

# Electrochemistry of Heteroleptic Tris(phthalocyaninato) Rare Earth(III) Complexes

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The electrochemical characteristics of a series of heteroleptic tris(phthalocyaninato) complexes with identical rare earths or mixed rare earths (Pc)M(OOPc)M(OOPc) [M = Eu...Lu, Y; H<sub>2</sub>Pc = unsubstituted phthalocyanine, H<sub>2</sub>(OOPc) = 3,4,12,13,21,22,30,31-octakis(octyloxy)phthalocyanine] and (Pc)Eu(OOPc)Er(OOPc) have been recorded and studied comparatively by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in CH<sub>2</sub>Cl<sub>2</sub> containing 0.1 M tetrabutylammonium perchlorate (TBAP). Up to five quasi-reversible one-electron oxidations and four one-electron reductions have been revealed. The half-wave potentials of the first, second and fifth oxidations depend on the size of the metal center, but the fifth changes in the opposite direction to that of the first two. Moreover, the difference in redox potentials of the first oxidation and first reduction for

(Pc)M(OOPc)M(OOPc), 0.85–0.98 V, also decreases linearly along with decreasing rare earth ion radius, clearly showing the rare earth ion size effect and indicating enhanced  $\pi$ – $\pi$  interactions in the triple-deckers connected by smaller lanthanides. This order follows the red-shift seen in the lowest energy band of triple-decker compounds. The electronic differences between the lanthanides and yttrium are more apparent for triple-decker sandwich complexes than for the analogous double-deckers. By comparing triple-decker, double-decker and mononuclear [Zn<sup>II</sup>] complexes containing the OOPc ligand, the HOMO–LUMO gap has been shown to contract approximately linearly with the number of stacked phthalocyanine ligands.

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## Introduction

Bis(phthalocyaninato) rare earth sandwich complexes have been extensively studied for potential applications in electronic devices.<sup>[1,2]</sup> The electrochemical properties of bis(phthalocyaninato) rare earth compounds have been systematically investigated from the viewpoint of electrochromic displays and to understand the nature of  $\pi$ – $\pi$  interactions in the molecules.<sup>[3–5]</sup> Recently, triple-decker (na)phthalocyaninato rare earth analogues have aroused interest for the same reasons.<sup>[6–9]</sup> The expected relatively weaker electronic interaction in triple-deckers, which have a larger ring-to-ring separation than the double-decker analogues, has been revealed by spectroscopic studies. In 1986, Kasuga isolated traces of Y<sub>2</sub>(Pc)<sub>3</sub> as a side-product in preparing double-decker Y(Pc)<sub>2</sub> and confirmed its triple-decker nat-

ure by mass spectrometry.<sup>[7a]</sup> Since 1993, Takahashi developed a new synthetic route for preparing homoleptic substituted tris(phthalocyaninato) rare earth compounds M<sub>2</sub>(OBPc)<sub>3</sub> (M = La, Dy, Yb, Lu) using the reaction between free base phthalocyanine H<sub>2</sub>(OBPc) and rare earth salt M(OAc)<sub>3</sub>·*n*H<sub>2</sub>O<sup>[7b,7c]</sup> (for abbreviations of ligands, see Table 1). L'Her has detailed the synthesis, characterization, and electrochemical behavior of the tris(1,2-naphthalocyaninato)dilutetium compound Lu<sub>2</sub>(1,2-Nc)<sub>3</sub>.<sup>[8]</sup> Ishikawa and co-workers have prepared homoleptic and heteroleptic

Table 1. Abbreviations for ligands

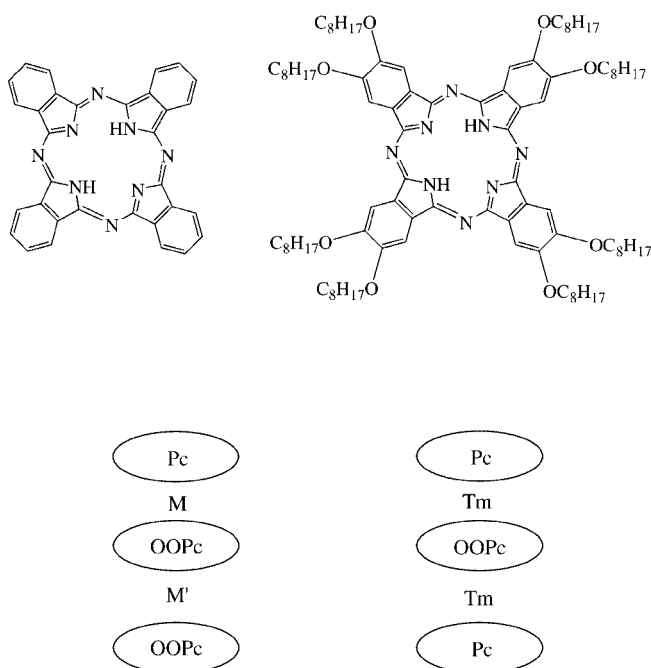
Abbreviation	Ligand
H <sub>2</sub> TPP	5,10,15,20-tetraphenylporphyrin
H <sub>2</sub> OEP	2,3,7,8,12,13,17,18-octaethylporphyrin
H <sub>2</sub> Pc	phthalocyanine
H <sub>2</sub> OOPc	2,3,9,10,16,17,24,25-octakis(octyloxy)phthalocyanine
H <sub>2</sub> OBPc	2,3,9,10,16,17,24,25-octakis(butyloxy)phthalocyanine
H <sub>2</sub> TBPc	2(3),9(10),16(17),24(25)-tetra- <i>tert</i> -butylphthalocyanine
H <sub>2</sub> [Pc(15C5) <sub>4</sub> ]	phthalocyanine with four 15-crown-5 (1,4,7,10,13-pentaoxacyclopentadecane) voids at the 2,3-positions
H <sub>2</sub> (1,2-Nc)	1,2-naphthalocyanine
H <sub>2</sub> (2,3-TBNc)	3(4),12(13),21(22),30(31)-tetra- <i>tert</i> -butyl-2,3-naphthalocyanine

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phthalocyaninato triple-decker complexes  $\text{Lu}_2(\text{Pc})_3$  and  $(\text{Pc})\text{Lu}[\text{Pc}(15\text{C}5)_4]\text{Lu}(\text{Pc})$  and studied their electronic absorption and MCD spectra.<sup>[9]</sup> Our group have reported a novel, versatile route for preparing a series of heteroleptic phthalocyaninato rare earth triple-deckers containing unsubstituted phthalocyaninato and 2,3,9,10,16,17,23,24-octakis(octyloxy)phthalocyaninato (OOPc) ligands<sup>[6a]</sup> and have systematically studied their NMR properties.<sup>[6b]</sup> Using a similar synthetic methodology, Ishikawa has prepared a series of similar heteroleptic tris(phthalocyaninato) rare earth compounds  $(\text{Pc})\text{M}(\text{Pc})\text{M}'(\text{OBPc})$  ( $\text{M} \neq \text{M}' = \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}, \text{Yb}, \text{Y}$ ) and studied the interaction between the f-electronic systems and phthalocyanine ligands in the dinuclear complexes of paramagnetic trivalent lanthanide ions as well as the f–f interactions between the metal ions by magnetic measurements.<sup>[10a,10b]</sup> However, of the reported triple-decker tris[(na)phthalocyaninato] rare earth compounds only five,  $\text{M}_2(\text{OBPc})_3$  ( $\text{M} = \text{La}, \text{Dy}, \text{Yb}, \text{Lu}$ )<sup>[7b,7c]</sup> and  $\text{Lu}_2(1,2\text{-Nc})_3$ ,<sup>[8b]</sup> have been investigated by electrochemical methods. The ring-to-ring interaction in these triple-decker molecules is worthy of systematic study from both theoretical and experimental viewpoints. We report here the electrochemical properties of a series of heteroleptic phthalocyaninato rare earth triple-decker complexes  $(\text{Pc})\text{M}(\text{OOPc})\text{M}(\text{OOPc})$  ( $\text{M} = \text{Eu} \dots \text{Lu}, \text{Y}$ ) and  $(\text{Pc})\text{Tm}(\text{OOPc})\text{Tm}(\text{Pc})$  (Scheme 1) by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). For comparison, the electrochemistry of the substituted (phthalocyaninato)zinc complex  $\text{Zn}(\text{OOPc})$  and double-decker rare earth compounds  $\text{M}(\text{Pc})_2$  and  $\text{M}(\text{OOPc})_2$  are also discussed. The latter two series and the analogues  $\text{M}(\text{TBPc})_2$  feature in our previous paper.<sup>[5]</sup>



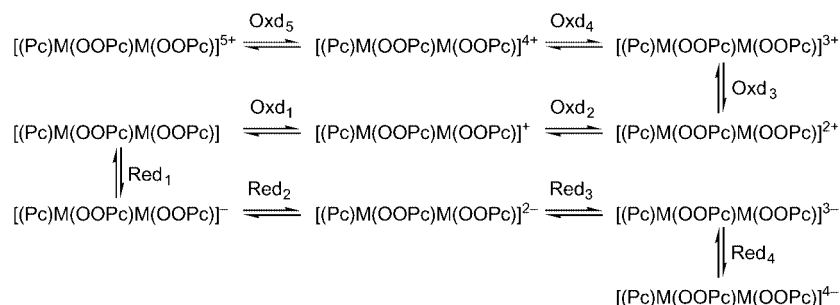
Scheme 1. Phthalocyanine ligands and schematic diagram of heteroleptic tris(phthalocyaninato) rare earth complexes  $(\text{Pc})\text{M}(\text{OOPc})\text{M}'(\text{OOPc})$  ( $\text{M} = \text{M}' = \text{Eu} \dots \text{Lu}, \text{Y}$ ;  $\text{M} = \text{Eu}, \text{M}' = \text{Er}$ ) and  $(\text{Pc})\text{Tm}(\text{OOPc})\text{Tm}(\text{Pc})$

## Results and Discussion

The electrochemical behavior of the triple-decker complexes together with monomeric  $\text{Zn}(\text{OOPc})$  was investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in  $\text{CH}_2\text{Cl}_2$ . While the monomeric compound  $\text{Zn}(\text{OOPc})$  undergoes two reversible to quasi-reversible one-electron oxidations and two reversible to quasi-reversible one-electron reductions, the triple-decker compounds display up to five one-electron oxidations and up to four one-electron reductions within the electrochemical window of  $\text{CH}_2\text{Cl}_2$  under the conditions employed. The reduction and oxidation peak potentials for each process are 60–90 mV apart. Since the oxidation state of the central zinc and trivalent rare earth ions in monomeric and triple-decker complexes, respectively, do not change, these processes are attributed to the successive removal, or addition, of one electron from, or to, the ligand-based orbitals of the redox states (Scheme 2). Oxidations are labeled  $\text{Oxd}_1$  to  $\text{Oxd}_5$  and the reductions  $\text{Red}_1$  to  $\text{Red}_4$ . The half-wave redox potentials vs. SCE are summarized in Table 2. Representative cyclic voltammograms and differential pulse voltammograms for  $(\text{Pc})\text{Tm}(\text{OOPc})\text{Tm}(\text{OOPc})$  are displayed in Figure 1. The observation of up to five cationic states for these triple-deckers supports the proposal of Lindsey that they are potential molecular materials for information storage.<sup>[11]</sup>

Our observations of the electrochemistry of these heteroleptic triple-deckers in  $\text{CH}_2\text{Cl}_2$  differ slightly from those reported for homoleptic tris(phthalocyaninato) rare earth analogues.<sup>[7b,7c]</sup> For instance, up to four oxidation and three reduction processes were observed for  $\text{M}_2(\text{OBPc})_3$  in  $\text{CH}_2\text{Cl}_2$  containing  $\text{TBAPF}_6$ .<sup>[7b,7c]</sup> However, under our experimental conditions, we observed two more oxidation states in some cases, particularly by DPV. Figure 2 shows the variation of the redox potentials of  $(\text{Pc})\text{M}(\text{OOPc})\text{M}(\text{OOPc})$  with the ionic radius of the rare earth metal center. While the half-wave potentials of the third and fourth oxidations of  $(\text{Pc})\text{M}(\text{OOPc})\text{M}(\text{OOPc})$  remain virtually unchanged, the half-wave potentials of the first, second and fifth oxidations of these triple-deckers correlate linearly with the ionic size of the rare earth metal center (Figure 2 and Table 2). The half-wave potentials of the first and second oxidations shift slightly in the cathodic direction with decreasing rare earth ion radius, while those of the fifth oxidation shift in the opposite direction.

As with bis(phthalocyaninato) rare earth compounds,<sup>[5]</sup> in the tris(phthalocyaninato) rare earth triple-decker molecules the close proximity of the three conjugated  $\pi$ -systems in a face-to-face configuration splits the doubly degenerate LUMO ( $e_g$ ) and HOMO ( $4a_u$ ) molecular orbitals derived from monophthalocyanines. This results in three pairs of doubly degenerate unoccupied frontier molecular orbitals (the bonding LUMO, second non-bonding LUMO and third anti-bonding LUMO) and three non-degenerate occupied frontier orbitals (the third bonding HOMO, second non-bonding HOMO and first anti-bonding HOMO) in the triple-deckers. The splitting of the filled MOs, actually the splitting between the first HOMO and second HOMO as



Scheme 2. One-electron redox processes of (Pc)M(OOPc)M(OOPc)

Table 2. Half-wave redox potentials of (Pc)M(OOPc)M'(OOPc) (M = M' = Eu...Lu, Y; M = Eu, M' = Er) together with (Pc)Tm(OOPc)Tm(Pc) and Zn(OOPc) (V vs. SCE) in CH<sub>2</sub>Cl<sub>2</sub> containing 0.1 M TBAP

	Oxd <sub>5</sub>	Oxd <sub>4</sub>	Oxd <sub>3</sub>	Oxd <sub>2</sub>	Oxd <sub>1</sub>	Red <sub>1</sub>	Red <sub>2</sub>	Red <sub>3</sub>	Red <sub>4</sub>	$\Delta E^\circ_{1/2}$ <sup>[a]</sup>
Eu	+1.45 <sup>[b]</sup>	+1.30	+1.14	+0.63	+0.26	−0.72	−1.10	−1.41 <sup>[b]</sup>		0.98
Gd	+1.49 <sup>[b]</sup>	+1.32 <sup>[b]</sup>	+1.18	+0.63	+0.25	−0.73	−1.09	−1.41 <sup>[b]</sup>	−1.66 <sup>[b]</sup>	0.98
Tb	+1.50 <sup>[b]</sup>	+1.32 <sup>[b]</sup>	+1.18	+0.62	+0.23	−0.75 <sup>[b]</sup>	−1.08 <sup>[b]</sup>	−1.43 <sup>[b]</sup>	−1.76 <sup>[b]</sup>	0.98
Dy	+1.66 <sup>[b]</sup>	+1.35	+1.19	+0.61	+0.21	−0.78	−1.13	−1.51	−1.75 <sup>[b]</sup>	0.99
Y	+1.50	+1.30	+1.14	+0.64	+0.27	−0.76	−1.06	−1.38		1.03
Ho			+1.19 <sup>[b]</sup>	+0.60	+0.21	−0.72 <sup>[b]</sup>	−1.05 <sup>[b]</sup>	−1.38 <sup>[b]</sup>		0.93
Er		+1.35	+1.19	+0.57	+0.18	−0.74	−1.06 <sup>[b]</sup>	−1.41 <sup>[b]</sup>	−1.60 <sup>[b]</sup>	0.92
Tm		+1.34	+1.16	+0.54	+0.14	−0.77	−1.13	−1.55	−1.80 <sup>[b]</sup>	0.91
Yb		+1.36	+1.18	+0.54	+0.14	−0.76	−1.09	−1.44	−1.62 <sup>[b]</sup>	0.90
Lu		+1.38	+1.20	+0.53	+0.13	−0.72	−1.07	−1.39		0.85
Eu/Er <sup>[c]</sup>		+1.43	+1.19	+0.62	+0.22	−0.74	−1.07	−1.49 <sup>[b]</sup>		0.96
Tm <sup>[d]</sup>	+1.76 <sup>[b]</sup>	+1.46 <sup>[b]</sup>	+1.28	+0.68	+0.27	−0.71	−0.97 <sup>[b]</sup>	−1.37 <sup>[b]</sup>	−1.67 <sup>[b]</sup>	0.98
Zn <sup>[e]</sup>				+1.27	+0.50	−1.14	−1.22			1.64

<sup>[a]</sup>  $\Delta E^\circ_{1/2}$  is the potential difference between the first oxidation and first reduction processes, i.e. the HOMO–LUMO gap of corresponding molecules, namely (Pc)M(OOPc)M(OOPc), (Pc)Tm(OOPc)Tm(Pc) and Zn(OOPc). <sup>[b]</sup> Recorded by DPV. <sup>[c]</sup> (Pc)Eu(OOPc)Er(OOPc). <sup>[d]</sup> (Pc)Tm(OOPc)Tm(Pc). <sup>[e]</sup> Zn(OOPc).

well as the second HOMO and third HOMO of triple-decker, increases with the lanthanide contraction due to the increase in the ring-to-ring interaction. Therefore, there is an increase in the energy of the anti-bonding HOMO and a corresponding decrease in the energy of the third bonding HOMO in the same order, but no change in the energy of the non-bonding second HOMO. This is why the half-wave potentials of the first and second oxidations (Oxd<sub>1</sub> and Oxd<sub>2</sub>) dealing with the first anti-bonding HOMO are shifted slightly to a more negative direction with decreasing rare earth radius, and those for the fifth oxidation of (Pc)M(OOPc)M(OOPc) (Oxd<sub>5</sub>) involving the third bonding HOMO are shifted slightly in the positive direction, in the same order. Conversely, those for the third and fourth oxidations, which are related to the second non-bonding HOMO, are essentially unchanged. This proposal is also well supported by the optical properties of (Pc)M(OOPc)M(OOPc). Previous studies have revealed that the lowest energy electronic absorption band at 683–714 nm in the electronic spectra of triple-decker tris(phthalocyaninato) rare earth complexes (Pc)M(OOPc)M(OOPc) (M = Pr...Tm), which involves the electronic transition from the HOMO to the degenerate LUMO, is red-shifted with decreasing rare earth ionic size.<sup>[5]</sup> It is noteworthy that the first and second oxidation

(HOMO-related) potentials of tris(phthalocyaninato) rare earth compounds depend in a similar way on the rare earth ionic size as do the first reduction and first oxidation (also involving the HOMO) of their double-decker counterparts. However, the sensitivity to ionic size is significantly less for the triple-deckers due to their larger inter-ring distances.<sup>[3–5]</sup>

The half-wave potentials of all the *reductions* for (Pc)M(OOPc)M(OOPc) appear to reveal no systematic trends with ionic size. These results also correspond well with those obtained for the bis(phthalocyaninato) rare earth double-deckers.<sup>[3–5]</sup>

The redox behavior of the heterodinuclear compound (Pc)Eu(OOPc)Er(OOPc) was also examined by CV and DPV, and parallels those of its counterparts with two identical metals (Table 2). The redox potentials, especially those involving the HOMO and LUMO of (Pc)Eu(OOPc)-Er(OOPc), i.e. the first and second oxidations and the first and second reductions, fit the linear correlation seen between the redox potentials and ionic radii for complexes with identical metals if the mean ionic radius of Eu and Er is employed. This corresponds well with the results of Weiss and co-workers on the electrochemistry of mixed (phthalocyaninato)(porphyrinato) rare earth triple-decker complexes containing mixed or identical rare earth metals, clearly indi-

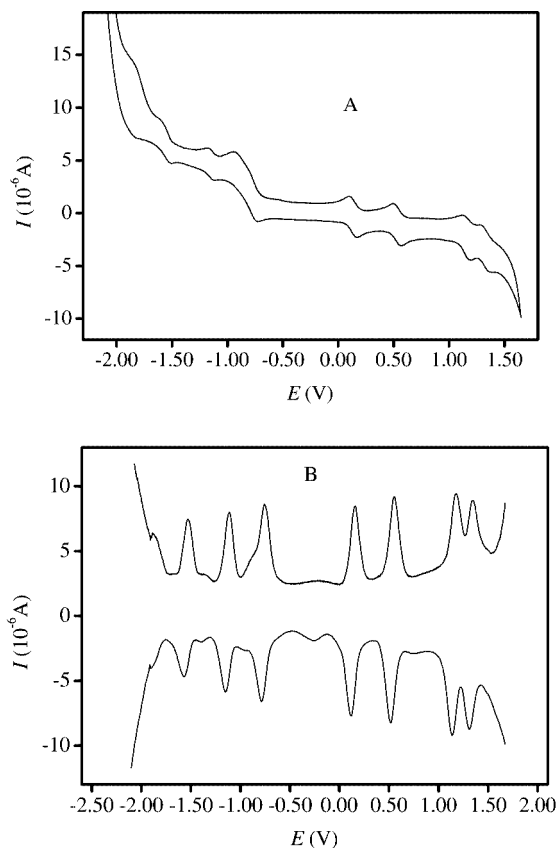


Figure 1. CV (A) and DPV (B) of (Pc)Tm(OOPc)Tm(OOPc) in  $\text{CH}_2\text{Cl}_2$  containing 0.1 M  $[\text{Bu}_4\text{N}][\text{ClO}_4]$  at scan rates of 20 and 10  $\text{mV}\cdot\text{s}^{-1}$ , respectively

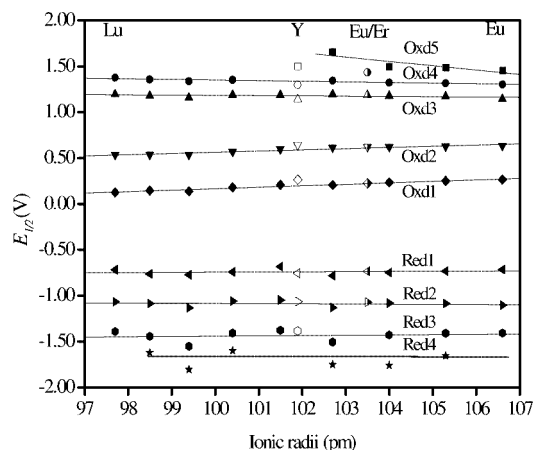


Figure 2. Half-wave potentials of redox processes of (Pc)M(OOPc)M(OOPc) (M = Eu...Lu) as a function of the ionic radius of  $\text{M}^{\text{III}}$

cating the involvement of all three phthalocyanine rings in the frontier molecular orbitals of heteroleptic tris(phthalocyaninato) rare earth compounds.<sup>[12]</sup>

The potential difference between the first oxidation and first reduction,  $\Delta E_{1/2}^{\circ}$ , for all these triple-decker compounds (Pc)M(OOPc)M(OOPc) (M = Eu...Lu) spans the relatively narrow range 0.85–0.99 V, which corresponds well with results for  $\text{M}_2(\text{OBPc})_3$  (M = Dy, Yb, Lu)

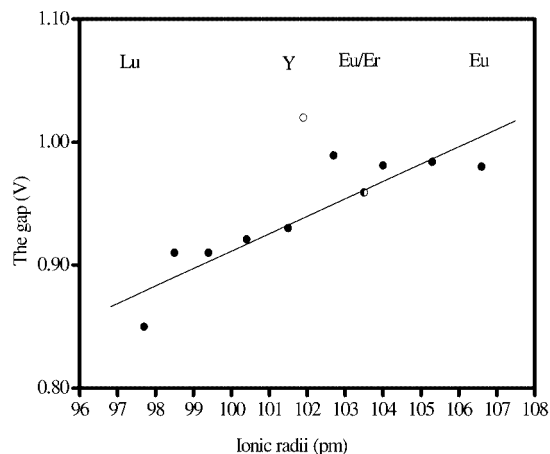


Figure 3. HOMO–LUMO gap between the half-wave potentials of the first oxidation and first reduction of (Pc)M(OOPc)M(OOPc) as a function of the ionic radius of  $\text{M}^{\text{III}}$

(0.98–1.09 V)<sup>[7b,7c]</sup> and  $\text{Lu}_2(1,2\text{-Nc})_3$ <sup>[8b]</sup> (0.86 V). Figure 3 shows this potential gap for (Pc)M(OOPc)M(OOPc) as a function of the trivalent rare earth ionic radii. Clearly, the difference between the first oxidation and first reduction processes for (Pc)M(OOPc)M(OOPc) decreases more or less linearly with decreasing rare earth ion size. The clear outlier (Pc)Y(OOPc)Y(OOPc) is not unexpected as yttrium is not an f-series lanthanide, and so its interaction with the  $\pi$  orbitals of conjugated tetrapyrrole ligands is fundamentally different. Electrochemical investigations of a series of rare earth *double-decker* compounds with different tetrapyrrole ligands in either neutral or reduced form, namely  $[\text{M}(\text{Pc})_2]^-$ <sup>[3,4]</sup> and  $\text{M}(\text{Pc}')_2$  (Pc' = Pc, TBPC, OOPc),<sup>[5]</sup>  $\text{M}(\text{TBNC})_2$ ,<sup>[13]</sup>  $\text{M}(\text{TPP})(\text{Pc})$ <sup>[14]</sup>  $\text{M}(\text{OEP})(\text{Nc})$ ,<sup>[15]</sup> and  $\text{M}(\text{OEP})_2$ ,<sup>[16]</sup> have found that the gap between the first oxidation and the first reduction potentials of the monoanionic reduced form of all these tetrapyrrole double-deckers decreases linearly with the lanthanide contraction. The deviation for yttrium double-decker compounds  $[\text{Y}(\text{Pc}')_2]^-$  (Pc' = Pc, TBPC, OOPc) is not so obvious as in the triple-decker series studied here. This is due to the magnifying effects of the f–f interaction between the metal centers in the lanthanide triple-deckers. Of course, such interaction is absent for yttrium, so a large deviation is not unexpected.

As  $\Delta E_{1/2}^{\circ}$  (Oxd<sub>1</sub> – Red<sub>1</sub>), representing the electrochemical HOMO–LUMO gap, reflects the interactions among the tetrapyrrole rings in the sandwich molecules, the decrease in  $\Delta E_{1/2}^{\circ}$  (Oxd<sub>1</sub> – Red<sub>1</sub>) with the lanthanide contraction clearly suggests enhanced ring–ring interactions in the same order. This view is strongly supported as the HOMO–LUMO gap for the mixed-metal complex (Pc)Eu(OOPc)Er(OOPc) lies between those of the compounds with two identical metals (Pc)Eu(OOPc)Eu(OOPc) and (Pc)Er(OOPc)Er(OOPc) (Table 2 and Figure 3).

Furthermore, the electrochemical data for triple-deckers (Pc)M(OOPc)M(OOPc) and the mononuclear compound  $\text{Zn}(\text{OOPc})$ , together with those of the double-deckers  $\text{M}(\text{Pc})_2$  and  $\text{M}(\text{OOPc})_2$  obtained previously, render it pos-



sible to compare the effect of the extension of the  $\pi$ -networks along an axis perpendicular to the phthalocyanine plane. It must be pointed out that in the neutral double-decker species  $M(Pc')_2$  ( $Pc' = Pc, OOPc$ ), one of the two  $Pc'$  rings is a monoanion radical ( $Pc'^{\cdot-}$ ), therefore the reduced double-decker species  $[M(Pc')_2]^-$  ( $Pc' = Pc, OOPc$ ) should be considered for comparison with the monomeric  $Zn(OOPc)$  and triple-decker  $(Pc)M(OOPc)M(OOPc)$ , so that all the phthalocyanine rings are in the dianionic form  $Pc'^{2-}$ .<sup>[8b]</sup> Comparison of the HOMO–LUMO gap for  $(Pc)M(OOPc)M(OOPc)$  ( $M = Eu...Lu$ ), 0.85–0.98 V, with that of 1.08–1.37 V for  $[M(Pc)_2]^-$  ( $M = La...Lu$ ) or 1.13–1.40 V for  $[M(OOPc)_2]^-$  ( $La...Lu$ ) from our previous work<sup>[5]</sup> and 1.64 V for  $Zn(OOPc)$  makes it clear that the extension of the bonding over more phthalocyanine rings has an obvious effect on the MO levels.  $Zn(OOPc)$  is used as a comparable representative mononuclear complex as its gap is the same as that for  $Lu(1,2-Nc)(OAc)$ ,<sup>[8b]</sup> likewise the gap for  $[Lu(1,2-Nc)_2]^-$  lies in the range for our double-decker anions, and that for  $Lu_2(1,2-Nc)_3$  is in the range for our triple-deckers.<sup>[8b]</sup> For a qualitative comparison, it therefore seems appropriate to use the Zn complex, and thus avoid recording the full series of mononuclear rare earth complexes. The increase in the number of macrocycles in the face-to-face stack from monomer to triple-decker via double-decker induces important modifications in the orbital systems of these complexes, manifested in the decrease in the HOMO–LUMO gap (Figure 4). Further axial extension of delocalization of the stacked  $\pi$ -conjugated molecules is therefore predicted to lead to corresponding molecular materials with narrower HOMO–LUMO gaps. According to Simon,<sup>[17]</sup> the potential difference between the first oxidation and first reduction processes,  $\Delta E_{1/2}^o$ , allows the prediction of electrical properties such as the thermal activation energy for the conduction process of the condensed phases derived from the corresponding molecular precursors. Therefore one can reasonably expect further improved electrical properties of stacked  $\pi$ -conjugated phthalocyanine-derived molecular systems, i.e. sandwich-type

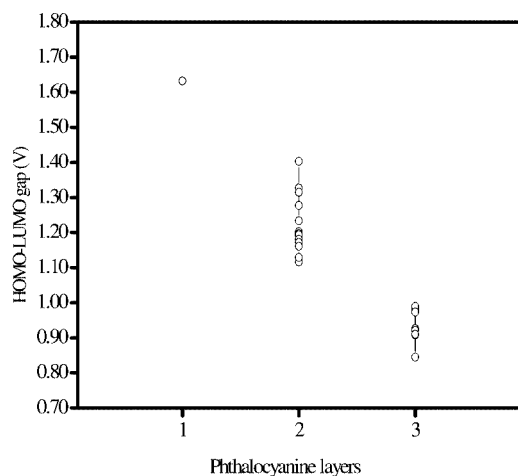


Figure 4. HOMO–LUMO gap of  $Zn(OOPc)$ ,  $[M(OOPc)_2]^-$  ( $M = La...Lu$ ;  $OOPc$ ) and  $(Pc)M(OOPc)M(OOPc)$  ( $M = Eu...Lu$ ) as a function of the number of phthalocyanine layers

(phthalocyaninato)metal oligomers or polymers, compared with those of double- and triple-deckers. So far no higher oligomers linked by metal ion connectors have been isolated, only systems linked by various axial ligands.<sup>[18]</sup>

CV and DPV studies revealed that  $(Pc)Tm(OOPc)Tm(Pc)$ , which is a representative of a series of more symmetrical heteroleptic tris(phthalocyaninato) rare earth compounds, also undergo five quasi-reversible one-electron oxidations and four quasi-reversible one-electron reductions (Table 2). In comparison with  $(Pc)Tm(OOPc)Tm(OOPc)$ , the symmetrical compound clearly undergoes oxidations less readily, as shown by the higher oxidation potentials, whereas the reductions occur more readily, both effects being due to the incorporation of only one electron-rich  $OOPc$  ring in the molecule. However, the difference between the first oxidation and first reduction potentials of  $(Pc)Tm(OOPc)Tm(Pc)$ , 0.97 V, is very similar to the 0.91 V for  $(Pc)Tm(OOPc)Tm(OOPc)$  and still lies in the range for the  $(Pc)M(OOPc)M(OOPc)$  series, indicating similar  $\pi$ – $\pi$  interactions in the two series. Similar results have also been observed for heteroleptic and homoleptic bis(phthalocyaninato) rare earth compounds containing substituted phthalocyanine ring(s), namely  $M(Pc)(Pc^*)$ <sup>[19]</sup> and  $M(Pc^*)_2$  ( $Pc^* = TBPC$ ,<sup>[5,19a]</sup>  $OOPc$ ,<sup>[5]</sup>  $OPPC$ ,<sup>[19b]</sup>  $OHPc$ <sup>[19b]</sup>) when compared with the electrochemical properties of  $M(Pc)_2$ .<sup>[3–5]</sup>

## Conclusions

Systematic studies of the electrochemical characteristics of heteroleptic tris(phthalocyaninato) rare earth complexes  $(Pc)M(OOPc)M(OOPc)$  have revealed that these compounds can undergo up to five quasi-reversible one-electron oxidations and up to four quasi-reversible one-electron reductions within the electrochemical window of  $CH_2Cl_2$ . The half-wave potentials of the first and second oxidations for these trivalent rare earth triple-deckers are metal-ion-size-dependent; the oxidations become easier with decreasing lanthanide ion size. Comparison among triple-deckers  $(Pc)M(OOPc)M(OOPc)$ , reduced double-deckers  $[M(Pc')_2]^-$  ( $Pc' = Pc, OOPc$ )<sup>[5]</sup> and mononuclear  $Zn(OOPc)$  shows that the HOMO–LUMO gap is decreased by extension of the delocalized bonding along the axis perpendicular to the macrocycle plane.

## Experimental

The monomeric (phthalocyaninato)zinc compound  $Zn(OOPc)$ <sup>[20]</sup> and heteroleptic phthalocyaninato rare earth triple-decker complexes  $(Pc)M(OOPc)M(OOPc)$  ( $M = Eu...Lu, Y$ ),  $(Pc)Eu(OOPc)Er(OOPc)$ , and  $(Pc)Tm(OOPc)Tm(Pc)$  were prepared according to published procedures.<sup>[6a]</sup> Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were carried out with a BAS CV-50 W voltammetric analyzer. The cell consists of inlets for a glassy carbon disk working electrode (2.0 mm in diameter)

and a silver-wire counter electrode. The Ag/Ag<sup>+</sup> reference electrode was connected to the solution by a Luggin capillary whose tip was placed close to the working electrode. Results were corrected for junction potentials by being referenced internally to the ferrocenium/ferrocene (Fe<sup>+</sup>/Fe) couple [ $E_{1/2}(\text{Fe}^+/\text{Fe}) = 0.50 \text{ V vs. SCE}$ ]. Potentials in this paper are referenced to the SCE. Typically, a 0.1 M solution of [Bu<sub>4</sub>N][ClO<sub>4</sub>] in CH<sub>2</sub>Cl<sub>2</sub> containing 0.5 mM of sample was purged with nitrogen for 10 min, and then the voltammograms were recorded at ambient temperature. The scan rate was 20 and 10 mV·s<sup>-1</sup> for CV and DPV, respectively.

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