

Controlling the Nature of Mixed (Phthalocyaninato)(porphyrinato) Rare-Earth(III) Double-Decker Complexes: The Effects of Nonperipheral Alkoxy Substitution of the Phthalocyanine Ligand

Rongming Wang,^[a] Renjie Li,^[a] Yong Li,^[a] Xianxi Zhang,^[a] Peihua Zhu,^[a] Pui-Chi Lo,^[b] Dennis K. P. Ng,^{*,[b]} Na Pan,^[a, c] Changqin Ma,^[a] Nagao Kobayashi,^[c] and Jianzhuang Jiang^{*,[a]}

Abstract: The half-sandwich rare-earth complexes $[M^{III}(\text{acac})(\text{TCIPP})]$ ($M = \text{Sm}, \text{Eu}, \text{Y}$; $\text{TCIPP} = \text{meso-tetrakis}(4\text{-chlorophenyl})\text{porphyrinate}$; $\text{acac} = \text{acetylacetonate}$), generated in situ from $[M(\text{acac})_3] \cdot n\text{H}_2\text{O}$ and $\text{H}_2(\text{TCIPP})$, were treated with 1,8,15,22-tetrakis(3-pentyl-oxy)phthalocyanine $[\text{H}_2\{\text{Pc}(\alpha\text{-OC}_5\text{H}_{11})_4\}]$ ($\text{Pc} = \text{phthalocyaninate}$) under reflux in *n*-octanol to yield both the neutral nonprotonated and protonated (phthalocyaninato)(porphyrinato) rare-earth double-decker complexes, $[M^{III}\{\text{Pc}(\alpha\text{-OC}_5\text{H}_{11})_4\}(\text{TCIPP})]$ (**1–3**) and $[M^{III}\text{H}\{\text{Pc}(\alpha\text{-OC}_5\text{H}_{11})_4\}(\text{TCIPP})]$ (**4–6**), respectively. In contrast, reaction

of $[Y^{III}(\text{acac})(\text{TCIPP})]$ with 1,4,8,11,15,18,22,25-octakis(1-butyloxy)-phthalocyanine $[\text{H}_2\text{Pc}(\alpha\text{-OC}_4\text{H}_9)_8]$ gave only the protonated double-decker complex $[Y^{III}\text{H}\{\text{Pc}(\alpha\text{-OC}_4\text{H}_9)_8\}(\text{TCIPP})]$ (**7**). These observations clearly show the importance of the number and positions of substituents on the phthalocyanine ligand in controlling the nature of the (phthalocyaninato)-

(porphyrinato) rare-earth double-deckers obtained. In particular, α -alkoxylation of the phthalocyanine ligand is found to stabilize the protonated form, a fact supported by molecular-orbital calculations. A combination of mass spectrometry, NMR, UV-visible, near-IR, MCD, and IR spectroscopy, and X-ray diffraction analyses, facilitated the differentiation of the newly prepared neutral nonprotonated and protonated double-decker complexes. The crystal structure of the protonated form has been determined for the first time.

Keywords: phthalocyanines • porphyrinoids • rare-earth elements • sandwich complexes • substitution effect

Introduction

Porphyryns and their non-naturally occurring analogues, phthalocyanines, are the most common and important tetrapyrrole derivatives.^[1] Both series of macrocycles can form complexes with almost all the metals in the Periodic Table. Rare earths, actinides, and some early transition metals and main-group elements form sandwich-type complexes with these ligands in the form of double- and triple-deckers, which are emerging as an important class of functional materials.^[2] The bis(phthalocyaninato) rare-earth sandwich complexes have been known since the mid 1960s,^[3] while studies of their bis(porphyrinato) counterparts began in the 1980s.^[4] To understand the nature of the ring-to-ring interactions in these bis- and tris(tetrapyrrole) metal complexes, a substantial number of heteroleptic sandwich compounds with different porphyrin and/or phthalocyanine ligands have been prepared and examined in recent years.^[5]

[a] R. Wang, R. Li, Y. Li, X. Zhang, P. Zhu, Dr. N. Pan, Prof. C. Ma, Prof. J. Jiang
Department of Chemistry, Shandong University
Jinan 250100 (China)
Fax: (+86) 531-856-5211
E-mail: jzjiang@sdu.edu.cn

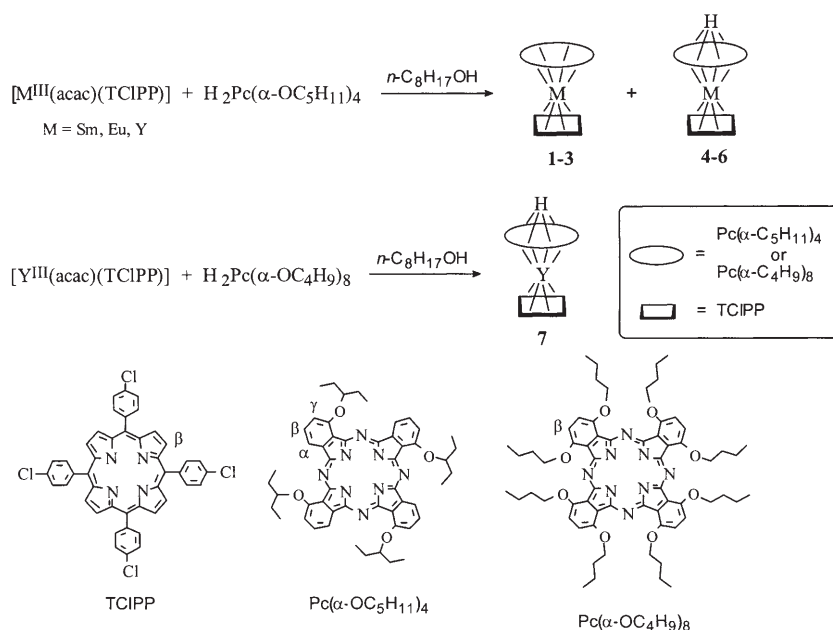
[b] P.-C. Lo, Prof. D. K. P. Ng
Department of Chemistry
The Chinese University of Hong Kong, Shatin
N.T., Hong Kong (China)
Fax: (+852) 2603-5057
E-mail: dkpn@cuhk.edu.hk

[c] Dr. N. Pan, Prof. N. Kobayashi
Department of Chemistry, Graduate School of Science
Tohoku University, Sendai 980-8578 (Japan)

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Bis(phthalocyaninato) rare-earth complexes are usually prepared by cyclic tetramerization of phthalonitriles with rare-earth salts in the presence of an organic base, such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), as a promoter. In these reactions, protonated double-deckers $[M^{III}H(Pc')_2]$ (Pc' = general phthalocyaninate) are believed to be the initial products that undergo oxidation in air to give the nonprotonated analogues $[M^{III}(Pc')_2]$.^[6] In the presence of reducing agents, some mono-anionic double-deckers such as $Li[M^{III}(Pc)_2]$ ($M = La-Yb$ except Ce),^[7] $(NBu_4)[M^{III}(Pc)_2]$ ($M = La, Ce, Pr, Nd, Sm, Gd, Ho, Lu$),^[8] and $(PNP)[M^{III}(Pc)_2]$ (PNP = bis(triphenylphosphino)iminium; $M = La, Gd, Tm$)^[8a,9] have been isolated and characterized. The synthesis of the bis(porphyrinato) complexes usually involves the treatment of metal-free porphyrins with rare-earth salts, such as $M(acac)_3 \cdot nH_2O$. The "reduced" protonated double-deckers, such as $[Pr^{III}H(TTP)_2]$ (TPP = *meso*-tetraphenylporphyrinate), $[Pr^{III}H(OEP)_2]$ (OEP = octaethylporphyrinate), $[M^{III}H(TPP)_2]$ ($M = La-Lu$ except Ce), and $[M^{III}H(OEP)-(TPP)]$ ($M = Nd-Lu$), and their neutral nonprotonated counterparts have also been isolated.^[10] Mixed (phthalocyaninato)(porphyrinato) rare-earth double-deckers are usually prepared by $[M^{III}(Por)(acac)]$ (Por = general porphyrinate)-induced cyclic tetramerization of phthalonitriles or by treating metal-free porphyrins with Li_2Pc in the presence of rare-earth salts. The reduced protonated species $[La^{III}H(Pc)(TPP)]$ ^[11] and $[M^{III}H(Pc)(TPyP)]$ [$M = Gd, Eu, Y$; $TpyP$ = *meso*-tetra(4-pyridyl)porphyrinate]^[12] and the lithiated analogues $Li[M^{III}(Pc)(TPyP)]$ ($M = Eu, Gd$)^[13] have been isolated and characterized, mainly by electronic absorption spectroscopy, and are proposed to be the intermediates in the formation of the neutral nonprotonated mixed-ring double-deckers. In the present paper, we describe in detail the isolation, spectroscopic, and structural characterization of the reduced protonated mixed-ring double-decker rare-earth(III) complexes $[M^{III}H\{Pc(\alpha-OC_5H_{11})_4\}(TCIPP)]$ ($M = Sm, Eu, Y$) (**4-6**) and $[Y^{III}H\{Pc(\alpha-OC_4H_9)_8\}(TCIPP)]$ (**7**), the formation of which was promoted by the use of α -alkoxyphthalocyanines. A comparison of the spectroscopic and structural data with that obtained for the available neutral complexes $[M^{III}\{Pc(\alpha-OC_5H_{11})_4\}(TCIPP)]$ ($M = Sm, Eu, Y$) (**1-3**) provides direct and unambiguous evidence for the formation of such reduced, protonated, mixed (phthalocyaninato)(porphyrinato), rare-earth(III) double-decker complexes.

The electrochemical and spectroscopic properties of phthalocyanine derivatives can be tuned by changing the type, number, and positions of the substituents on the macrocycle ligands. However, to the best of our knowledge, no study of the influence of the substituents of the phthalocyanine ligand on the formation of the corresponding sandwich rare-earth complexes has been made. To this end, mixed-ring double-decker rare-earth complexes $M(TCIPP)[Pc(\alpha-OC_5H_{11})_4]$ ($M = Sm, Eu, Y$) (**1-3**), $MH(TCIPP)[Pc(\alpha-OC_5H_{11})_4]$ ($M = Sm, Eu, Y$) (**4-6**), and $YH(TCIPP)[Pc(\alpha-OC_4H_9)_8]$ (**7**), Scheme 1, have been designed, prepared, and



Scheme 1. Synthesis of mixed double-decker complexes.

characterized. The TCIPP ligand is the same in all complexes; complexes **1-7** differ only in the nature and number of alkoxy groups at the non-peripheral positions of the phthalocyanine ligand. The effect of alkoxy substituents at these positions on the properties of the isolated mixed (phthalocyaninato)(porphyrinato) rare-earth complexes is discussed in relation to the properties of analogous complexes containing *unsubstituted* phthalocyanine ligand.^[14,15] This constitutes the first attempt towards understanding the effect of substituents of the phthalocyanine ligand on the formation chemistry of the corresponding rare-earth sandwich complexes.

Results and Discussion

Synthesis of heteroleptic double-deckers 1-7: Treatment of the half-sandwich complexes $[M^{III}(acac)(TCIPP)]$ ($M = Sm, Eu, Y$), which were generated in situ from the corresponding $[M(acac)_3] \cdot nH_2O$ ($M = Sm, Eu, Y$) and H_2TCIPP , with the metal-free phthalocyanine $H_2Pc(\alpha-OC_5H_{11})_4$ in refluxing

n-octanol for seven hours gave a mixture of the nonprotonated double-deckers $[M^{III}\{Pc(\alpha-OC_5H_{11})_4(TCIPP)\}]$ ($M = Sm, Eu, Y$; **1–3**, respectively) and their protonated analogues $[M^{III}H\{Pc(\alpha-OC_5H_{11})_4(TCIPP)\}]$ ($M = Sm, Eu, Y$; **4–6**, respectively), Scheme 1. These compounds were soluble in common organic solvents, such as $CHCl_3$, CH_2Cl_2 , and toluene, and could be separated by column chromatography. Interestingly, when $[Y^{III}(acac)(TCIPP)]$ was treated with the octa- α -substituted phthalocyanine $H_2Pc(\alpha-OC_4H_9)_8$, only the protonated double-decker $[Y^{III}H\{Pc(\alpha-OC_4H_9)_8(TCIPP)\}]$ (**7**) was isolated. Heteroleptic triple-decker complexes were not detected in any of these reactions. It is worth noting that treatment of $[M^{III}(acac)(TCIPP)]$ ($M = Y, La-Er$ except Ce and Pm) with $Li_2(Pc)$ results in a mixture of the triple-deckers $[M^{III}_2(Pc)(TCIPP)_2]$ and $[M^{III}_2(Pc)_2(TCIPP)]$ together with a small amount of $[M^{III}(Pc)(TCIPP)]$.^[14] In contrast, reaction of $[M^{III}(acac)(TCIPP)]$ ($M = Y, La-Lu$ except Ce and Pm) with phthalonitrile in the presence of DBU affords neutral nonprotonated double-deckers $[M^{III}(Pc)(TCIPP)]$ via the intermediate protonated $[M^{III}H(Pc)(TCIPP)]$ species.^[15] These results clearly show that the α -alkoxy substituents of the phthalocyanine ligand can stabilize the protonated double-deckers.

For comparative studies of the effects of α -substitution, we used the β -substituted 2(3),9(10),16(17),24(5)-tetrakis(3-pentyloxy)phthalocyanine $[H_2Pc(\beta-OC_5H_{11})_4]$ and 2,3,9,10,16,17,23,24-octakis(1-pentyloxy)phthalocyanine $[H_2Pc(\beta-OC_5H_{11})_8]$ as starting materials. Similar reaction conditions to those described above yielded mixed triple-deckers as the main reaction products together with a trace amount of nonprotonated double-deckers.^[16] It is likely that the protonated intermediate products are easily oxidized by air and that the resulting neutral nonprotonated double-deckers further complex with the half-sandwich phthalocyaninato or porphyrinato complexes to form the triple-deckers. These observations clearly show the importance of the number and position of substituents on the phthalocyanine ligand in controlling the nature of the isolated mixed (phthalocyaninato)(porphyrinato) rare-earth double-deckers.

Spectroscopic characterization: Compounds **1–7** gave satisfactory elemental analysis data, which are presented in Table 1 together with the product yields. The table also

shows the MALDI-TOF mass-spectral data. Under the same experimental conditions, the mass of the monoisotopic protonated molecular ion ($[MH]^+$) for the protonated double-deckers **4–6** shifts by one mass unit compared to that of the nonprotonated counterparts **1–3**. In the table, the masses of the molecular ion of the protonated and nonprotonated Sm and Y complexes differ by only 0.3 and 0.1, respectively. The isotopic pattern is in good agreement with the simulated spectrum for all these compounds, as exemplified by the spectrum of the protonated europium analogue **5** (Figure 1).

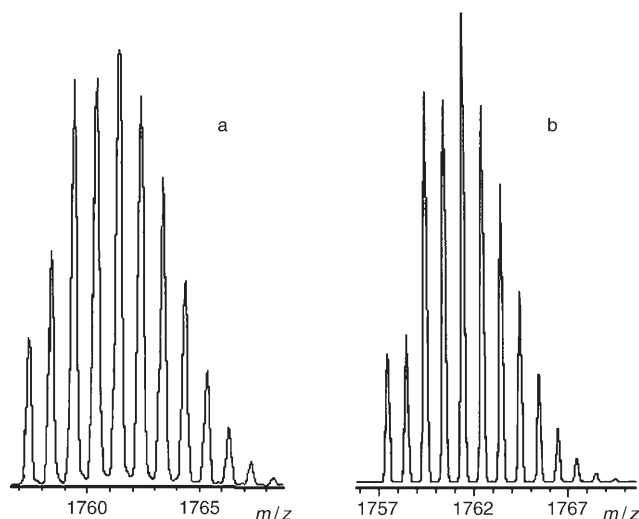


Figure 1. a) Experimental and b) simulated isotopic pattern for the molecular ion of $[Eu^{III}H\{Pc(\alpha-OC_5H_{11})_4(TCIPP)\}]$.

Like other nonprotonated bis(tetrapyrrole) rare-earth(III) complexes,^[2] the double-deckers **1–3** can be regarded as single-hole complexes in which an unpaired electron is present in one of the macrocyclic ligands. This was demonstrated by the EPR spectrum of $[Y^{III}\{Pc(\alpha-OC_5H_{11})_4(TCIPP)\}]$ (**3**), which showed a characteristic signal for organic radicals at $g=2.000$. In contrast, the protonated yttrium analogues **6** and **7** were EPR silent, showing that these compounds are diamagnetic. The samarium and europium complexes **1** and **2** were also EPR silent due to the interaction between the ring's unpaired electron and the paramagnetic metal center.

Table 1. Analytical and mass spectroscopic data for the heteroleptic double-deckers **1–7**.

Compound	Yield [%]	$[MH]^+$ (m/z) ^[a,b]	Analysis (%) ^[a]		
			C	H	N
$[Sm^{III}\{Pc(\alpha-OC_5H_{11})_4(TCIPP)\}]$ (1) ^[c]	16	1758.7 (1759.4)	64.98 (64.87)	4.63 (4.54)	9.27 (9.44)
$[Eu^{III}\{Pc(\alpha-OC_5H_{11})_4(TCIPP)\}]$ (2) ^[c]	19	1760.2 (1760.4)	64.62 (64.80)	4.63 (4.53)	9.13 (9.43)
$[Y^{III}\{Pc(\alpha-OC_5H_{11})_4(TCIPP)\}]$ (3) ^[c]	24	1695.8 (1696.4)	67.32 (67.19)	4.92 (4.70)	9.41 (9.77)
$[Sm^{III}H\{Pc(\alpha-OC_5H_{11})_4(TCIPP)\}]$ (4) ^[d]	24	1760.0 (1760.4)	63.33 (63.73)	4.51 (4.52)	8.83 (9.24)
$[Eu^{III}H\{Pc(\alpha-OC_5H_{11})_4(TCIPP)\}]$ (5) ^[d]	31	1761.4 (1761.5)	63.22 (63.67)	4.54 (4.51)	8.82 (9.23)
$[Y^{III}H\{Pc(\alpha-OC_5H_{11})_4(TCIPP)\}]$ (6) ^[d]	61	1696.9 (1697.4)	65.47 (65.96)	4.71 (4.68)	9.15 (9.56)
$[Y^{III}H\{Pc(\alpha-OC_4H_9)_8(TCIPP)\}]$ (7)	52	1930.4 (1930.6)	66.60 (67.72)	5.32 (5.48)	8.70 (8.71)

[a] Calculated values given in parentheses. [b] By MALDI-TOF mass spectrometry. The value corresponds to the most abundant isotopic peak of the protonated molecular ion ($[MH]^+$). [c] Contains 0.2 equiv of solvated $CHCl_3$. [d] Contains 0.5 equiv of solvated $CHCl_3$.

Due to the presence of the unpaired electron and the paramagnetic nature of some of the rare-earth ions, NMR data for single-hole bis(tetrapyrrole) rare-earth(III) complexes are difficult to obtain.^[2] Surprisingly, satisfactory NMR spectra were not be obtained for the apparently diamagnetic protonated double-deckers **4–7**. To illustrate this, Figure 2a

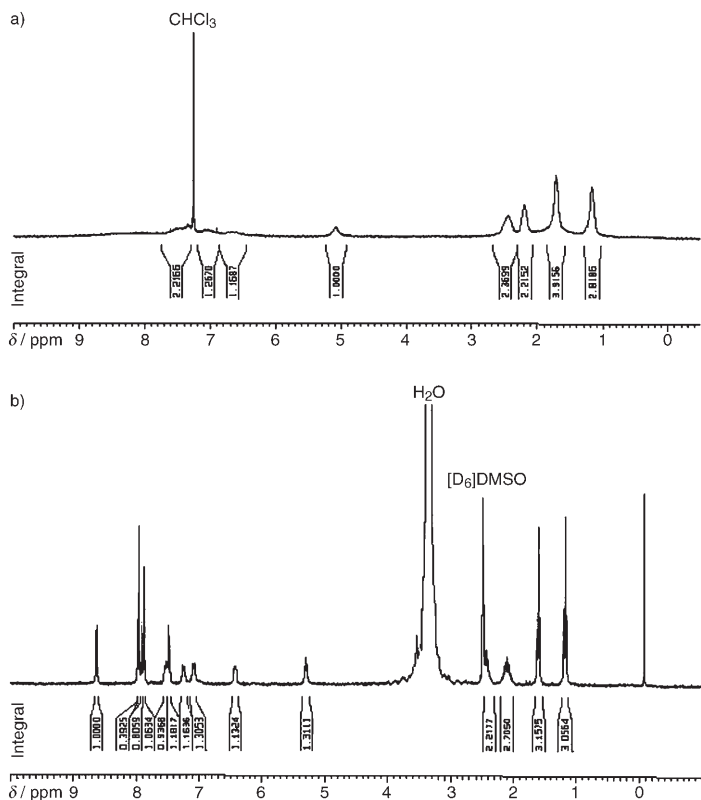


Figure 2. ¹H NMR spectra of [Y^{III}H{Pc(α-OC₅H₁₁)₄}(TCIPP)] (**6**) in a) CDCl₃ and b) CDCl₃/DMSO (1:1) in the presence of approximately 1% hydrazine hydrate.

shows the ¹H NMR spectrum of the yttrium complex **6** in CDCl₃. Only few broad signals are observed (at δ = 5.1 and 1.2–2.5 ppm) for the 3-pentyloxy substituents. However, upon addition of about 1% hydrazine hydrate, a common reducing agent for acquiring NMR data for nonprotonated double-deckers,^[17] a well-resolved spectrum was obtained, giving virtually all the expected signals. As shown in Figure 2b, the doublets at δ = 8.63 and 7.48 ppm are due to the α and γ ring protons of Pc(α-OC₅H₁₁)₄. The signals for the β protons of Pc(α-OC₅H₁₁)₄ and TCIPP overlap in the region δ = 7.86–7.99 ppm. As a result of the disposition of the 3-pentyloxy substituents about the C₄ axis, the TCIPP β protons are no longer equivalent. Due to the restricted rotation of the 4-chlorophenyl ring around the C(*meso*)–C(*ipso*) bond in TCIPP, and the 3-pentyloxy group about the C(*ipso*)–O bond in Pc(α-OC₅H₁₁)₄, four broad doublets (at δ = 7.54, 7.25, 7.09, and 6.43 ppm) are observed for the C₆H₄Cl ring protons, while the 3-pentyloxy group resonates

as three multiplets at δ = 5.28–5.33 (OCH), 2.36–2.50 (CH₂), and 2.00–2.20 ppm (CH₂), and two triplets at δ = 1.61 and 1.19 ppm (CH₃). The assignments were unambiguously confirmed by the ¹H–¹H COSY spectrum. It is likely that the acidic proton in **6** is weakly bound to one of the nitrogen atoms and that the slow tautomerization leads to a broadening of the signals. Addition of hydrazine hydrate converts the protonated species to the diamagnetic mono-anionic double-decker [Y^{III}{Pc(α-OC₅H₁₁)₄}(TCIPP)][–], so that a satisfactory spectrum is observed.

The spectra for the samarium and europium analogues **4** and **5** are similar to that of **6**, except that the signals occur in narrower and wider regions, respectively, due to the paramagnetic nature of the metal centers. The data and assignments are given in Tables 2 and 3. Note that the spectra of **4–6** obtained in this manner are virtually identical to those of the corresponding nonprotonated analogues **1–3**, with and without hydrazine hydrate. This suggests that, for both series of complexes, the species under study are actually the mono-anionic double-deckers.

The ¹H NMR spectrum of [Y^{III}H{Pc(α-OC₄H₉)₈}(TCIPP)] (**7**) treated with hydrazine hydrate was also satisfactorily assigned. The β protons of Pc(α-OC₄H₉)₈ gave rise to a singlet at δ = 7.49 ppm. The β protons of TCIPP are equivalent, giving a singlet at δ = 7.92 ppm, while the four C₆H₄Cl protons gave three broad multiplets at δ = 6.4–7.6 ppm. The OCH₂ protons are diastereotopic in this environment, giving two multiplets at δ = 5.01–5.10 and 4.92–4.98 ppm. The remaining methylene and methyl protons gave the typical resonance patterns (Table 3).

The electronic absorption (Table 4) and magnetic circular dichroism (MCD) spectra of compounds **1–7** were measured in CHCl₃ (Figure 3). The spectra of the nonprotonated double-deckers [M^{III}{Pc(α-OC₅H₁₁)₄}(TCIPP)] (M = Sm, Eu, Y; **1–3**, respectively) exhibit features typical of single-hole (phthalocyaninato)(porphyrinato) double-decker complexes.^[2,5a] All three absorption spectra show medium to strong bands at 309–310 and 406–410 nm, which can be attributed to the Soret bands of the phthalocyanine and porphyrin ligands, respectively. The Faraday A-term-like dispersion in the MCD spectra of the corresponding signals supports this assignment. The absorptions at 469–470 and 989–1033 nm can be attributed to the electronic transitions involving the semi-occupied molecular orbital (SOMO). An additional marker band for single-hole double-deckers in the near-IR region (1174–1220 nm) shifts toward the blue as the size of the metal center decreases.

The absorption spectra of the protonated analogues [M^{III}H{Pc(α-OC₅H₁₁)₄}(TCIPP)] (M = Sm, Eu, Y; **4–6**, respectively; Figure 4) resemble those of double-deckers containing two dianionic ligands, such as [Ce^{IV}(Pc)(TPP)],^[18] [M^{IV}(Pc)(Por)] (M = Zr, Hf, Th, U),^[19] and Li[M^{III}(Pc)(TPyP)] (M = Eu, Gd).^[13] The spectra show medium to strong phthalocyanine and porphyrin Soret bands at 315 and 413–416 nm, respectively, and several Q bands in the 567–944 nm region. The spectra also display a band of medium intensity at 490–492 nm, which is attributed to a transition

Table 2. ^1H NMR data (δ [ppm]) for the aromatic protons in heteroleptic double-deckers **4–7** in $\text{CDCl}_3/[\text{D}_6]\text{DMSO}$ (1:1) in the presence of approximately 1% hydrazine hydrate.

H_β	Signals for TCIPP		H_α	Signals for $\text{Pc}(\alpha\text{-OC}_5\text{H}_{11})_4$ or $\text{Pc}(\alpha\text{-OC}_4\text{H}_9)_8$	
	H_{aryl}			H_β	H_γ
4	7.08–7.13 (m, 12H) ^[a]	6.78 (brd, $J=7.2$ Hz, 4H), 5.98 (brd, $J=7.2$ Hz, 4H)	8.11 (d, $J=7.5$ Hz, 4H)	7.65 (t, $J=7.5$ Hz, 4H)	7.22–7.24 (m, 8H) ^[a]
5	7.20–7.28 (m, 8H), ^[a] 7.13 (d, $J=4.8$ Hz, 4H)	10.96–11.00 (m, 4H) 8.68–8.72 (m, 4H), 6.76–6.80 (m, 4H)	10.04 (d, $J=7.5$ Hz, 4H)	8.42 (t, $J=7.5$ Hz, 4H)	– ^[b]
6	7.86–7.99 (m, 12H) ^[c]	7.54 (brd, $J=7.2$ Hz, 4H), 7.25 (brd, $J=7.2$ Hz, 4H), 7.09 (brd, $J=7.2$ Hz, 4H), 6.43 (brd, $J=7.2$ Hz, 4H)	8.63 (d, $J=7.5$ Hz, 4H)	–	7.48 (d, $J=7.5$ Hz, 4H)
7	7.92 (s, 8H)	7.48–7.62 (m, 4H), 7.06–7.24 (m, 8H), 6.42–6.54 (m, 4H)	–	7.49 (s, 8H)	–

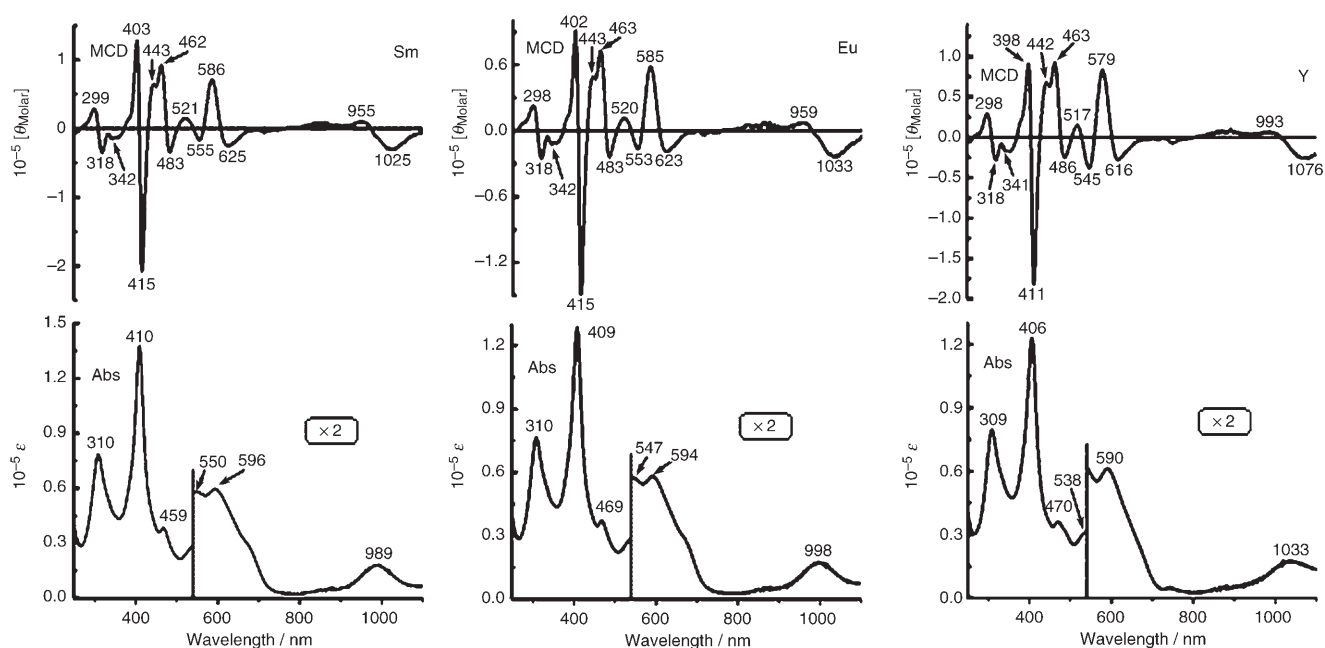
[a] Overlapped with one of the TCIPP H_{aryl} signals. [b] Obscured by the strong residual CHCl_3 signal at $\delta=7.95$ ppm. [c] Overlapped with the H_β signal of $\text{Pc}(\alpha\text{-OC}_5\text{H}_{11})_4$.

Table 3. ^1H NMR data (δ [ppm]) for the side chain protons in heteroleptic double-deckers **4–7** in $\text{CDCl}_3/[\text{D}_6]\text{DMSO}$ (1:1) in the presence of approximately 1% hydrazine hydrate.

	OCH (or OCH_2)	Signals for $\text{Pc}(\alpha\text{-OC}_5\text{H}_{11})_4$ or $\text{Pc}(\alpha\text{-OC}_4\text{H}_9)_8$	
		CH_2	CH_3
4	4.72–4.78 (m, 4H)	1.98–2.08 (m, 8H) 1.76–1.90 (m, 8H)	1.18 (t, $J=7.2$ Hz, 12H) 1.04 (t, $J=7.2$ Hz, 12H)
5	5.98–6.02 (m, 4H)	3.50–3.68 (m, 8H) 2.85–2.98 (m, 8H)	2.82 (t, $J=7.5$ Hz, 12H) 1.64 (t, $J=7.5$ Hz, 12H)
6	5.28–5.33 (m, 4H)	2.36–2.50 (m, 8H) 2.00–2.20 (m, 8H)	1.61 (t, $J=7.5$ Hz, 12H) 1.19 (t, $J=7.5$ Hz, 12H)
7	5.01–5.10 (m, 8H) 4.92–4.98 (m, 8H)	2.06–2.15 (m, 16H) 1.65–1.76 (m, 16H)	1.08 (t, $J=7.5$ Hz, 24H)

Table 4. Electronic absorption data for double-deckers **1–7** in CHCl_3 .

	$\lambda_{\text{max}} \text{ nm}^{-1} (\log \epsilon)$								
1	310 (3.89)	410 (4.14)	469 (3.58)	551 (3.46)	596 (3.47)	679 (3.15)	989 (2.96)	1220 (2.70)	
2	310 (3.88)	409 (4.11)	469 (3.57)	547 (3.46)	594 (3.46)	671 (3.17)	998 (2.94)	1211 (2.71)	
3	309 (3.90)	406 (4.09)	470 (3.56)	538 (3.49)	590 (3.48)	646 (3.25)	1033 (2.94)	1174 (2.78)	
4	315 (3.81)	416 (4.36)	492 (3.73)	567 (3.23)	613 (3.52)	849 (3.13)	898 (3.14)		
5	315 (3.81)	415 (4.33)	492 (3.74)	569 (3.23)	614 (3.53)	849 (3.11)	907 (3.13)		
6	315 (3.83)	413 (4.35)	490 (3.84)	576 (3.24)	617 (3.59)	849 (3.03)	944 (3.09)		
7	323 (4.85)	418 (5.40)	498 (4.75)	571 (4.20)	627 (4.56)	848 (sh)	954 (4.20)		

Figure 3. Electronic absorption and MCD spectra of $[\text{M}^{\text{III}}\{\text{Pc}(\alpha\text{-OC}_5\text{H}_{11})_4\}(\text{TCIPP})]$ ($\text{M}=\text{Sm}, \text{Eu}, \text{Y}; \mathbf{1}\text{--}\mathbf{3}$, respectively) in CHCl_3 .

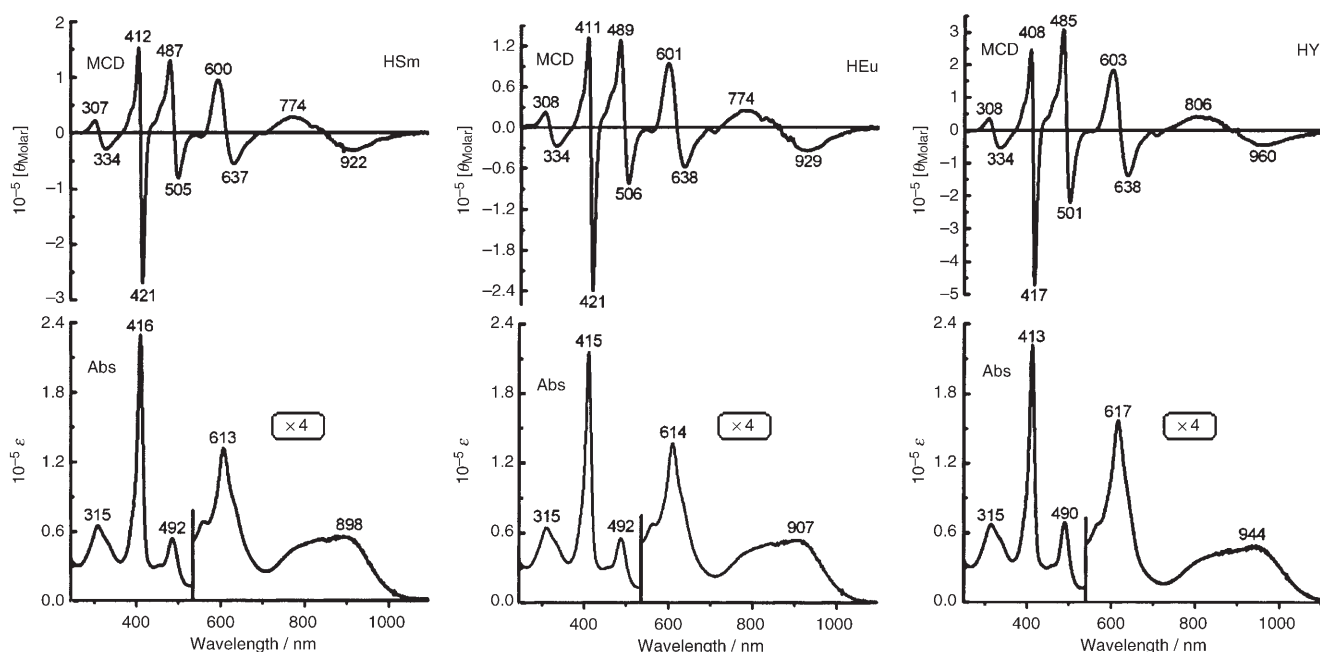


Figure 4. Electronic absorption and MCD spectra of $[M^{III}H[Pc(\alpha\text{-OC}_5\text{H}_{11})_4](\text{TCIPP})]$ ($M=\text{Sm, Eu, Y; 4-6}$; respectively) in CHCl_3 .

involving a delocalized orbital.^[19,20] A near-IR absorption band at approximately 1200 nm, characteristic of the non-protonated complexes, was not detected for **4-6**, thus confirming the “reduced” nature of these double-deckers. The MCD spectra of **4-6** (Figure 4) are simpler than those of **1-3** due to the reduced number of possible transitions associated with the fully occupied HOMO and the degenerate LUMO of the protonated complexes. The Faraday A-term-like dispersion for all the Soret and Q absorption bands is indicative of transitions from HOMO or low-lying occupied molecular orbitals to the degenerate LUMO or higher unoccupied degenerate orbitals. Compound **7** has similar spectral characteristics and can be assigned similarly. The data are collected in Table 4.

The IR spectra of **1-3** showed an intense band at 1308–1310 cm^{-1} , which is a marker band for the phthalocyanine π -radical anion.^[21] The TCIPP⁻ marker band at about 1270–1300 cm^{-1} was not observed. The results suggest that the unpaired electron resides mainly on the phthalocyanine ligand, as is reported for many (phthalocyaninato)(porphyrinato) rare-earth(III) double-deckers.^[2,5a,15b] For the protonated complexes **4-7**, the phthalocyanine π -radical-anion marker band is shifted to approximately 1325 cm^{-1} , which is characteristic of dianionic phthalocyanine ligands.^[21] Hence both of the macrocyclic ligands in **4-7** are regarded as dianions. For comparison, the IR spectra of the nonprotonated and protonated yttrium complexes **3** and **6** are provided in Supporting Information (Figure S1).

Structural studies: The molecular structures of the nonprotonated double-deckers **1** and **2**, and their protonated counterparts **4-6** were determined by X-ray diffraction analyses. The latter are the first structurally characterized protonated

(phthalocyaninato)(porphyrinato) double-decker complexes. Single crystals of these compounds were obtained by slow diffusion of MeOH into the corresponding solutions of the complexes in CHCl_3 . The C_4 symmetry of these double-decker molecules means that they are intrinsically chiral, as are the bis(phthalocyaninato) analogues $[M^{III}(\text{Pc})\{\text{Pc}(\alpha\text{-OC}_5\text{H}_{11})_4\}]$.^[22] However, attempts to resolve the two enantiomers of the samarium compounds **1** and **4** by HPLC using a silica gel column coated with cellulose 2,3,6-tris(3,5-dimethylphenylcarbamate) were unsuccessful due to their limited solubility in hexane-containing solvent systems [note that organic solvents other than hexane will dissolve and remove the active material of cellulose 2,3,6-tris(3,5-dimethylphenylcarbamate) coated on silica gel].^[23]

Compounds **1** and **2** crystallize in the orthorhombic system, with two pairs of enantiomeric double-deckers per unit cell. On the other hand, compounds **4-6** crystallize in the triclinic system with one pair of enantiomeric molecules per unit cell. The crystal structures of these protonated double-deckers also contain two solvated CHCl_3 molecules. Figure 5 shows the molecular structures of the samarium compounds **1** and **4** viewed along the C_4 axis. Both compounds adopt a slightly distorted square-antiprismatic structure around the metal center. However, the average twist angle, defined as the rotation angle of one macrocycle away from the eclipsed conformation of the two macrocycles, was found to be larger for **1** and **2** (43.8–44.1° vs 38.3–38.9° for **4-6**). These data together with other structural parameters for these compounds are summarized in Table 5, from which the structural differences between the two series of double-deckers are evident. Apart from the average twist angle, the distance between the metal and the N_4 plane of TCIPP, for example, is also significantly larger for the protonated

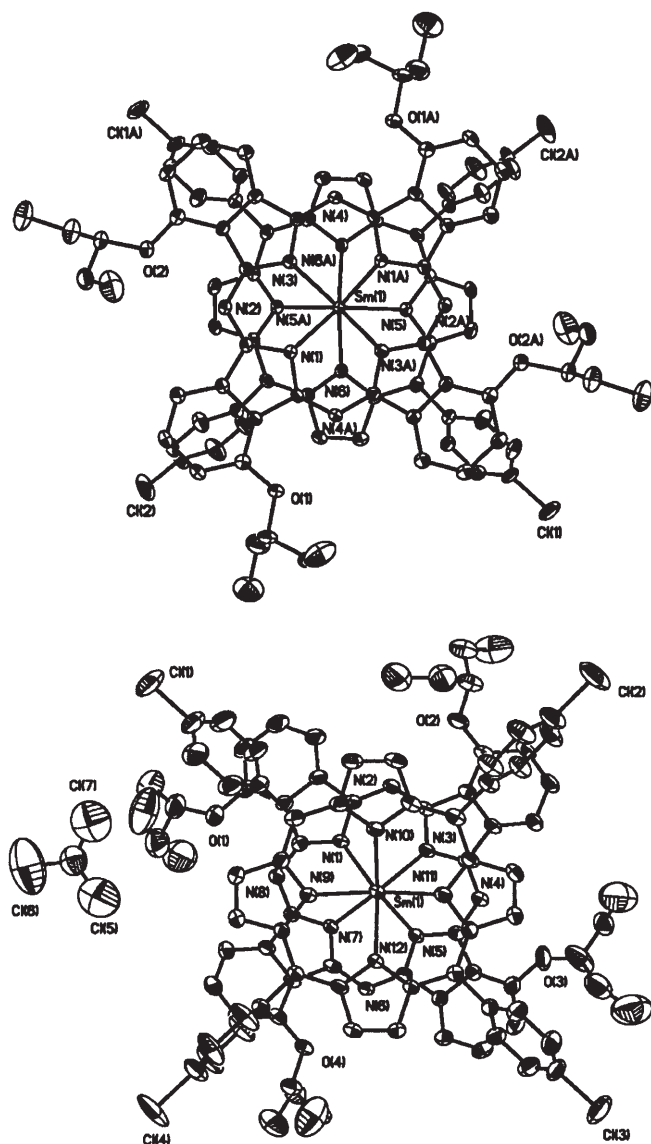


Figure 5. Molecular structure of $[\text{Sm}^{\text{III}}\{\text{Pc}(\alpha\text{-OC}_5\text{H}_{11})_4\}(\text{TCIPP})]$ (**1**) (top) and $[\text{Sm}^{\text{III}}\text{H}\{\text{Pc}(\alpha\text{-OC}_5\text{H}_{11})_4\}(\text{TCIPP})]$ (**4**) (below) viewed along the C_4 axis. Hydrogen atoms are omitted for clarity and the ellipsoids are drawn at the 30% probability level.

Table 5. Comparison of the structural data for double-deckers **1**, **2**, and **4–6**.

	1	2	4	5	6
average M–N(TCIPP) bond length [Å]	2.474	2.452	2.471	2.472	2.439
average M–N $[\text{Pc}(\alpha\text{-OC}_5\text{H}_{11})_4]$ bond length [Å]	2.528	2.502	2.523	2.519	2.479
M–N $_4$ (TCIPP) plane distance [Å]	1.334	1.312	1.363	1.349	1.304
M–N $_4$ $[\text{Pc}(\alpha\text{-OC}_5\text{H}_{11})_4]$ plane distance [Å]	1.557	1.533	1.558	1.545	1.496
interplanar distance [Å]	2.891	2.845	2.921	2.894	2.800
dihedral angle between the two N $_4$ planes [°]	0.0	0.0	0.9	1.0	0.8
average dihedral angle φ for the TCIPP ring [°] ^[a]	11.0	11.5	11.8	11.8	12.6
average dihedral angle φ for the $\text{Pc}(\alpha\text{-OC}_5\text{H}_{11})_4$ ring [°] ^[a]	13.8	14.2	11.5	12.8	13.4
average twist angle [°] ^[b]	43.8	44.1	38.3	38.4	38.9

[a] The average dihedral angle of the individual pyrrole or isoindole rings with respect to the corresponding N $_4$ mean plane. [b] Defined as the rotation angle of one macrocycle away from the eclipsed conformation of the two macrocycles.

double-deckers than for their nonprotonated counterparts, leading to a greater ring-to-ring separation.

As shown in the crystal-packing diagram for $[\text{Sm}^{\text{III}}\text{H}\{\text{Pc}(\alpha\text{-OC}_5\text{H}_{11})_4\}(\text{TCIPP})]$ (**4**) (Figure S2a in Supporting Information), the two enantiomeric molecules appear to be bound to each other to form a pseudo-quadruple-decker supramolecular structure through the two $\text{Pc}(\alpha\text{-OC}_5\text{H}_{11})_4$ ligands. The ring-to-ring separation of the mean planes of the two virtually parallel N(isoindole) $_4$ moieties in $\text{Pc}(\alpha\text{-OC}_5\text{H}_{11})_4$ is 4.40 Å (4.45 and 4.53 Å for the europium and yttrium analogues **5** and **6**, respectively). This value is comparable with the distance 4.23 Å reported previously for the slipped pseudo-quadruple-decker complex of phthalocyanines $[(\text{Pc})\text{Sm}^{\text{III}}\{\text{Pc}(\alpha\text{-OC}_4\text{H}_9)_8\}\text{Na}_2\{\text{Pc}(\alpha\text{-OC}_4\text{H}_9)_8\}\text{Sm}^{\text{III}}(\text{Pc})]$ (**8**), a complex in which the two heteroleptic bis(phthalocyaninato) units are linked by two sodium atoms through the $\text{Pc}(\alpha\text{-OC}_4\text{H}_9)_8$ rings.^[24] The distance between the two C_4 axes of each $[\text{Sm}^{\text{III}}\text{H}\{\text{Pc}(\alpha\text{-OC}_5\text{H}_{11})_4\}(\text{TCIPP})]$ unit is 4.04 Å (4.95 and 4.61 Å for **5** and **6**, respectively), which is much shorter than that of **8** (6.97 Å).^[24] These results suggest the presence of a significant and effective π – π interaction between the two phthalocyanine rings due to their close proximity in the supramolecular structure. In contrast, the N(pyrrole) $_4$ planes of TCIPP in adjacent molecules are separated by 7.22 Å (7.26 and 7.35 Å for **5** and **6**, respectively), indicating that the intermolecular π – π interaction between the TCIPP rings is insignificant.

The nonprotonated analogue $[\text{Sm}^{\text{III}}\{\text{Pc}(\alpha\text{-OC}_5\text{H}_{11})_4\}(\text{TCIPP})]$ (**1**) has a different crystal packing (Figure S2b in the Supporting Information) and the large separation between the two C_4 axes of adjacent $[\text{Sm}^{\text{III}}\{\text{Pc}(\alpha\text{-OC}_5\text{H}_{11})_4\}(\text{TCIPP})]$ units (8.01 Å) prevents an effective interaction between the π systems.

Electrochemical properties: The redox behavior of the nonprotonated double-deckers **1–3** was studied by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) with CH_2Cl_2 as the solvent. All compounds exhibited three quasi-reversible one-electron oxidations and three quasi-reversible one-electron reductions, all of which can be attributed to ligand-based redox processes. The half-wavelength potentials are summarized in Table 6. Apart from a slight shift in the potentials, the electrochemical properties of these compounds are similar to those of $[\text{M}^{\text{III}}(\text{Pc})(\text{TCIPP})]$.^[15b]

The protonated complexes **4–7** exhibited redox behavior typical of protonated bis(tetrapyrrole) rare-earth compounds;^[10b–e] however, this behavior is more complicated and difficult to interpret than that of the nonprotonated complexes. The shapes of some of the voltammograms are not well-defined, but nevertheless

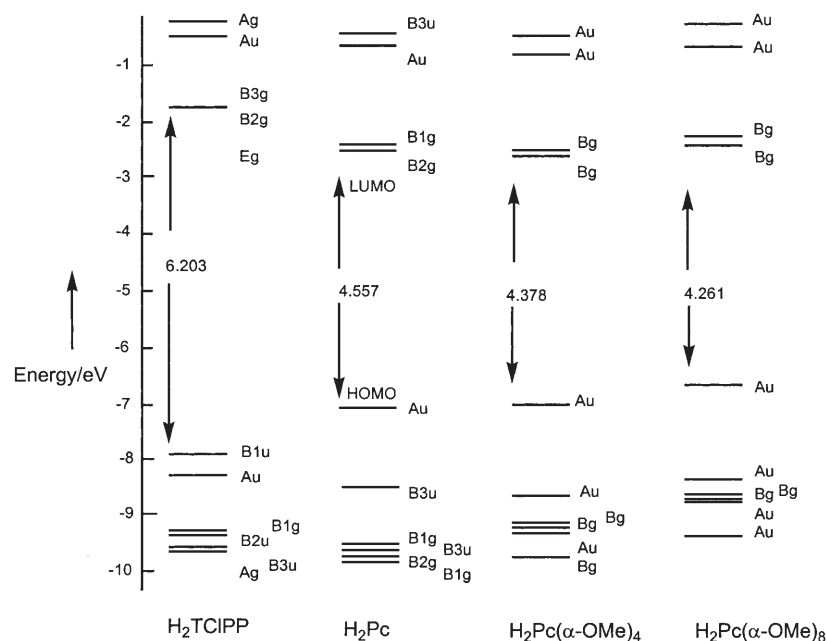
Table 6. Electrochemical data for the non-protonated double-deckers **1–3**.^[a]

	Oxd ₃	Oxd ₂	Oxd ₁	Red ₁	Red ₂	Red ₃
1	+1.56	+1.24	+0.59	+0.06	−1.39	−1.83
2	+1.56	+1.23	+0.57	+0.05	−1.39	−1.86
3	+1.56	+1.22	+0.48	−0.04	−1.46	−1.94

[a] Recorded with [Bu₄N][ClO₄] as electrolyte in CH₂Cl₂ (0.1 mol dm^{−3}) at ambient temperature. Potentials were obtained by cyclic voltammetry with a scan rate of 20 mV s^{−1}, and are expressed as half-wave potentials (*E*_{1/2}) in V relative to SCE unless otherwise stated.

show roughly 10 redox couples in CH₂Cl₂. The addition of triethylamine did simplify the voltammograms slightly; however assignments were difficult to make and further analysis is required to fully understand the electrochemical behavior of the complexes.

Molecular-orbital calculations: In an attempt to rationalize the effect of α -substitution of the phthalocyanine ligand on the formation of these double-decker complexes, we performed molecular-orbital calculations for H₂TCIPP and the metal-free phthalocyanines H₂Pc, H₂Pc(α -OMe)₄, and H₂Pc(α -OMe)₈ within the framework of the PM3 approximation. Figure 6 shows partial orbital-energy diagrams for these


 Figure 6. Partial energy diagram for H₂TCIPP, H₂Pc, H₂Pc(α -OMe)₄, and H₂Pc(α -OMe)₈ obtained by PM3 calculations.

macrocycles. The energy of the HOMO increases significantly in the order: H₂Pc, H₂Pc(α -OMe)₄, H₂Pc(α -OMe)₈, while the LUMO energy of H₂Pc lies between that of H₂Pc(α -OMe)₄ and H₂Pc(α -OMe)₈. The energy difference between the HOMO levels of H₂TCIPP and the substituted phthalocyanines is larger than that between the HOMOs of H₂TCIPP and H₂Pc, suggesting a weaker π – π interaction in

the double-deckers containing substituted phthalocyanine ligand. This will decrease the extent of delocalization of the unpaired electron over the two macrocycles. In other words, the SOMO will have a higher phthalocyanine character for complexes with α -substituted phthalocyanine ligands, compared with [M^{III}(Pc)(TCIPP)].^[15b] This in turn facilitates the formation of protonated (and “reduced”) species. Hence, by using H₂Pc(α -OC₅H₁₁)₄ as the starting material, both non-protonated (**1–3**) and protonated (**4–6**) double-deckers were formed, while the use of H₂Pc(α -OC₄H₉)₈ gave only the protonated double-decker **7**.

Revealing the location of the proton in complexes 4–7: An interesting problem in relation to these protonated double-deckers is the question of the location of the acidic proton. As in the case of [M^{III}H(OEP)(TPP)],^[10] satisfactory ¹H NMR spectra could not be obtained, probably due to tautomerization, and the proton could not be located using this technique.

Although crystallographic studies could not directly reveal the location of this proton, a detailed examination of the structural parameters may shed some light on the matter. As mentioned in the previous section, the protonated double-deckers form a pseudo-quadruple-decker supra-

molecular structure in the crystal lattice. The close separation between the Pc(α -OC₅H₁₁)₄ rings in adjacent molecules (4.40–4.53 Å) seems to suggest that weak hydrogen bonds may exist linking the enantiomeric molecules through these macrocycles. In addition, the average twist angle of the two ligands in **4–6** (38.3–38.9°) deviates from the fully staggered conformation observed for the nonprotonated analogues. This suggests that the nonbonding interaction between the 4-chlorophenyl groups of TCIPP and the 3-pentyloxy groups of Pc(α -OC₅H₁₁)₄ is stronger in the protonated complexes, which may lead to a larger deformation in the two macrocyclic ligands. As shown in Table 5, the average dihedral angle φ for the TCIPP ring marginally increases (by 0.3–0.8°), while that of the Pc(α -OC₅H₁₁)₄

ring significantly decreases (by 1.4–2.3°) upon protonation. The larger change in deformation of the Pc(α -OC₅H₁₁)₄ ring may also suggest that the proton resides on the phthalocyanine rather than on the porphyrin ligand, as it is known that the presence of additional tetrapyrrole ligand to bis(tetrapyrrole) rare-earth complexes significantly reduces the deformation of the central tetrapyrrole ligand in the tris(tetra-

pyrrole) rare-earth compounds thus formed.^[25] This is further supported by the observation that for the nonprotonated double-deckers, the four M–N(isoindole) and the four M–N(pyrrole) bond lengths are very similar (differing by less than 0.01 Å), but for the protonated counterparts, the four M–N(isoindole) bond lengths span a wider range (differing by ca. 0.05 Å) than the four M–N(pyrrole) bond lengths (differing by ca. 0.02 Å).

Aside from these observations, it seems sensible that the acidic proton should reside at the more basic phthalocyanine ligand. In accordance with the electrochemical data and molecular-orbital calculations described earlier, each of the three phthalocyanines are more electron rich than TCIPP, and should therefore more readily accommodate the proton in the double-decker complex.

Conclusion

In summary, we have prepared a series of nonprotonated and protonated (phthalocyaninato)(porphyrinato) double-decker complexes **1–7**. The use of α -alkoxyphthalocyanines enhances the formation of the protonated form. On the basis of the spectroscopic and structural data obtained, the nonprotonated and protonated double-deckers could be differentiated, and the protonated heteroleptic (phthalocyaninato)(porphyrinato) rare-earth(III) double-decker complexes could be unambiguously characterized for the first time. Most importantly, we show that the nature of the mixed (phthalocyaninato)(porphyrinato) rare-earth double-decker complexes isolated is controlled by the number and position of alkoxy groups on the phthalocyanine ligand.

Experimental Section

General: *n*-Octanol was distilled from sodium. Hexane used for chromatography was distilled from anhydrous CaCl₂. Column chromatography was carried out on silica gel columns (Merck, Kieselgel 60, 70–230 mesh) with the eluents indicated. The electrolyte [Bu₄N][ClO₄] was recrystallized twice from tetrahydrofuran. Dichloromethane for voltammetric studies was freshly distilled from CaH₂ under nitrogen. All other reagents and solvents were used as received. The compounds H₂TCIPP,^[26] H₂Pc(α -OC₅H₁₁)₄,^[27] H₂Pc(α -OC₄H₉)₈,^[28] and [M(acac)₃] \cdot *n*H₂O^[29] were prepared according to the literature procedures.

Electronic absorption spectra were recorded on a Hitachi U-4100 spectrophotometer. Magnetic circular dichroism (MCD) measurements were made with a JASCO J-725 spectrodichrometer equipped with a JASCO electromagnet that produced magnetic fields (both parallel and antiparallel) of up to 1.09 T. Its magnitude is expressed in terms of molar ellipticity per Tesla [θ]_M/10⁴ deg mol⁻¹ m³ cm⁻¹ T⁻¹. IR spectra were recorded on KBr-matrix pellets on a BIORAD FTS-165 spectrometer with a resolution of 2 cm⁻¹. MALDI-TOF mass spectra were taken on a Bruker BIFLEX III ultra-high-resolution Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer with α -cyano-4-hydroxycinnamic acid as matrix. Elemental analyses were performed by the Institute of Chemistry, Chinese Academy of Sciences. Electrochemical measurements were carried out with a BAS CV-50W voltammetric analyzer. The cell comprised inlets for a glassy-carbon-disk working electrode of 2.0 mm in diameter and a silver-wire counter electrode. The reference electrode was Ag/Ag⁺, 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 being referenced internally to the ferrocenium/ferrocene (Fe⁺/Fe) couple ($E_{1/2}$ [Fe⁺/Fe] = 501 mV vs SCE). Typically, a 0.1 mol dm⁻³ solution of [Bu₄N][ClO₄] in CH₂Cl₂ containing 0.5 mmol dm⁻³ of sample was purged with nitrogen for 10 min. The voltammograms were then recorded at ambient temperature. The scan rate was 20 and 10 mV s⁻¹ for CV and DPV, respectively.

[M^{III}{Pc(α -OC₅H₁₁)₄}(TCIPP)] (M = Sm, Eu, Y; **1–3**, respectively) and [M^{III}H{Pc(α -OC₅H₁₁)₄}(TCIPP)] (M = Sm, Eu, Y; **4–6**, respectively): A mixture of [M(acac)₃] \cdot *n*H₂O (M = Sm, Eu, Y) (25 mg, ca. 0.05 mmol) and H₂TCIPP (38 mg, 0.05 mmol) in *n*-octanol (4 mL) was heated to reflux under nitrogen for about 4 h. The mixture was cooled to room temperature, then treated with H₂Pc(α -OC₅H₁₁)₄ (0.05 mmol) under reflux for an-

Table 7. Crystallographic data for **1**, **2**, and **4–6**.

	1	2	4-CHCl₃	5-CHCl₃	6-CHCl₃
formula	C ₉₆ H ₈₀ N ₁₂ O ₄ Cl ₄ Sm	C ₉₆ H ₈₀ N ₁₂ O ₄ Cl ₄ Eu	C ₉₇ H ₈₂ N ₁₂ O ₄ Cl ₇ Sm	C ₉₇ H ₈₂ N ₁₂ O ₄ Cl ₇ Eu	C ₉₇ H ₈₂ N ₁₂ O ₄ Cl ₇ Y
<i>M_r</i>	1757.87	1759.48	1878.25	1879.86	1816.81
crystal size [mm ³]	0.42 × 0.21 × 0.13	0.38 × 0.23 × 0.11	0.42 × 0.35 × 0.14	0.35 × 0.24 × 0.08	0.43 × 0.30 × 0.16
crystal system	orthorhombic	orthorhombic	triclinic	triclinic	triclinic
space group	<i>Pbcn</i>	<i>Pbcn</i>	<i>P1</i>	<i>P1</i>	<i>P1</i>
<i>a</i> [Å]	15.961(16)	15.87(9)	14.23(3)	14.294(10)	14.29(2)
<i>b</i> [Å]	33.03(3)	32.92(18)	17.68(4)	17.739(12)	17.64(3)
<i>c</i> [Å]	16.223(16)	16.02(9)	18.94(4)	19.044(13)	19.01(3)
α [°]	90	90	112.49(3)	112.790(9)	112.68(2)
β [°]	90	90	97.31(3)	96.654(9)	96.56(3)
γ [°]	90	90	97.40(3)	97.734(10)	97.87(2)
<i>V</i> [Å ³]	8554(15)	8368(79)	4286(15)	4336(5)	4308(11)
<i>Z</i>	4	4	2	2	2
<i>F</i> (000)	3608	3612	1922	1924	1876
ρ_{calcd} [mgm ⁻³]	1.365	1.397	1.456	1.440	1.401
μ [mm ⁻¹]	0.871	0.938	0.965	1.000	0.955
θ range [°]	1.89–25.07	1.77–25.03	1.75–25.03	2.54–25.03	1.96–25.03
total reflns	41 421	41 001	22 049	22 656	17 624
independent reflns	7423 ($R_{\text{int}} = 0.0791$)	7287 ($R_{\text{int}} = 0.1635$)	14 726 ($R_{\text{int}} = 0.0288$)	14 955 ($R_{\text{int}} = 0.0297$)	13 732 ($R_{\text{int}} = 0.0607$)
parameters	528	528	1090	1090	1085
<i>R</i> 1 [$I > 2\sigma(I)$]	0.0433	0.0460	0.0535	0.0550	0.0763
<i>wR</i> 2 [$I > 2\sigma(I)$]	0.0718	0.0648	0.1272	0.1251	0.1849
goodness of fit	1.022	0.859	0.978	0.961	0.884

other 7 h. After a brief cooling, the mixture was evaporated under reduced pressure and the residue was subjected to chromatography on a silica-gel column. A small amount of unreacted H₂TCIPP was separated by using CHCl₃/hexane (1:2) as eluent, then the column was eluted with CHCl₃. A small green band containing the metal-free phthalocyanine followed by another green band containing the nonprotonated and protonated double-deckers were developed. The latter fraction was collected and subjected to chromatography again using ethyl acetate/petroleum ether (b.p.: 60–90°C) (5:95) as eluent. The first brown band containing the nonprotonated double-decker and the second green band containing the protonated analogue were collected and evaporated. The products were further purified by recrystallization from CHCl₃/MeOH.

Note that the reaction yields for compounds 1–7 are given in Table 1.

[Y^{III}H{Pc(α-OC₄H₉)₄}(TCIPP)] (7): Following the above procedure and by using H₂Pc(α-OC₄H₉)₈ instead of H₂Pc(α-OC₅H₁₁)₄ as the starting material, this product was isolated in 52% yield. The nonprotonated counterpart was not detected during chromatography.

X-ray crystallographic analyses of 1, 2, 4–6: Crystal data and details of data collection and structure refinement are given in Table 7. Data were collected on a Bruker SMART CCD diffractometer with an MoK_α sealed tube (λ = 0.71073 Å) at 293 K, using a ω scan mode with an increment of 0.3°. Preliminary unit cell parameters were obtained from 45 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 by using the preliminary cell-orientation matrix. The SMART software was used for collecting frames of data, indexing reflections, and determination of lattice constants; SAINT-PLUS for the integration of intensity of the reflections and scaling;^[30] SADABS for the absorption correction;^[31] and SHELXL for space group and structure determination, refinements, graphics, and structure reporting.^[32] CCDC-202238, 202446, and 210752–210754 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

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- [1] *The Porphyrin Handbook, Vols. 1–20* (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), Academic Press, San Diego, **2000** and **2003**.
- [2] a) J. W. Buchler, D. K. P. Ng in *The Porphyrin Handbook, Vol. 3* (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), Academic Press, San Diego, **2000**, pp. 245–294; b) J. Jiang, K. Kasuga, D. P. Arnold in *Supramolecular Photosensitive and Electroactive Materials* (Ed.: H. S. Nalwa), Academic Press, New York, **2001**, pp. 113–210; c) J. Jiang, W. Liu, D. P. Arnold, *J. Porphyrins Phthalocyanines* **2003**, *7*, 459–473.
- [3] I. S. Kirin, P. N. Moskalev, Y. A. Makashev, *Russ. J. Inorg. Chem.* **1965**, *10*, 1065–1066.
- [4] J. W. Buchler, H.-G. Kapellmann, M. Knoff, K.-L. Lay, S. Pfeifer, *Z. Naturforsch. B.* **1983**, *38*, 1339–1345.
- [5] See, for example: a) D. K. P. Ng, J. Jiang, *Chem. Soc. Rev.* **1997**, *26*, 433–442; b) Y. Bian, J. Jiang, Y. Tao, M. T. M. Choi, R. Li, A. C. H. Ng, P. Zhu, N. Pan, X. Sun, D. P. Arnold, Z. Zhou, H.-W. Li, T. C. W. Mak, D. P. K. Ng, *J. Am. Chem. Soc.* **2003**, *125*, 12257–12267; c) Z. Liu, A. A. Yasser, J. S. Lindsey, D. F. Bocian, *Science* **2003**, *302*, 1543–1545; d) L. Wei, K. Padmaja, W. J. Youngblood, A. B. Lysenko, J. S. Lindsey, D. F. Bocian, *J. Org. Chem.* **2004**, *69*, 1461–1469.
- [6] W. Liu, J. Jiang, D. Du, D. P. Arnold, *Aust. J. Chem.* **2000**, *53*, 131–136.
- [7] A. Iwase, C. Harnood, Y. Kameda, *J. Alloys Compd.* **1993**, *192*, 280–283.
- [8] a) M. S. Haghghi, H. Homborg, *Z. Naturforsch. B. Chem. Sci.* **1991**, *46*, 1641–1649; b) N. Koike, H. Uekusa, Y. Ohashi, C. Harnood, F. Kitamura, T. Ohsaka, K. Tokuda, *Inorg. Chem.* **1996**, *35*, 5798–5804; c) M. Moussavi, A. De Cian, J. Fischer, R. Weiss, *Inorg. Chem.* **1988**, *27*, 1287–1291; d) H. Hückstädt, A. Tutab, M. Goldner, U. Cornelissen, H. Homborg, *Z. Anorg. Allg. Chem.* **2001**, *627*, 485–497.
- [9] M. S. Haghghi, A. Franken, H. Homborg, *Z. Naturforsch. B. Chem. Sci.* **1994**, *49*, 812–820.
- [10] a) J. W. Buchler, B. Scharbert, U. Englert, J. Strähle, *Chem. Ber.* **1988**, *121*, 2077–2082; b) G. A. Spyroulias, A. G. Coutsolelos, C. P. Raptopoulou, A. Terzis, *Inorg. Chem.* **1995**, *34*, 2476–2479; c) G. A. Spyroulias, C. P. Raptopoulou, D. de Montauzon, A. Mari, R. Poilblanc, A. Terzis, A. G. Coutsolelos, *Inorg. Chem.* **1999**, *38*, 1683–1696; d) J.-H. Agondanou, G. A. Spyroulias, J. Purans, G. Tsikalas, C. Souleau, A. G. Coutsolelos, S. Benazeth, *Inorg. Chem.* **2001**, *40*, 6088–6096; e) G. A. Spyroulias, A. G. Coutsolelos, *Inorg. Chem.* **1996**, *35*, 1382–1385.
- [11] D. Chabach, M. Tahiri, A. De Cian, J. Fischer, R. Weiss, M. El Malouli Bibout, *J. Am. Chem. Soc.* **1995**, *117*, 8548–8556.
- [12] J. Jiang W. Liu, X. Sun, D. K. P. Ng, *Chem. Res. Chin. Univ.* **2001**, *17*, 134–142.
- [13] J. Jiang, T. C. W. Mak, D. K. P. Ng, *Chem. Ber.* **1996**, *129*, 933–936.
- [14] X. Sun, R. Li, D. Wang, J. Dou, P. Zhu, F. Lu, C. Ma, C.-F. Choi, D. Y. Y. Cheng, D. K. P. Ng, N. Kobayashi, J. Jiang, *Eur. J. Inorg. Chem.* **2004**, 3806–3813.
- [15] a) J. Jiang, M. T. M. Choi, W.-F. Law, J. Chen, D. K. P. Ng, *Polyhedron* **1998**, *17*, 3903–3908; b) F. Lu, X. Sun, R. Li, D. Liang, P. Zhu, X. Zhang, C.-F. Choi, D. K. P. Ng, T. Fukuda, N. Kobayashi, J. Jiang, *New J. Chem.* **2004**, *28*, 1116–1122.
- [16] J. Jiang, R. Wang, R. Li, unpublished results.
- [17] a) A. Pondaven, Y. Cozien, M. L’Her, *New J. Chem.* **1992**, *16*, 711–718; b) F. Guyon, A. Pondaven, P. Guenot, M. L’Her, *Inorg. Chem.* **1994**, *33*, 4787–4793; c) C. Cadiou, A. Pondaven, M. L’Her, P. Jehan, P. Guenot, *J. Org. Chem.* **1999**, *64*, 9046–9050.
- [18] a) M. Lachkar, A. De Cian, J. Fischer, R. Weiss, *New J. Chem.* **1988**, *12*, 729–731; b) T.-H. Tran-Thi, T. A. Mattioli, D. Chabach, A. De Cian, R. Weiss, *J. Phys. Chem.* **1994**, *98*, 8279–8288.
- [19] K. M. Kadish, G. Moninot, Y. Hu, D. Dubois, A. Ibnlfassi, J.-M. Barbe, R. Guilard, *J. Am. Chem. Soc.* **1993**, *115*, 8153–8166.
- [20] R. Guilard, J.-M. Barbe, A. Ibnlfassi, A. Zrineh, V. A. Adamian, K. M. Kadish, *Inorg. Chem.* **1995**, *34*, 1472–1481.
- [21] a) J. Jiang, D. P. Arnold, H. Yu, *Polyhedron* **1999**, *18*, 2129–2139; b) F. Lu, M. Bao, C. Ma, X. Zhang, D. P. Arnold, J. Jiang, *Spectrochim. Acta Part A* **2003**, *59*, 3273–3286; c) M. Bao, P. Pan, C. Ma, D. P. Arnold, J. Jiang, *Vib. Spectrosc.* **2003**, *32*, 175–184; d) M. Bao, Y. Bian, L. Rintoul, R. Wang, D. P. Arnold, C. Ma, J. Jiang, *Vib. Spectrosc.* **2004**, *34*, 283–291.
- [22] a) Y. Bian, R. Wang, J. Jiang, C.-H. Lee, J. Wang, D. K. P. Ng, *Chem. Commun.* **2003**, 1194–1195; b) Y. Bian, R. Wang, D. Wang, P. Zhu, R. Li, J. Dou, W. Liu, C.-F. Choi, H.-S. Chan, C. Ma, D. K. P. Ng, J. Jiang, *Helv. Chim. Acta* **2004**, *87*, 2581–2596.
- [23] N. Kobayashi, T. Nonomura, *Tetrahedron Lett.* **2002**, *43*, 4253–4255.
- [24] H. Zhang, R. Wang, P. Zhu, J. Han, F. Lu, C.-H. Lee, D. K. P. Ng, X. Cui, C. Ma, J. Jiang, *Inorg. Chem.* **2004**, *43*, 4740–4742.
- [25] a) J. Jiang, Y. Bian, F. Furuya, W. Liu, M. T. M. Choi, N. Kobayashi, H.-W. Li, Q. Yang, T. C. W. Mak, D. K. P. Ng, *Chem. Eur. J.* **2001**, *7*, 5059–5069; b) P. Zhu, N. Pan, R. Li, J. Dou, Y. Zhang, D. Y. Y. Cheng, D. Wang, D. K. P. Ng, J. Jiang, *Chem. Eur. J.* **2005**, *11*, 1425–1432.
- [26] G. H. Barnett, M. F. Hudson, K. M. Smith, *J. Chem. Soc. Perkin Trans. I* **1975**, 1401–1403.
- [27] K. Kasuga, M. Kawashima, K. Asano, T. Sugimori, K. Abe, T. Kikawa, T. Fujiwara, *Chem. Lett.* **1996**, 867–868.

- [28] M. J. Cook, A. J. Dunn, S. D. Howe, A. J. Thomson, *J. Chem. Soc. Perkin Trans. 1* **1988**, 2453–2458.
- [29] J. G. Stites, C. N. McCarty, L. L. Quill, *J. Am. Chem. Soc.* **1948**, *70*, 3142–3143.
- [30] SMART and SAINT for Windows NT Software Reference Manuals, Version 5.0, Bruker Analytical X-Ray Systems, Madison, WI, **1997**.
- [31] G. M. Sheldrick, SADABS, A Software for Empirical Absorption Correction, University of Göttingen, Germany, **1997**.
- [32] SHELXL Reference Manual, Version 5.1, Bruker Analytical X-Ray Systems, Madison, WI, **1997**.

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