The Electronic Absorption Characteristics of Mixed Phthalocyaninato Porphyrinato Rare Earth(III) Triple-Deckers $M_2(TPyP)_2(Pc)$

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Mixed phthalocyaninato tetrakis(4-pyridyl)porphyrinato rare earth triple-decker complexes $M_2(TPyP)_2(Pc)$ [M = La (**1**), Eu (**2**)] have been prepared by condensation between M(TPyP)acac generated in situ and $M(Pc)_2$. Their symmetrical structure (TPyP)M(Pc)M(TPyP) was verified by ^1H NMR (1D and 2D) spectra in $CDCl_3$ solutions. The electronic absorption spectra of these two compounds were recorded in the UV/Vis and near-IR region. A weak absorption in the near-IR region at 860 and 942 nm for **1** and **2**, respectively, was observed as the lowest energy band and is attributed to the electronic transition from HOMO to LUMO for these mono(phthalocyaninato) bis(porphyrinato) rare earth complexes. Their electrochemical properties were investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). Analysis of the relationship between the optical and redox properties of $M_2(TPyP)_2(Pc)$ reveals that the HOMO and LUMO of $M_2(TPyP)_2(Pc)$ have both porphyrin and phthalocyanine character.

Introduction

Sandwich-type phthalocyaninato and/or porphyrinato metal complexes have been intensively studied.[1−3] These species comprise two or three aromatic macrocyclic ligands held in close proximity by eight-coordinate metal ions in the +3 or +4 oxidation state. They exhibit a wide range of intriguing physical and chemical properties which render them useful in molecular (semi)conductors, molecular electronics and electrochromic displays.[4−5] Although heteroleptic and mixed tetrapyrrole ring complexes containing different phthalocyaninato and porphyrinato ligands have aroused increasing interest in recent years, relatively little is known about their optical, electrochemical and functional properties.[3] As part of our continuing exploration of this novel class of compounds, we have developed several effective pathways for preparing heteroleptic bis(phthalocyaninato) rare earth and mixed (na)phthalocyaninato porphyrinato rare earth double- and triple-deckers and systematically investigated their structural, electrochemical and spectroscopic (both electronic and vibrational) properties.[6−8]

Electronic absorption is one of the most powerful methods to characterize sandwich-type tetrapyrrole metal complexes. With regard to the optical properties of mixed phthalocyaninato porphyrinato rare earth sandwich complexes, it is worth pointing out that we have been intrigued by the significant difference in the appearance of the electronic absorption spectra of $(Por)M^{III}(Pc)M^{III}(Por)$ (for a list of abbreviations, see Table 1) from those of $[M^{III}(Por)(Pc)]^-$ since the very beginning of our research in this field.[9,10]

Table 1. List of abbreviations for ligands

Abbreviation	Ligand
P	general phthalocyaninato or porphyrinato
Pc	phthalocyaninato
Por, Por′	general porphyrinato
TPyP	5,10,15,20-tetrakis(4-pyridyl)porphyrinato
TPP	5,10,15,20-tetraphenylporphyrinato
TClPP	5,10,15,20-tetrakis(4-chlorophenyl)porphyrinato
TBPP	5,10,15,20-tetrakis(4-*tert*-butylphenyl)porphyrinato
TOMPP	5,10,15,20-tetrakis(4-methoxyphenyl)porphyrinato
OEP	2,3,7,8,12,13,17,18-octaethylporphyrinato
Nc	2,3-naphthalocyaninato (linearly annelated tetrabenzophthalocyaninato)

It is well known that an absorption band in the near-IR region is the most prominent feature in the electronic

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absorption spectra of all the neutral homoleptic and heteroleptic tetrapyrrole double-decker rare earth(III) complexes. Such complexes contain an unpaired electron on one ring thus can be depicted as a monoanion radical $P^{\cdot-}$ (P = Por, Pc).[1,2] This near-IR band has been attributed to the ring-to-ring intramolecular charge transfer (RRCT) from the dianion P^{2-} electron donor to the monoanion radical $P^{\cdot-}$ electron acceptor.[3,11] In the spectra of the one-electron reduced form $[M^{III}(Por)(Pc)]^-$, no absorption band has ever been observed in the near-IR region beyond 800 nm, presumably due to the absence of an unpaired electron.[1−3] The reduced mixed ring complexes $[M^{III}(Por)(Pc)]^-$ display electronic absorption features common to both $[M^{III}(Por)_2]^-$ and $[M^{III}(Pc)_2]^-$ or $[M^{IV}(Pc)_2]$.[9,11−13] Thus, except for a weak absorption at ca. 480 nm assigned to a new π-π* transition arising from molecular orbitals delocalized over both rings, the porphyrin Soret band in $Li[M^{III}(TPyP)(Pc)]$ (M = Eu, Gd) appears at ca. 411 nm, whereas the phthalocyanine Soret and Q bands appear at ca. 330 and 584, 635, and 800 nm, respectively.[9]

The electronic absorption spectra of mixed phthalocyaninato porphyrinato rare earth triple-decker compounds $M^{III}_2(Por)_2(Pc)$ [having the constitution (Por)M(Pc)M(Por)] (Por = TPP, TClPP, TBPP, TOMPP) are usually recorded in the region of 300−800 (at most to 900) nm.[10] As these compounds are composed of two $[M^{III}(Por)(Pc)]^-$ moieties, which possess a common Pc^{2-} unit strongly interacting with two outer Por^{2-} rings, their absorption features should be easily understood on the basis of the electronic absorption spectra of $[M^{III}(Por)(Pc)]^-$. However, due to the increased ring-ring separation and consequently decreased ring-ring interaction in triple-deckers $M^{III}_2(Por)_2(Pc)$, all the absorption bands are expected to shift to the red as compared with those in the reduced double-decker counterparts $[M^{III}(Por)(Pc)]^-$. The absorptions at ca. 354 and 420 nm for $Eu_2(Por)_2(Pc)$ (Por = TPP, TClPP, TBPP, TOMPP) can be assigned to the phthalocyaninato and porphyrinato Soret bands, respectively. The band at around 490 nm has been compared to the similar weak absorption at ca. 480 nm for $Li[M^{III}(TPyP)(Pc)]$ (M = Eu, Gd) and similarly assigned to the π-π* transition arising from molecular orbitals delocalized over both rings. The remaining absorptions in the visible region at 539−551 and 603−605 nm for the various $Eu_2(Por)_2(Pc)$ complexes are mainly contributed by the Q bands of the phthalocyanine ring. Apparently, no absorption band similar to that at ca. 800 nm for reduced double-decker $Li[M^{III}(TPyP)(Pc)]$ has been found in the electronic absorption spectra of these triple-deckers. It is this phenomenon that has appeared anomalous to the primary authors of our group for a long time.

Researchers in this field including ourselves have not paid sufficient attention to the characteristic absorption of (Por)M^{III}(Pc)M^{III}(Por) in the near-IR region beyond 800 nm. One reason for this oversight is the hypothesis that there would be no absorptions in the near-IR region because there is no unpaired electron (hole) in such sandwich triple-deckers. Another reason for overlooking absorption in the near-IR region is the very low intensity of this absorption band (see below), which might be related to the decreased ratio of phthalocyanine to porphyrin in this kind of triple-deckers as well as the generally very weak absorption of porphyrins in the near-IR region. The last reason for missing the near-IR absorption is that the work in mixed phthalocyaninato porphyrinato rare earth triple-deckers thus far has mainly focused on the complexes of Sm, Eu, and Gd,[10] whose lowest energy absorption in the near-IR region is beyond 900 nm.

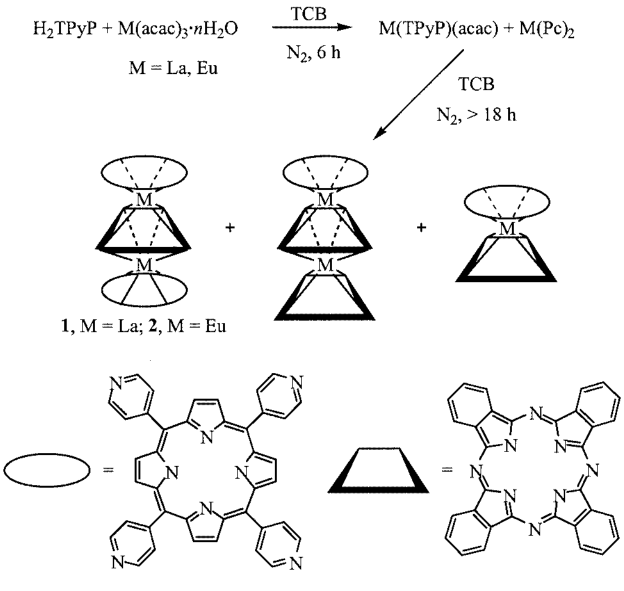
Our recent work on the 2,3-naphthalocyanine-containing mixed ring sandwiches revealed that $M_2(OEP)_2(Nc)$ [(OEP)M^{III}(Nc)M^{III}(OEP)][8a] complexes exhibit a rather intense near-IR absorption (1000−1100 nm) associated with the HOMO−LUMO electron transition. This encouraged us to re-investigate the electronic absorption characteristics of triple-decker compounds (Por)M^{III}(Pc)M^{III}(Por) and finally led to the discovery of the weak near-IR absorption band in the region of 860−960 nm for the mixed ring triple-decker complexes $M_2(TPyP)_2(Pc)$ (M = La, Eu). Herein we report these results, together with associated electrochemical and NMR characterization data.

Results and Discussion

Synthesis

There are several possible synthetic pathways to rare earth(III) triple-decker complexes with mixed tetrapyrrole ligands $M_2^{III}(Por)_2(Pc)$.[1,3] The most commonly used method involves direct condensation between $H_2(Por)$ and $Li_2(Pc)$ in the presence of $M(acac)_3{\cdot}nH_2O$. However, in addition to the target mixed ring triple-deckers M_2^{III}-$(Por)_2(Pc)$, double-decker M^{III}(Por)(Pc) together with another form of triple-decker $M_2^{III}(Por)(Pc)_2$ were also isolated by this method. The second familiar route is the so-called raise-by-one-story method in which the mono(porphyrinato) compound M(Por)acac generated in situ is treated with mixed ring double-decker M(Por)(Pc). By using this synthetic route, both homo- and heterodinuclear metal triple-deckers $M_2^{III}(Por)_2(Pc)$ or (Por)M(Pc)M′(Por′) can be isolated.[14] The third path to $M_2^{III}(Por)_2(Pc)$ developed recently by our group involves the tetramerization of phthalonitriles on the template of mono(porphyrinato) rare earth complex M(Por)acac in *n*-octanol catalyzed by the organic base DBU.[15]

However, it is worth mentioning that none of the above-mentioned procedures works for the tetrakis(4-pyridyl)porphyrin ligand. No $M_2(TPyP)_2(Pc)$ has ever been isolated for rare earths other than cerium thus far. The condensation between H_2TPyP and Li_2Pc with $M(acac)_3{\cdot}nH_2O$ (M = Eu, Gd) usually leads to the formation and isolation of reduced mixed ring double-deckers Li[M(TPyP)(Pc)] together with trace amounts of $M_2(TPyP)(Pc)_2$.[9] In the recent work in which we tried to prepare the mixed ring triple-decker $Eu_2(TPyP)(Pc)_2$ starting with H_2TPyP and $Eu(Pc)_2$ in the presence of $Eu(acac)_3{\cdot}nH_2O$ in refluxing TCB, unexpectedly the triple-decker $Eu_2(TPyP)_2(Pc)$ (**2**) was isolated as the primary product after refluxing the mixture for 18 h. Later it was found that the other form of triple-decker $Eu_2(TPyP)(Pc)_2$ could only be isolated as the main product after a relatively short reaction time, say less than 12 h. Moreover, pre-preparation of the mono(porphyrinato) compound M(TPyP)acac was found to be unnecessary. More systematic and careful studies revealed that the one-pot reaction of H_2TPyP, $M(Pc)_2$ and $M(acac)_3{\cdot}nH_2O$ could lead directly to the formation of $M_2(TPyP)_2(Pc)$, $M_2(TPyP)(Pc)_2$ and some M(TPyP)(Pc) (M = La, Eu), the relative yields of which were determined by the refluxing time. This indicates that the neutral double-decker M(TPyP)(Pc) produced by degradation of the triple-decker $M_2(TPyP)(Pc)_2$ formed in the first step (Scheme 1) is the intermediate. The neutral double-decker reacts further with M(TPyP)acac formed in situ to generate the mono(phthalocyaninato) bis(porphyrinato) triple-decker compound $M_2(TPyP)_2(Pc)$. This postulate is supported by the isolation of a large amount of $Eu_2(TPyP)(Pc)_2$ when the mixture of H_2TPyP, $Eu(Pc)_2$ and $Eu(acac)_3{\cdot}nH_2O$ is refluxed for a short time (6 h) and relatively high yield of neutral double-decker Eu(TPyP)(Pc) after reflux for a relatively long time (10 h). The fact that Li[M(TPyP)(Pc)] (M = Eu, Gd) could not directly form triple-deckers $M_2(TPyP)_2(Pc)$ seems to suggest that the reduced double-decker Li[M(TPyP)(Pc)] is quite stable and the lithium cation is located on the top of the Pc ring, which prevents the reduced double-decker from reacting further with M(TPyP)acac. The relatively high stability of the reduced form of TPyP-containing double-deckers $[M^{III}(TPyP)(Pc)]^-$ is further confirmed by the isolation of protonated mixed [tetrakis(4-pyridyl)porphyrinato]-(phthalocyaninato) rare earth double-deckers $HM^{III}(TPyP)(Pc)$ (M = Eu, Gd, Y) formed by tetramerization of phthalonitrile on the template of the mono(porphyrinato) compound M(TPyP)acac.[13]



Scheme 1. Synthesis of rare earth triple-deckers

It has been found that among the whole series of rare earth metals, only the lighter rare earths with large enough ionic radius could connect three OEP rings to form homoleptic triple-deckers $M_2(OEP)_3$ (M = La, ..., Tb except for Pm).[1,16,17] This is also true for the formation of mixed ring triple-deckers $M_2(TPyP)_2(Pc)$ as will be detailed elsewhere. The lower yield of $Eu_2(TPyP)_2(Pc)$ (**2**) than $La_2(TPyP)_2(Pc)$ (**1**) is thus rationalized by the smaller ionic size of Eu.

These two compounds were fully characterized by various spectroscopic methods. The MALDI-TOF mass spectrum of **2** and the predicted isotope pattern are shown in the Electronic Supporting Information. However, satisfactory elemental analysis results could not be obtained for these two compounds as is usual for sandwich-type phthalocyaninatoand/or porphyrinato metal complexes and has been reported by different research groups.[15,18]

^{1}H NMR Spectra of $M^{III}{}_2(TPyP)_2(Pc)$ [M = La (1), Eu (2)]

The molecular structures of the newly prepared triple-decker complexes were clearly demonstrated to be of the form (TPyP)M(Pc)M(TPyP) (M = La, Eu) by their NMR spectra recorded in $CDCl_3$. The chemical shift data for the TPyP β-pyrrole, pyridyl, and Pc α- and β-protons are collected in Table 2, together with the T_1 values for protons in **2**. The assignments of the spectra for both the diamagnetic lanthanum complex and the weakly paramagnetic europium complex were achieved by virtue of the resolved multiplicity in the signals for the Pc α- and β-protons, the availability of spectra for related triple-deckers[10,15,19,20] and the 2D spectra. The positions on the pyridyl rings are labeled *ortho* and *meta* with respect to the bond to the porphyrin *meso*-carbon atom, and the terms *exo* and *endo* refer to the two possible environments with respect to the neighboring (inner) Pc ring. The *exo*/*endo* positions are exchanged by rotation about the bond between the pyridyl *ipso*-carbon atom and the porphyrin *meso*-carbon atom, but at room temperature, rotation is slow enough, as usual for *meso*-tetraarylporphyrins, that the usual AA′XX′ pattern is split into two pairs of signals. We show the ^{1}H NMR spectra of **1** and **2** in Figure 1 and the COSY spectrum of **1** in the Electronic Supporting Information. The sequence of assignments was as follows. The Pc proton signals could be readily identified by their integrals, their characteristic downfield positions, and the double-doublet signals (for **1**) at δ = 9.40 and 8.50 ppm for the α- and β-protons, respectively. The β-porphyrin signal was obvious as a unique 8-proton singlet at δ = 7.35 ppm. The *endo*- and *exo*-*ortho*- and *endo*- and *exo*-*meta*-proton signals appear as broad peaks and were readily assigned as *ortho*/*meta* pairs according to the COSY spectrum. At 30 °C the β-Pc signal overlaps with one of the py signals. For the paramagnetic Eu complex **2**, the assignment of the pair of *ortho*-protons is obvious from measurement of T_1 − faster relaxation is consistent with average proximity to the paramagnetic ion. In addition, an NOESY experiment with short mixing time (150 ms), showed positive cross peaks relating the protons in chemical exchange (EXSY), confirming these assignments. The only remaining ambiguity is the assignment of *exo*/*endo* for each pair of resonances. This has yet to be confirmed and will

Table 2. ^{1}H NMR spectroscopic chemical shifts (T_1 [ms] for Eu complex) for the triple-deckers (TPyP)M(Pc)M(TPyP) in $CDCl_3$ (300 MHz, 30 °C)

Complex[a][b]	Por β	*endo,ortho*	*endo,meta*	*exo,ortho*	*exo,meta*	Pc α	Pc β
1 La,La	7.36 s	9.52 b	9.11 b	6.48 b	8.51 b[c]	9.40 dd	8.50 dd
2 Eu,Eu	3.97 s	11.41 d	10.29 d	4.91 d	8.14 d	12. 56 d	10.73 d
	(150)	(190)	(760)	(190)	(760)	(140)	(390)

[a] Multiplicities: s = singlet, d = doublet, dd = double doublet, b = broad. [b] Assignments of *endo*/*exo* tentative (see text). [c] Signal overlapped with that of the Pc β-proton signals.

require variable-temperature ROESY experiments. The present assignments for **2** are based on the expected strong downfield pseudo-contact shift near the coordinated ion, i.e. on the *endo* side of the py ring. The assignments for **1** have been aligned with those for **2**. In the spectrum of compound **2**, the Pc α- and β-proton signals are less resolved than in analogue **1** because of broadening due to the paramagnetic europium ion. Conversely, the signals of the pyridyl protons of **2** are narrower than those in triple-decker **1** despite the presence of the paramagnetic europium ion. This is attributed to the slower rotation of pyridyl groups about the bond between the pyridyl *ipso*-carbon atom and the porphyrin *meso*-carbon atom associated with the smaller Eu^{III} ion and thus shorter ring−ring distance in compound **2**.

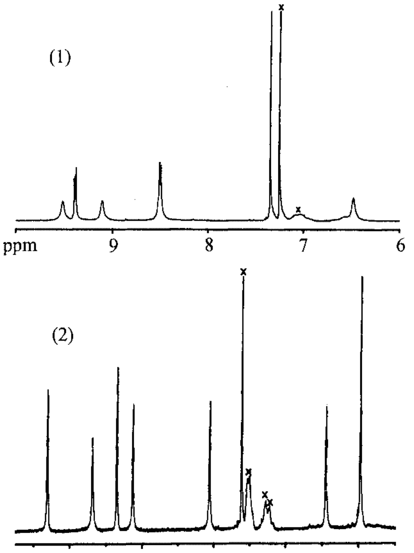


Figure 1. ^{1}H NMR spectra of $La_2(TPyP)_2(Pc)$ (**1**) and $Eu_2(TPyP)_2(Pc)$ (**2**) in $CDCl_3$

Electronic Absorption Spectra of $M^{III}_2(TPyP)_2(Pc)$ [M = La (1), Eu (2)]

The electronic absorption spectra of the mixed phthalocyaninato porphyrinato rare earth triple-decker compound **2** together with that of Li[Eu(TPyP)(Pc)] and the related triple-decker $Eu_2(TPyP)(Pc)_2$ are displayed in Figure 2. $M^{III}_2(TPyP)_2(Pc)$ shows similar features in the region from 300 to 800 nm to those of previously reported analogues $M_2(Por)_2(Pc)$ (Por = TPP, TClPP, TOMPP, TBPP).[10] However, in the near-IR region, a weak absorption band was also observed at 860 and 942 nm for **1** and **2**, respectively. It is noteworthy that re-examination of the electronic absorption spectra of previously reported $M_2(Por)_2(Pc)$ (M = Ce, Sm, Eu, Gd; Por = TPP, TClPP, TOMPP, TBPP) showed that this near-IR absorption at 860−960 nm is common for these mixed ring triple-decker compounds although it had been ignored by most previous studies for the reasons mentioned in the Introduction. After carefully re-examining the documents in this field, the sole work that ever mentioned this absorption before the present report appears to be that of Tran-Thi, who drew the absorption of $Ce_2(TPP)_2(Pc)$ at 890 nm in a schematic representation of the electronic absorption bands for this compound.[12] However, this band was not discussed further.

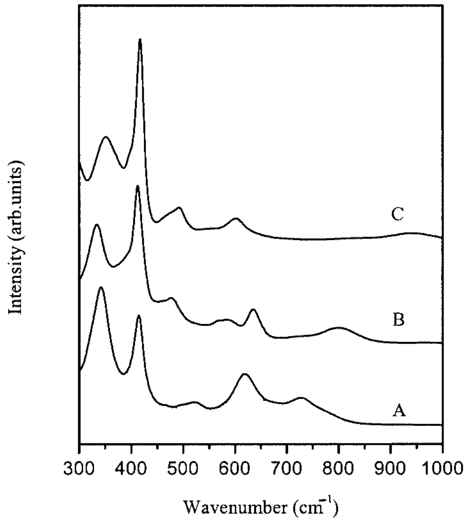


Figure 2. Electronic absorption spectra of (A) $Eu_2(TPyP)(Pc)_2$ in $CHCl_3$, (B) Li[Eu(TPyP)(Pc)] in MeOH, and (C) $Eu_2(TPyP)_2(Pc)$ (**2**) in $CHCl_3$

As expected, since compound $Eu_2(TPyP)_2(Pc)$ (**2**) consists of two units of $[(TPyP)Eu(Pc)]^-$, **2** indeed exhibits very similar electronic absorption spectrum to the corresponding double-decker Li[Eu(TPyP)(Pc)].[9] The Pc^{2-} and Por^{2-} Soret bands of **2** appear at 351 and 417 nm, respectively. The Pc^{2-} Q bands, which also contain some contributions from the Por ligands, appear at 602 and 942 nm, respectively. The absorption assigned to another π-π* transition arising from molecular orbitals delocalized over both Pc and Por macrocycles is located at 492 nm. Compared with the spectra of the corresponding double-decker Li[Eu(TPyP)(Pc)], all of the corresponding absorption bands in **2** have been found to red-shift to some extent, indicating the decreased ring-ring interaction in the triple-decker because of the increased ring-ring distance.

For the purposes of comparison, the electronic absorption spectrum of another mixed tetrapyrrole triple-decker species $Eu^{III}_2(TPyP)(Pc)_2$ [(TPyP)Eu(Pc)Eu(Pc)] is also shown in Figure 2. This compound can be regarded as composed of $[(TPyP)Eu(Pc)]^-$ and $[(Pc)Eu(Pc)]^-$. However, the absorption spectrum is not simply a superposition of the spectra of the constituent double-decker species $[(TPyP)Eu(Pc)]^-$ and $[(Pc)Eu(Pc)]^-$, indicating apparent ring−ring interaction between the one Por and the two Pc moieties. The Soret bands of $Eu^{III}_2(TPyP)(Pc)_2$ appear to be composed of two peaks at 340 and 415 nm, which are mainly derived from Pc and TPyP Soret bands, respectively. The prominent Q bands appear at 621 and 740 nm, respectively. Based on similarities in the appearance as well as the relative absorption intensities of these two absorptions to those of phthalocyaninato rare earth triple-decker compounds $M_2(Pc')_3$ at 630−650 and 680−710 nm,[20] these two Q bands are considered to arise mainly from the two neighboring Pc chromophores connected by one europium cation $[(Pc)Eu(Pc)]^-$. Comparison between the electronic absorption spectra of $Eu^{III}_2(TPyP)(Pc)_2$ and $Eu^{III}_2(TPyP)_2(Pc)$ (**2**) clearly reveals that the remaining weak band in the spectrum of the former compound at ca. 520 nm is mainly contributed by $[(TPyP)Eu(Pc)]^-$.

Correlation between Optical and Redox Properties of $M^{III}_2(TPyP)_2(Pc)$ [M = La (1), Eu (2)]

The redox properties of mixed phthalocyaninato porphyrinato rare earth triple-decker compounds $M^{III}_2(Por)_2(Pc)$ [M = La (**1**), Eu (**2**)] were investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in CH_2Cl_2. The half-wave redox potentials vs. SCE are summarized in Table 3. The cyclic voltammetry of compounds **1** and **2** is similar to that of known analogues.[10] Both these triple-deckers undergo two quasi-reversible one-electron oxidations and two quasi-reversible one-electron reductions under the present conditions. By analogy with the electrochemical properties of related sandwich complexes, especially (na)phthalocyaninato and/or porphyrinato rare earth sandwich complexes, all these processes can be attributed to successive electron removal from or addition to the ligand-based orbitals which are represented by the following five redox states: $[M_2(TPyP)_2(Pc)]/[M_2(TPyP)_2(Pc)]^+$, $[M_2(TPyP)_2(Pc)]^+/[M_2(TPyP)_2(Pc)]^{2+}$, $[M_2(TPyP)_2(Pc)]/[M_2(TPyP)_2(Pc)]^-$, and $[M_2(TPyP)_2(Pc)]^-/[M_2(TPyP)_2(Pc)]^{2-}$.

The potential difference between the first oxidation and the first reduction process, $\Delta E°_{1/2}$(oxd.1−red.1), is an important value for sandwich phthalocyaninato and/or porphyrinato complexes. As the first oxidation step and first reduction step, respectively, involve the HOMO and the LUMO of the molecule, the energy difference between these two redox processes corresponds to the electrochemical molecular band gap. The value $\Delta E°_{1/2}$(oxd.1−red.1) should reflect the energy necessary for the transition of an electron from the HOMO to the LUMO of respective sandwich species and therefore should correlate with the lowest energy optical transition. The equation $\Delta E°_{1/2}(\text{oxd.1}-\text{red.1}) - h\nu = 0.01$ eV was established between the redox characteristics and the lowest energy bands of monomeric metalloporphyrins M(Por).[21] According to this equation and the $\Delta E°_{1/2}$(oxd.1−red.1) values of 1.71 and 1.51 V for **1** and **2**, respectively, these two triple-decker compounds should show the lowest energy band at 729 and 827 nm, respectively. However, these results are far away from the observed maxima of 860 and 942 nm for **1** and **2**, respectively, perhaps indicating the significant contribution from the phthalocyanine ring to the frontier orbitals of $M^{III}_2(Por)_2(Pc)$. Moreover, the discrepancy between the experimental and calculated data for these two triple-deckers $M_2(TPyP)_2(Pc)$ is larger than that for double-deckers $[M^{III}(Por)(Pc)]^-$,[11] which seems to suggest that the frontier molecular orbitals of $M_2(TPyP)_2(Pc)$ contain more phthalocyanine contribution. This appears difficult to understand at first glance as the ratio of phthalocyanine to porphyrin in triple-decker $M_2(TPyP)_2(Pc)$ is lower than in double-decker $[M^{III}(Por)(Pc)]^-$. However, this result could be rationalized by the fact that the central Pc ring interrupts direct interaction between the two TPyP ligands in $M_2(TPyP)_2(Pc)$ and the Por and Pc ring-to-ring distance in triple-deckers is larger than in double-deckers. It may also be that such a correlation is inappropriate for sandwich complexes in general. However, it is noteworthy that the maxima of the lowest energy electronic band for naphthalocyanine-containing mixed ring triple-decker analogues $M_2(OEP)_2(Nc)$ correspond well with the calculated values based on their redox data according to the above equation.[8a] This correspondence may well be fortuitous due to the similar redox properties of OEP and Nc rings and is unlikely to mean

Table 3. Electrochemical data for the triple-decker complexes

Compound[a]	$E°_{1/2}$(oxd.2)	$E°_{1/2}$(oxd.1)	$E°_{1/2}$(red.1)	$E°_{1/2}$(red.2)	$\Delta E°_{1/2}$(oxd.1−red.1)
$La_2(TPyP)_2(Pc)$ (**1**)	1.42	0.97	−0.74	−1.27	1.71 V
$Eu_2(TPyP)_2(Pc)$ (**2**)	1.19	0.75	−0.76	−1.27	1.51 V

[a] Recorded with $[Bu_4N][PF_6]$ as electrolyte in CH_2Cl_2 (0.1 M) at ambient temperature. Potentials were determined by cyclic voltammetry with a scan rate of 100 mV s^{-1}, and are expressed as half-wave potentials ($E_{1/2}$) in volts relative to SCE.

that the molecular orbitals, especially the HOMO and LUMO of $M_2(OEP)_2(Nc)$, possess only porphyrin character.

Conclusion

In summary, the HOMO and LUMO of mixed ring triple-deckers $M_2(TPyP)_2(Pc)$ (M = La, Eu) consist of contributions from both macrocycles. However, the research into this subject for mixed phthalocyaninato porphyrinato metal derivatives is relatively undeveloped at this stage due to the lack of systematic investigation into the optical and redox properties of such kinds of compounds. It is clear that the unexpected existence of near-IR absorption for neutral mixed ring triple-deckers warrants further experimental and theoretical attention, and work in this regard is in progress.

Experimental Section

General: $CHCl_3$ and CH_3OH were used as received from Beijing Chemical Reagents. H_2TPyP was purchased from Aldrich. $M(acac)_3 \cdot nH_2O$[22] and $M(Pc)_2$[23] were prepared according to published procedures. The electronic absorption spectra were recorded with Hitachi U-3300 and Hitachi 3100 spectrophotometers. ^1H NMR spectra were recorded with a Bruker Avance 400 spectrometer at the Centre for Molecular Architecture, Central Queensland University, in $CDCl_3$ solutions at ca. 30 °C. Electrochemical measurements were carried out with a BAS CV-50 W voltammetric analyzer. The cell comprised a platinum-sphere working electrode, a silver-wire counter electrode, and an $Ag/AgNO_3$ (0.1 M in MeCN) reference electrode, which was connected to the solution by a Luggin capillary whose tip was placed close to the working electrode. Typically, a 1.0 mM sample solution containing 0.1 M $[Bu_4N][ClO_4]$ in CH_2Cl_2 was purged with nitrogen for 20 min, then the voltammograms were recorded at ambient temperature. Potentials were referenced to the Ag/Ag^+ couple in MeCN, which was taken as +0.31 V vs. SCE as determined for this system previously using ferrocene as an internal standard.[24]

Preparation of Triple-Decker $La_2(TPyP)_2(Pc)$ (1): A mixture of $La(acac)_3 \cdot nH_2O$ (15 mg, 0.03 mmol), H_2TPyP (18 mg, 0.03 mmol) and $La(Pc)_2$ (23 mg, 0.02 mmol) in 1,2,4-trichlorobenzene (TCB) (4 mL) was refluxed overnight (> 18 h) under nitrogen to give a dark-blue solution. The volatiles were then removed under reduced pressure and the residue was chromatographed on a silica gel column with $CHCl_3$ to remove trace amounts of unchanged $La(Pc)_2$ as the first fraction. The column was then eluted with $CHCl_3$/MeOH (100:1−5) to elute triple-decker $La_2(TPyP)(Pc)_2$ and the desired triple-decker $La_2(TPyP)_2(Pc)$ as the second and third fractions, respectively. The crude product was repeatedly purified by the same chromatographic procedure, followed by recrystallization from a mixture of $CHCl_3$ and MeOH to afford dark blue microcrystals. Yield 14 mg (47%). MS (MALDI-TOF): an isotopic cluster peaking at m/z = 2025 $[M + H]^+$. IR (KBr): $\tilde{\nu} = 1328\ cm^{-1}$ (Pc^{2-}).

Preparation of Triple-Decker $Eu_2(TPyP)_2(Pc)$ (2): This compound was prepared by the above procedure with $Eu(acac)_3 \cdot H_2O$ (15 mg, 0.03 mmol), H_2TPyP (18 mg, 0.03 mmol) and $Eu(Pc)_2$ (23 mg, 0.02 mmol) as starting materials. Yield 16 mg (51%). MS (MALDI-TOF): an isotopic cluster peaking at m/z = 2051 $[M + H]^+$. IR (KBr): $\tilde{\nu} = 1331\ cm^{-1}$ (Pc^{2-}).

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[1] J. Jiang, K. Kasuga, D. P. Arnold, in *Supramolecular Photosensitive and Electroactive Materials* (Ed.: H. S. Nalwa), Academic Press, New York, **2001**, chapter 2, pp. 113−210.

[2] 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**, vol. 3, chapter 20, pp. 245−294.

[3] D. K. P. Ng, J. Jiang, *Chem. Soc. Rev.* **1997**, *26*, 433−442.

[4] J. Simon, S. Sirlin, *Pure Appl. Chem.* **1989**, *61*, 1625−1629.

[5] [5a] M. Mardru, G. Guilaud, M. Al. Sadoun, M. Maitrot, C. Clarisse, M. Le Contellec, J.-J. Andre, J. Simon, *Chem. Phys. Lett.* **1987**, *142*, 103−105. [5b] R. Madru, G. Guilaud, M. Al. Sadoun, M. Maitrot, J.-J. Andre, J. Simon, R. Even, *Chem. Phys. Lett.* **1988**, *145*, 343−346.

[6] [6a] J. Jiang, W. Liu, L. Lin, W. F. Law, D. K. P. Ng, *Inorg. Chim. Acta* **1998**, *268*, 49−52. [6b] J. Jiang, J. Xie, M. T. M. Choi, D. K. P. Ng, *J. Porphyrins Phthalocyanines* **1999**, *3*, 322−328.

[7] J. Jiang, M. T. M. Choi, J. Chen, D. K. P. Ng, *Polyhedron* **1998**, *17*, 3903−3908.

[8] [8a] J. Jiang, Y. Bian, F. Furuya, W. Liu, M. T. M. Choi, H. W. Li, N. Kobayashi, Q. Yang, T. C. W. Mak, D. K. P. Ng, *Chem. Eur. J.* **2001**, *7*, 5059−5069. [8b] J. Jiang, W. Liu, K.-L. Cheng, K.-W. Poon, D. K. P. Ng, *Eur. J. Inorg. Chem.* **2001**, 413−417. [8c] F. Furuya, N. Kobayashi, Y. Bian, J. Jiang, *Chem. Lett.* **2001**, 944−945. [8d] J. Jiang, D. Du, D. K. P. Ng, J. Xie, *Chem. Lett.* **1999**, 261−262.

[9] J. Jiang, T. C. W. Mak, D. K. P. Ng, *Chem. Ber.* **1996**, *129*, 933−936.

[10] [10a] J. Jiang, R. L. C. Lau, T. W. D. Chan, T. C. W. Mak, D. K. P. Ng, *Inorg. Chim. Acta* **1997**, *155*, 59−64. [10b] R. L. C. Lau, J. Jiang, D. K. P. Ng, T. W. D. Chan, *J. Am. Soc. Mass Spectrom.* **1997**, *8*, 161−169. [10c] J. Jiang, W. Liu, W.-F. Law, D. K. P. Ng, *Inorg. Chim. Acta* **1998**, *268*, 141−145.

[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] T.-H. Tran-Thi, T. A. Mattioli, D. Chabach, A. De Cian, R. Weiss, *J. Phys. Chem.* **1994**, *98*, 8279−8288.

[13] J. Jiang, W. Liu, X. Sun, X. Zhang, D. K. P. Ng, *Chem. Res. Chin. Univ.* **2001**, *17*, 134−142.

[14] D. Chabach, A. De Cian, J. Fischer, R. Weiss, M. El Malouli Bibout, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 898−889.

[15] N. Pan, J. Jiang, X. Cui, D. P. Arnold, *J. Porphyrins Phthalocyanines* **2002**, *6*, 347−358.

[16] G. A. Spyroulias, C. P. Raptopoulou, D. de Montauzon, A. Mari, R. Poilblanc, A. Terzis, A. G. Coutsolelos, *Inorg. Chem.* **1999**, *38*, 1683−1696.

[17] [17a] J. W. Buchler, A. De Cian, J. Fischer, M. Kihn-Botulinski, H. Paulus, R. Weiss, *J. Am. Chem. Soc.* **1986**, *108*, 3652−3659. [17b] J. W. Buchler, B. Scharbert, *J. Am. Chem. Soc.* **1988**, *110*, 4272−4276.

[18] T. Gross, F. Chevalier, J. S. Lindsey, *Inorg. Chem.* **2001**, *40*, 4762−4774.

[19] D. P. Arnold, J. Jiang, *Chem. Lett.* **1999**, 483−484.

[20] [20a] W. Liu, J. Jiang, N. Pan, D. P. Arnold, *Inorg. Chim. Acta*

2000, *310*, 140−146. [20b] D. P. Arnold, J. Jiang, *J. Phys. Chem. A* **2001**, *105*, 7525−7533.

[21] J.-H. Fuhrhop, K. M. Kadish, D. G. Davis, *J. Am. Chem. Soc.* **1973**, *95*, 5140−5147.

[22] J. G. Stites, C. N. McCarty, L. L. Quill, *J. Am. Chem. Soc.* **1948**, *70*, 3142−3143.

[23] A. De Cian, M. Moussavi, J. Fischer, R. Weiss, *Inorg. Chem.* **1985**, *24*, 3162−3167.

[24] J. Jiang, W. Liu, K.-W. Poon, D. Du, D. P. Arnold, D. K. P. Ng, *Eur. J. Inorg. Chem.* **2000**, 205−209.

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