, this synthetic scheme afforded compounds **2a** and **2b** in good overall yields (Table 1). It is worth mentioning that all attempts to obtain **2** directly from $^{HO,Bu}PcH_2$ were not successful, and led to the gradual thermal decomposition of the initial free-base phthalocyanine even under an inert gas, which is also consistent with the low thermal stability of **2**; the control experiments confirmed this hypothesis (Footnote S1 in the Supporting Information).

Table 1. Yields and high-resolution MALDI-TOF mass spectrometry data for complexes **1** and **2**.

	Formula	Yield [%]	*m/z* $[M]^{+[a]}$
1a	$C_{126}H_{140}N_{16}O_2Eu$	81	2061.7041 (2062.0557)
1b	$C_{126}H_{140}N_{16}O_2Lu$	78	2084.7595 (2085.0786)
2a	$C_{112}H_{128}N_{16}O_2Eu$	71	1881.5466 (1881.9618)
2b	$C_{112}H_{128}N_{16}O_2Lu$	98	1904.5760 (1904.9847)

[a] Calculated values given in parentheses.

Newly prepared homoleptic double-decker complexes **1** and **2** have been characterized by MALDI-TOF mass spectrometry, electronic absorption and ^{1}H NMR spectroscopic techniques. The MALDI-TOF mass spectra of these compounds (Table 1, Figures 1 and S1–S3 in the Supporting Information), with DCTB {2-[(2*E*)-3-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene]malonitrile} as the matrix, revealed intense molecular ion $[M]^+$ peaks with characteristic isotopic patterns that are in good accordance with the simulated spectra. It is also noteworthy that no additional fragmentation of the $[M]^+$ ion was observed under laser ionization with DCTB for compounds **1** that bear chemically labile benzyloxy groups (Figure 1), although spectra recorded with DHB (2,5-dihydroxybenzoic acid) as the matrix displayed secondary ion peaks.

Electronic Absorption Spectra

The UV/Vis spectroscopic study of bis(phthalocyanine) complexes **1** and **2** confirms that they are neutral π-radical-containing species. The spectra were recorded on C_6H_6 solutions of the complexes, and the data are summarized in Table 2. Figure 2 displays the UV/Vis spectra of the hydroxy derivatives **2** that are characterized by split Soret bands in the 327–356 nm region, weaker π-radical bands at 471–485 nm, and a strong single Q-band at 673–684 nm that has nicely resolved vibrational satellites. Furthermore, an expected hypsochromic shift of the absorption bands in the spectrum for the Eu complex with respect to the bands in the spectrum for the Lu complex is clearly observed, whereas the deprotection of the peripheral OH groups has

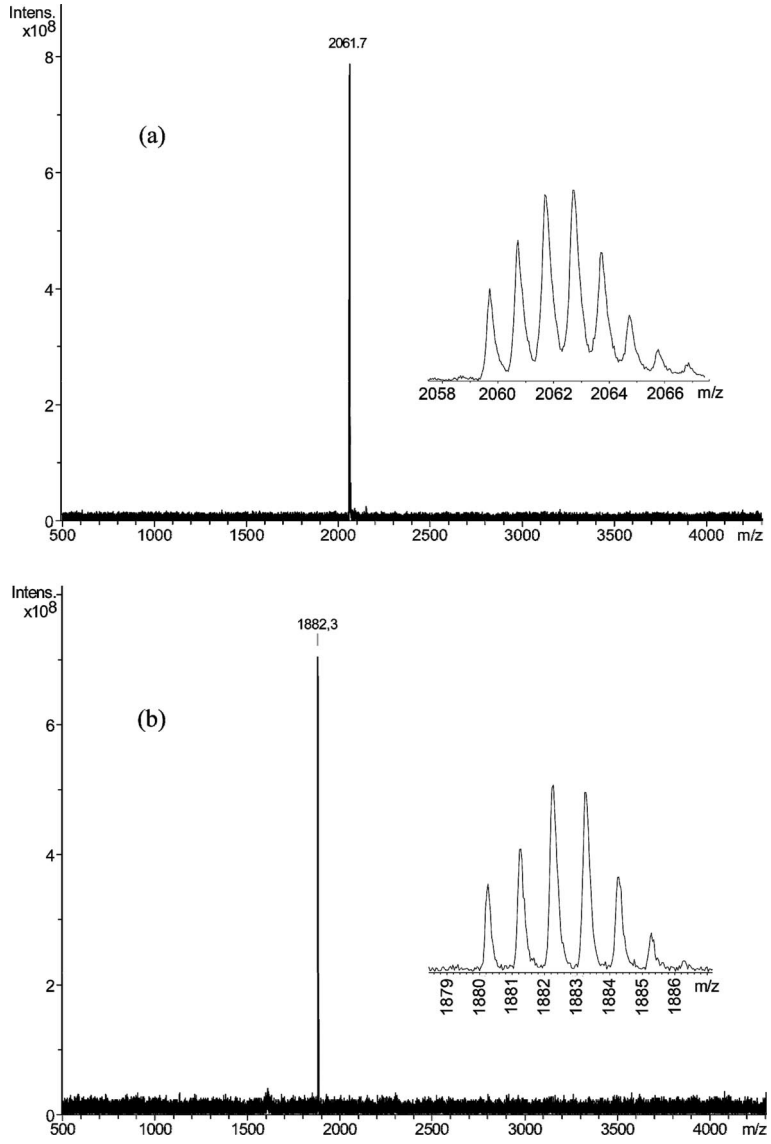

Figure 1. MALDI-TOF mass spectra of compounds **1a** (a) and **2a** (b) and isotopic patterns for the corresponding molecular ions (insets).

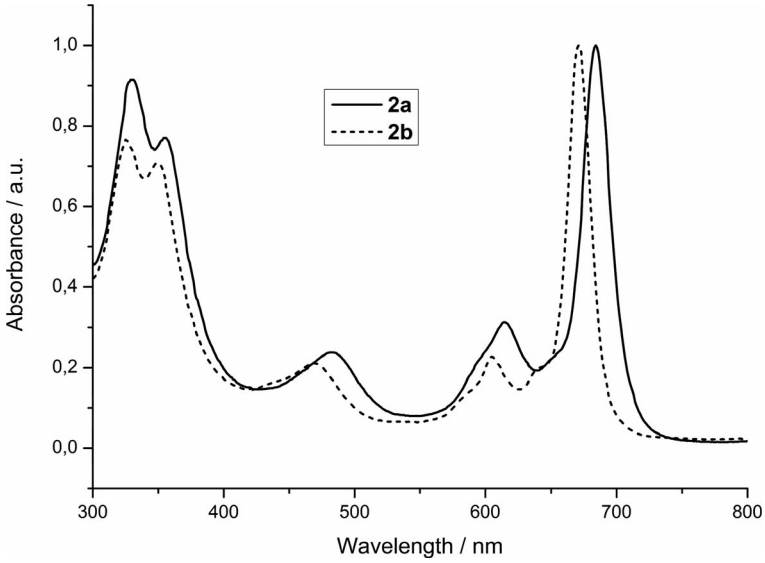

Figure 2. Electronic absorption spectra of compounds **2a** and **2b** in C_6H_6.

virtually no effect on the band positions, which reflects the similar electron-donating properties of benzyloxy and hydroxy substituents (Table 2). Investigation of the transmittance spectra in the NIR region also revealed no difference between the hydroxy and benzyloxy complexes, showing the same positions for the red valence (RV) and intervalence (IV) bands (Figures S4, S5 and Table S1 in the Supporting Information). Note that certain spectral changes in the NIR regions in the spectra of the Eu and Lu complexes are observed, namely, a bathochromic shift of the RV band, whereas the IV band shifts hypsochromically. Such changes are in good accordance with previously published data in the literature for HOMO–LUMO molecular orbital substructure of bis(phtahlocyanine) sandwich complexes.[13]

Table 2. Electronic absorption data for double-decker complexes **1** and **2** in C_6H_6.

	λ_{max} [nm] (I/I_{max})				
	B (Soret)		π-Radical	Q_{vib}	Q
1a	331 (0.980)	356 (0.852)	485 (0.251)	615 (0.344)	684 (1.000)
1b	327 (0.749)	351 (0.753)	471 (0.213)	606 (0.228)	673 (1.000)
2a	329 (0.917)	355 (0.776)	483 (0.257)	614 (0.330)	684 (1.000)
2b	327 (0.766)	351 (0.709)	471 (0.211)	607 (0.227)	673 (1.000)

NMR Spectra

During the last decades NMR spectroscopy has become an important tool in the structural determination of sandwich-type bis(phthalocyanine) complexes as the difficulties associated with radical extinction and insufficient solubility to enable spectrum acquisition have been overcome. For the freshly prepared double-decker compounds **1** and **2** that were prepared as inseparable mixture of structural isomers, and for which it is impossible to form single crystals suitable for X-ray analysis, the role of NMR spectroscopy is crucial. The ^{1}H NMR spectra of complexes **1** and **2** (Figures 3, 4, S6–S13 and Table S2 in the Supporting Information) were recorded at room temperature with the complexes dissolved in a $CDCl_3$/[D_6]DMSO (1:1, v/v) mixture in the presence of 1–2 vol.-% hydrazine hydrate, which reduces the π-radical species to the corresponding dianions.

The full assignment of NMR signals was made on a basis of published data[11] for the symmetrically substituted complexes $^{Bu}Pc_2Ln$ (Ln = Eu, Lu) and ^{1}H–^{1}H COSY experiments. Thus, in the spectrum of compound **1a** (Figure 3) the aromatic protons of the phthalocyanine rings H^{Ar} are revealed as a sum of singlets at δ = 11 ppm. The peaks associated with the α-H^{Ar} protons overlap with the H^{Ar} signal and have intercorrelated signals with the β-H^{Ar} protons (Figure 4) that enabled their assignment, while the signal at δ = 10.75 ppm is assigned to the α′-H^{Ar} protons. The signals in the δ = 7.5–8.5 ppm region are clearly due to the aromatic protons of the benzyloxy substituent (H^{Ph}), and their assignment was also provided by the 2D NMR spectrum (Figure 4). The CH_2 protons of the benzyloxy groups are revealed as signals at δ = 6.45 and 6.8 ppm and have cross-peaks in the COSY spectrum; these peaks are assigned to the *exo*- and *endo*-protons, respectively, as the *exo*-protons are subjected to a greater degree of deshielding than the *endo*-protons, because they are closer to the paramagnetic Eu^{III} ion. The signals in the aliphatic region belonging to the butyl chain protons can be assigned clearly from the COSY spectrum (Figure S6) and show a good correlation with data obtained for the $^{Bu}Pc_2Eu$ complex.[11] A similar approach was applied to fully assign the peaks in the NMR spectrum of the lutetium complex **1b** (Figures S7–S9 in the Supporting Information); however, no additional deshielding of the protons was observed, in contrast to **1a**, due to the diamagnetic nature of the Lu^{III} ion.

The ^{1}H NMR spectra of the double-decker complexes **2a** and **2b** are characterized by the disappearance of benzyloxy group signals (Figures S10–S13 and Table S2 in the Supporting Information) that are present in the spectra for **1a**

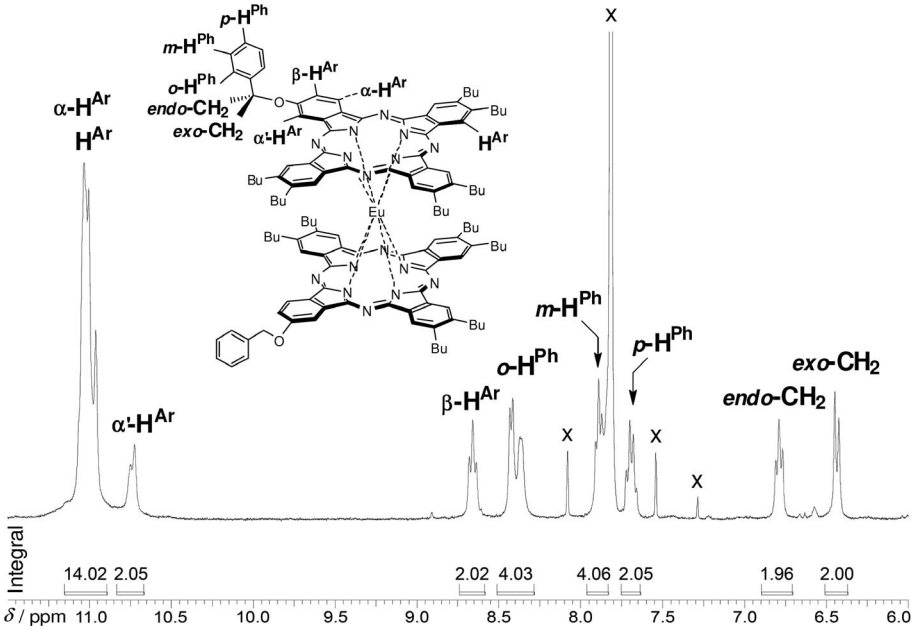

Figure 3. ^{1}H NMR spectrum of compound **1a** (aromatic region) in $CDCl_3$/[D_6]DMSO (1:1, v/v) with the addition of 1–2 vol.-% $N_2H_4 \cdot H_2O$; "×" indicates signals from residual $CHCl_3$.

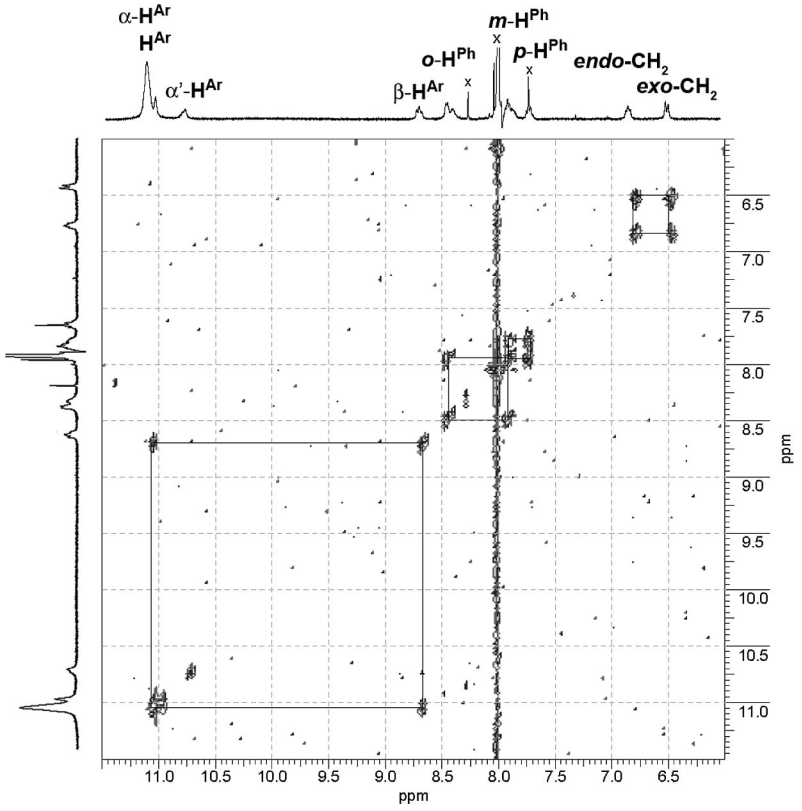

Figure 4. ^{1}H–^{1}H COSY NMR spectrum of compound **1a** (aromatic region) in $CDCl_3$/[D_6]DMSO (1:1, v/v) with the addition of 1–2 vol.-% $N_2H_4 \cdot H_2O$; "×" indicates signals from residual $CHCl_3$.

and **1b**. The protons of the phthalocyanine core are slightly shielded by 0.1–0.2 ppm indicating the similar electron-donating properties of the benzyloxy and hydroxy substituents. However, in the case of the europium complex **2a** the β-H^{Ar} proton signal demonstrated unexpected significant deshielding compared to the corresponding peak in the spectrum of the benzyloxy-protected compound **1a**, and also revealed the dependence of the chemical shift and peak

resolution on the solvent system used for data collections (Figures S10, S10a, S10b and Table S3 in the Supporting Information).

The NMR data can be rationalized by taking into account two processes competing in solution, namely, the dissociation of the hydroxy groups in **2a** and **2b** and the reduction of the complexes to negatively charged diamagnetic species. The first process seems to dominate for **2a** resulting in the delocalization of negative charge over the bis(phthalocyanine) moiety, while the remaining radical moves to the oxygen atom and, consequently, may influence the nearby protons. Furthermore, the signal of the β-protons should reveal a greater downfield shift than that of the α-protons, since they are strongly influenced by the core macrocyclic π-conjugated system. In turn, due to the smaller Lu ionic radius compared to the Eu ion, **2b** is characterized by a closer ligand arrangement then **2a**. This enhances the π–π interactions facilitating radical delocalization and, consequently, results in the lower acidity of the hydroxy groups that assists the reduction process mentioned above. Thus, direct radical extinction takes place for **2b**, which causes no significant changes in chemical shifts of the signals of the remaining protons compared with corresponding peaks in the spectrum of benzyloxy-protected **1b**. Nevertheless, these statements require more detailed physicochemical studies, which lie beyond the scope of the current investigation.

Electrochemistry

The redox properties of bis(phthalocyanine) complexes **1** and **2** were studied in *o*-dichlorobenzene (DCB) by cyclic voltammetry (CV) with a platinum disk electrode in the potential range from –2.4 to 1.1 V (vs. Fc/Fc^+). The compounds underwent up to three quasi-reversible ($i_p \approx v^{1/2}$, $\Delta E_p \approx 0.1$ V) reduction processes, labeled R_1, R_2, and R_3, as well as one reversible and one irreversible, i.e. no back peak was observed, oxidation processes labeled Ox_1 and Ox_2, respectively. Table 3 lists the half-wave potentials ($E_{1/2}$), and Figure 5 shows the CV curves for the reversible couples.

Table 3. Half-wave potentials for **1** and **2** in DCB.

	$E_{1/2}$ [V] (vs. Fc/Fc^+)				
	R_3	R_2	R_1	Ox_1	Ox_2[a]
1a		–1.76	–0.57	–0.15	1.02
1b	–2.16	–1.74	–0.66	–0.23	1.05
2a		–2.10	–0.57	–0.20	0.76
2b		–2.12	–0.67	–0.29	0.86

[a] Approximate values.

The negative shift of the redox potentials for the Eu (**a**) with respect to the Lu (**b**) complexes is in good agreement with previous reports,[14,15] and can be explained by the increased interaction between the phthalocyanine rings due to the distance between the macrocycles shortening along with a decreasing REE ionic radius. The redox potentials

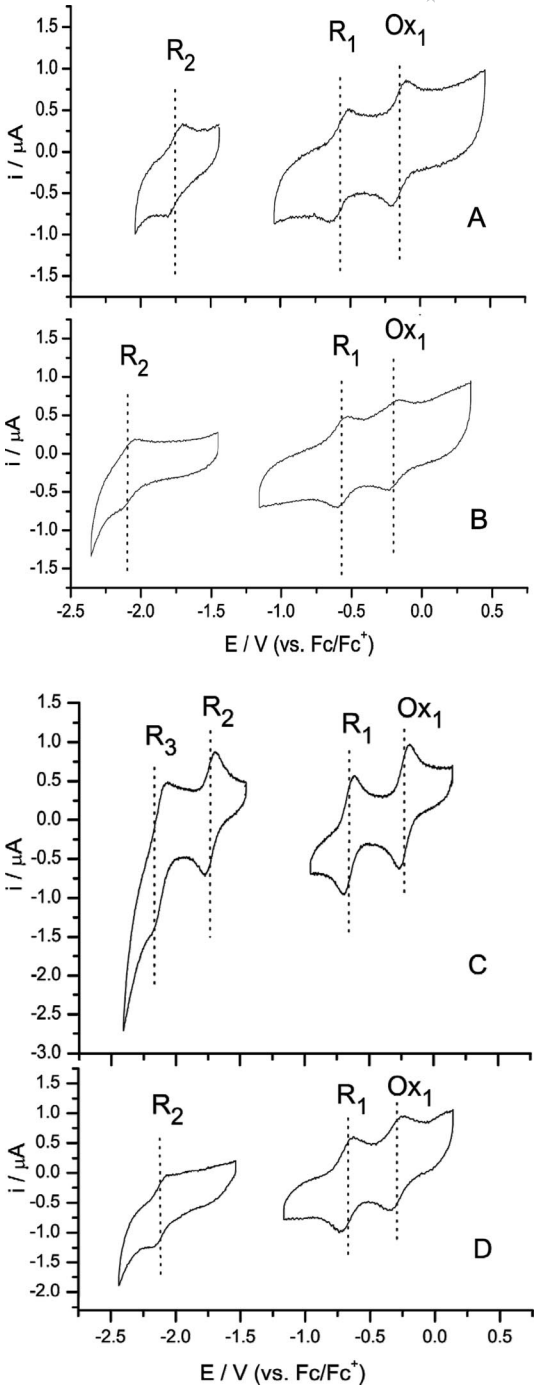

Figure 5. Cyclic voltammograms for reversible couples in DCB containing 0.2 M $[BuN_4][BF_4]$, with scan rate = 0.20 $V s^{-1}$: (A) **1a** ($^{BnO,Bu}Pc_2Eu$); (B) **2a** ($^{HO,Bu}Pc_2Eu$); (C) **1b** ($^{BnO,Bu}Pc_2Lu$); (D) **2b** ($^{HO,Bu}Pc_2Lu$).

of **1**, and especially the gaps between the first two oxidation and reduction peaks lie close to the literature values[14,15] for similar phthalocyanine complexes.

Debenzylation of complexes **1** to generate the corresponding complexes **2** results in a cathodic shift of the Ox_1, Ox_2 and R_1, R_2 peaks by 50–60 mV, 200–250 mV and 5–15 mV, 340–380 mV, respectively. This shift indicates a noticeable destabilization of complexes **2** compared to com-

plexes **1**, since less energy is required for the oxidation and more for the reduction processes. A similar effect has been noted previously[14] for phthalocyanines with electron-donating peripheral groups, and an opposite effect has been mentioned[16] in the case of acceptor substituents. The shift of the R_2 peak by ca. 350 mV in the voltammograms of complexes **2** compared to the corresponding peak in the voltammograms of **1** is stronger than expected from the debenzylation. The electron-donating effect of the hydroxy groups can be enhanced by the solvent and electrolyte that can induce polarization along the H–O bond, apparently leading to the formation of ionic pairs, thus increasing the negative charge on the oxygen atoms. However, taking into account the completely identical UV/Vis/NIR spectra of the initial neutral forms of **1** and **2**, and also the very similar UV/Vis spectra of both the one-electron-reduced and -oxidized forms, as described in the next section, the redox couple labeled as R_2 for **2** could be considered as an analogue of the R_3 reduction observed for **1**, whereas the real R_2 could remain undetectable due to the poor electrochemical reversibility of R_2 due to the presence of the hydroxy groups.

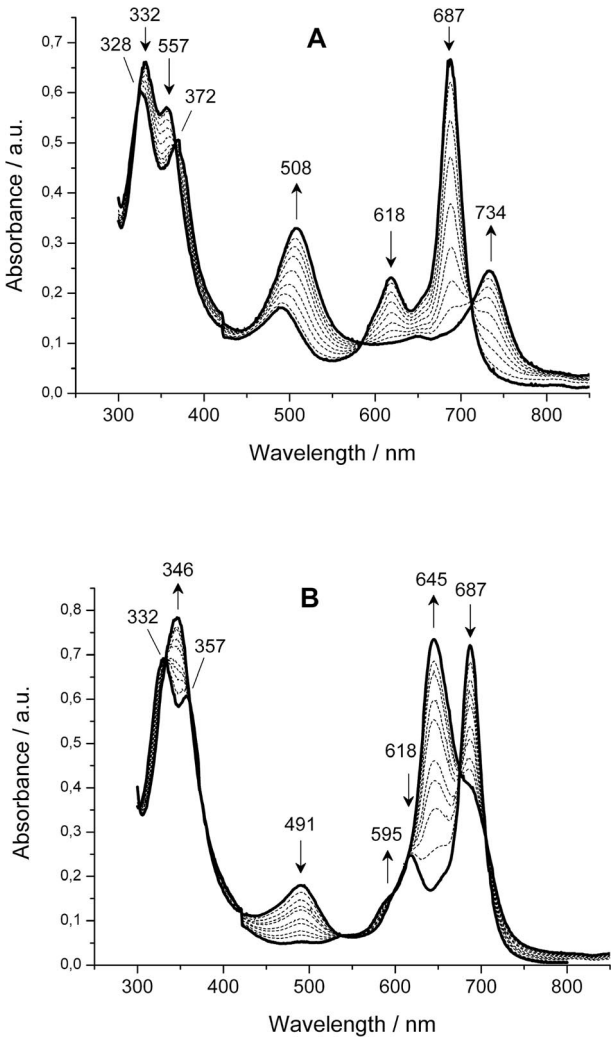

Figure 6. UV/Vis spectral changes for **2a** ($^{HO,Bu}Pc_2Eu$) in DCB containing 0.4 M $[BuN_4][BF_4]$ during (A) controlled potential oxidation (+0.15 V) and (B) reduction (–0.85 V).

Spectroelectrochemistry

It is well known that phthalocyanines reveal strong changes in their electronic absorption spectra while undergoing oxidation and reduction, providing opportunities for different applications. UV/Vis spectral changes for complex **2a** ($^{HO,Bu}Pc_2Eu$) during controlled potential electrolysis at +0.15 and –0.85 V (Figure 6) reflect the transformation of the neutral double-decker phthalocyanine to the one-electron-oxidized and -reduced forms,[15,17] respectively. The data for **1a** ($^{BnO,Bu}Pc_2Eu$) obtained under the same conditions gave identical band positions for all redox states (Table 4).

Table 4. Electronic absorption data for the neutral, oxidized, and reduced forms of **1a** and **2a**.

	State	λ_{max} [nm]			
		B (Soret)	π-Radical	Q_{vib}	Q
1a	$[^{BnO,Bu}Pc_2Eu]^0$	331, 357	492	618	687
	$[^{BnO,Bu}Pc_2Eu]^+$	328, 372	510	649	732
	$[^{BnO,Bu}Pc_2Eu]^-$	347		598[a]	645, 693sh
2a	$[^{HO,Bu}Pc_2Eu]^0$	332, 357	491	618	687
	$[^{HO,Bu}Pc_2Eu]^+$	331, 371	508	649	734
	$[^{HO,Bu}Pc_2Eu]^-$	346		595[a]	645, 691sh

[a] Approximate position.

Thus, the removal of the benzyloxy protecting group in **1** that leads to the hydroxy-substituted complexes **2** does not noticeably change the distances between the energy levels, at least for those that give rise to bands found in the UV/Vis spectra, but the energy of the whole system is probably increased since considerable cathodic shifts of the redox potentials were observed. After complete electrolysis, the initial neutral forms of the phthalocyanines were fully recovered by back oxidation/reduction. This demonstrates the good stability of the oxidized and reduced forms in solution, also implying that the double-decker complexes obtained are promising electrochromic materials.

Conclusions

Starting from 2-benzyloxy-9,10,16,17,23,24-hexa-*n*-butylphthalocyanine we have prepared a series of A_3B-type ligand based homoleptic REE–bis(phthalocyanine) complexes, including hydroxy-substituted derivatives, which are inaccessible directly from the corresponding 9,10,16,17,23,24-hexa-*n*-butyl-2-hydroxyphthalocyanine ligand. The phenolic hydroxy group containing complexes were found to be stable π-radicals as well as conventional bis(phthalocyanines), which is unambiguously supported by spectral as well as electrochemical data. An investigation of the application of these complexes as synthetic building blocks is currently underway and will be discussed elsewhere.

Experimental Section

General: Column chromatography was carried out on silica gel columns (Merck, Silicagel 60, 0.040–0.063 mm) with the eluents indicated. Preparative TLC was performed with flexible plates: Merck Silica Gel 60, Merck Silica Gel 60 F_{254}, and Merck Aluminium Oxide F_{254} neutral. Gel permeation chromatography was accomplished on polymeric support Bio-Beads S-X1 (BIORAD) with C_6H_6 as the eluent. The electrolyte for voltammetric and spectroelectrochemical studies, $[Bu_4N][BF_4]$ (Sigma–Aldrich), was recrystallized twice from ethyl acetate/hexane (9:1, v/v) and dried under vacuum at 70 °C, the *o*-dichlorobenzene (DCB, 99%, Sigma–Aldrich, HPLC-grade) for these studies was used as received. All other reagents and solvents were obtained or distilled according to standard procedures. The compounds $[M(acac)_3]\cdot nH_2O$,[18] 4,5-dibutylphthalonitrile[19] and 4-benzyloxyphthalonitrile[9a] were prepared according to literature procedures. The salts $[M(acac)_3]\cdot nH_2O$ and $Mg(OAc)_2\cdot 4H_2O$ were dried immediately before use in vacuo, in a desiccator, at 50 °C for 5 h and at 110 °C for 10 h, respectively. The $^{Bu}PcH_2$ ligand as well as the corresponding magnesium complex $^{Bu}PcMg$ were obtained as by-products during the synthesis of $^{HO,Bu}PcH_2$, and had spectral characteristics that are identical to published data.[11,20] All the reactions were monitored by TLC and UV/Vis and were continued until complete disappearance of starting reagents was observed, unless otherwise specified.

Electronic absorption (UV/Vis) spectra were recorded with a ThermoSpectronic Helios-α spectrophotometer with 0.5 cm quartz cells with the samples dissolved in C_6H_6, $CHCl_3$, CCl_4 or DCB. UV/Vis/NIR measurements were made with a Hitachi-230 instrument with 0.5 cm quartz cells with the samples dissolved in CCl_4. MALDI-TOF mass spectra were taken with a VISION-2000 mass spectrometer with 2-[(2*E*)-3-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene]malonitrile (DCTB) or 2,5-dihydroxybenzoic acid (DHB) as the matrix. High-resolution MALDI mass spectra were recorded with a Bruker ULTRAFLEX II TOF/TOF instrument with DCTB as the matrix. ^1H NMR and ^1H–^1H COSY spectra were recorded with a Bruker AVANCE 400 spectrometer (400.13 MHz) with the initial ligand samples dissolved in $[D_8]$THF. The complex samples were dissolved in $CDCl_3$/$[D_6]$DMSO (1:1, v/v) mixture to which $N_2H_4\cdot H_2O$ (1–2 vol.-%) was added at 20 °C, unless otherwise specified. Chemical shifts are given in ppm relative to $SiMe_4$. Coupling constants *J* are given in Hz. FT-IR spectra were recorded on KBr-matrix pellets with a Nicolet NEXUS IR-FURJE spectrometer with a resolution of 2 cm^{-1}.

Electrochemical measurements were carried out with an IPC-Pro potentiostat (Econix, Russia). Cyclic voltammetry (CV) was performed in a conventional three-electrode cell with a Pt-disk (2.0 mm in diameter) working and Pt-foil counter electrodes. The Ag|AgCl reference electrode was connected to the solution through a salt bridge and a Luggin capillary, the tip of which was placed close to the working electrode. The junction potentials were corrected for by a ferrocenium$^+$/ferrocene (Fc^+/Fc) couple. The sample (0.1–0.5 mmol dm^{-3}) was dissolved in a 0.2 mol dm^{-3} solution of $[Bu_4N][BF_4]$ in DCB, the solution was purged with argon for 20 min before measurements were taken. The open circuit potential of the working electrode when immersed in the phthalocyanine solutions was approximately –0.3 V. The scan rate was varied from 0.05 to 1.00 V s^{-1}. All measurements were performed at ambient temperature (22 ± 1 °C).

Spectroelectrochemical experiments were performed with a quartz electrochemical cell composed of three separated compartments. The rectangular compartment with a path length of 9.3 mm contained a Pt-net working electrode, which was placed near the side-wall of the cell to avoid it interfering with the light beam. A Luggin capillary and a capillary for argon purging were placed close to the working electrode. A reference Ag|AgCl electrode was connected to the cell through a salt bridge. A Pt-counter electrode with a surface area larger than the area of the working electrode was placed in a separate compartment and connected to the working space through a glass tube fitted with a frit. Sample solutions contained 0.4 mol dm^{-3} of $[Bu_4N][BF_4]$ and 0.01 mmol dm^{-3} of sample. Pure argon was passed through the sample solution to remove oxygen and to stir the solution gently during the electrolysis process.

Preparation of $[^{HO,Bu}PcMg]$: A mixture of 4,5-dibutylphthalonitrile (547.2 mg, 2.28 mmol), 4-benzyloxyphthalonitrile (88.9 mg, 0.38 mmol) and lithium methoxide (187.7 mg, 4.94 mmol) in isoamyl alcohol (15 mL) was heated under reflux for about 3 h. The solution was cooled to room temperature and concentrated under reduced pressure. The residue was washed with MeOH (3 × 50 mL), dried at 50 °C for 1 h, then dissolved in concentrated H_2SO_4 and poured onto ice. The resulting precipitate was filtered off, washed with water to obtain a neutral pH, and dried at 80 °C for 2 h. The obtained solid powder (254 mg, and according to MALDI-TOF spectrometry a mixture of $^{HO,Bu}PcH_2$ and $^{Bu}PcH_2$, which was poorly soluble and hard to separate) was suspended in DCB (10 mL), then DBU (0.329 mL, 1.33 mmol) and $Mg(OAc)_2\cdot 4H_2O$ (244 mg, 1.14 mmol) were added, and the mixture was then kept under reflux for 2 h. The resulting solution was concentrated under reduced pressure, and 50 mL of MeOH was subsequently added. The precipitate formed after 2 h was filtered off. The mother liquor was treated with acetic acid to obtain a neutral pH, and another fine precipitate formed that according to MALDI-TOF was pure $^{HO,Bu}PcMg$. Both precipitates were washed with boiling 80% aqueous MeOH (3 × 50 mL), filtered, and dried in vacuo. The first precipitate (which according to MALDI-TOF spectrometry was a mixture of $^{HO,Bu}PcMg$ and $^{Bu}PcMg$) was dissolved in $CHCl_3$ and subjected to chromatography on silica gel. The by-product $^{Bu}PcMg$ was separated from the mixture with $CHCl_3$/pyridine (100:1) as the eluent, and then the column was eluted with $CHCl_3$/Py (20:1) to isolate the $^{HO,Bu}PcMg$ complex, the solvent evaporated, and the residue dried in vacuo. The total reaction yield for $^{HO,Bu}PcMg$ was 158.8 mg (47%). ^1H NMR ($[D_8]$THF): δ = 8.64–9.33 (m, 9 H, Pc-H), 3.95 (br. t, *J* = 7.3 Hz, 12 H, α-CH_2), 1.95–2.12 (m, 12 H, β-CH_2), 1.52–1.64 (m, 12 H, γ-CH_2), 1.13 (br. t, *J* = 7.3 Hz, 18 H, CH_3) ppm. FT-IR (KBr): $\tilde{\nu}$ = 3220–3450 (OH) cm^{-1}. UV/Vis (C_6H_6): λ_{max} (I/I_{max}) = 355 (0.868), 627 (0.332), 688 (1.000) nm. MS (MALDI-TOF, DHB): calcd. for $C_{56}H_{65}N_8OMg$ $[M + H]^+$ 889.5; found 889.1.

Preparation of $[^{HO,Bu}PcH_2]$: The magnesium complex $^{HO,Bu}PcMg$ (25 mg, 0.028 mmol) was dissolved in concentrated H_2SO_4 and kept for 5 min, then poured onto ice. The precipitate was filtered, washed consecutively with H_2O, to obtain a neutral pH, and 80% aqueous MeOH (3× 20 mL), and dried in vacuo. Yield 22 mg (98%). ^1H NMR ($[D_8]$THF): δ = 8.73–9.24 (m, 9 H, Pc-H), 3.86 (br. t, *J* = 7.3 Hz, 12 H, α-CH_2), 2.05–2.19 (m, 12 H, β-CH_2), 1.54–1.66 (m, 12 H, γ-CH_2), 1.19 (br. t, *J* = 7.3 Hz, 18 H, CH_3) ppm. FT-IR (KBr): $\tilde{\nu}$ = 3210–3400 (OH) cm^{-1}. UV/Vis (C_6H_6): λ_{max} (I/I_{max}) = 347 (0.757), 614 sh (0.348), 649 (0.523), 669 (0.934), 705 (1.000) nm. MS (MALDI-TOF, DHB): calcd. for $C_{56}H_{66}N_8O$ $[M]^+$ 866.5; found 866.2.

Preparation of $[^{BnO,Bu}PcH_2]$: NaH (10 mg, 0.417 mmol) was added to a solution of $^{HO,Bu}PcH_2$ (72 mg, 0.083 mmol) in DMF (3 mL), and the mixture was stirred under sonication at ambient temperature for 30 min. After that, benzyl chloride (0.04 mL, 0.348 mmol) was added, and stirring was continued for another 1 h. The solu-

tion was treated with H_2O (10 mL), a precipitate formed, which was filtered and washed consecutively with H_2O (3× 30 mL) and MeOH (2× 30 mL). Yield 65 mg (82%). UV/Vis (C_6H_6): λ_{max} (I/I_{max}) = 348 (0.690), 614sh (0.283), 650 (0.455), 670 (0.889), 706 (1.000) nm. MS (MALDI-TOF, DHB): calcd. for $C_{63}H_{72}N_8O$ $[M]^+$ 956.6, $[M - Bn]^+$ 865.5; found 956.5, 865.5.

Preparation of [$^{BnO,Bu}Pc_2Ln$] [Ln = Eu (1a), Lu (1b)]: A mixture of ligand $^{BnO,Bu}PcH_2$ (25 mg, 0.026 mmol), MeOLi (3 mg, 0.078 mmol), $[Eu(acac)_3]\cdot 3H_2O$ (6.5 mg, 0.013 mmol) and 100 mg of *n*-hexadecanol (cetyl alcohol) was heated under argon to 180 °C for 20 min (Scheme 1, pathway A). In the same fashion, a mixture of $^{BnO,Bu}PcH_2$ (25 mg, 0.026 mmol), $[Lu(acac)_3]\cdot 3H_2O$ (6.8 mg, 0.013 mmol) and 100 mg of cetyl alcohol was heated under argon to 210 °C for 30 min (Scheme 1, pathway B). The mixtures were cooled to room temperature, then diluted with C_6H_6 (5 mL), the insoluble components were filtered off, and the solvents evaporated. The residues were repeatedly washed with boiling MeOH (4× 30 mL) and dried in vacuo. The greenish solids that were obtained were dissolved in C_6H_6 and subjected to gel permeation chromatography from which the green bands containing the target double-decker complexes were collected.

Preparation of [$^{HO,Bu}Pc_2Ln$] [Ln = Eu (2a), Lu (2b)]: The lanthanide complexes [$^{BnO,Bu}Pc_2Ln$] (25 mg, ca. 0.012 mmol) were dissolved in concentrated H_2SO_4 (2 mL) and immediately poured onto ice. The precipitates were filtered, washed consecutively with H_2O to obtain a neutral pH and 80% aqueous MeOH (3× 30 mL), and then dried in vacuo. The greenish solids that were obtained were dissolved in C_6H_6 and subjected to gel permeation chromatography from which the green bands containing the target complexes were collected.

The reaction yields for compounds **1** and **2** are given in Table 1.

Supporting Information (see footnote on the first page of this article): MALDI-TOF and HR mass spectra, UV/Vis/NIR spectra and data, ^1H and ^1H–^1H COSY NMR spectra and data for the double-decker complexes **1** and **2**; details of the control experiments on thermal stability of ligand $^{HO,Bu}PcH_2$ and complexes **2**.

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