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Synthesis, spectroscopic properties and electrochemistry of (2,9,16,23-tetrasubstituted phthalocyaninato) erbium complexes

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Abstract

Two homoleptic bis(phthalocyaninato) erbium(III) complexes $Er[Pc(\beta\text{-}OR/R)_4]_2$ and two half-sandwich phthalocyaninato erbium(III) complexes $(acac)Er[Pc(\beta\text{-}OR/R)_4]$ (OR = 1-*n*-pentyloxy and R = *tert*-butyl) have been synthesized and characterized by MALDI-TOF-MS as well as by various spectroscopic methods. The introduction of different substituents (alkoxy or alkyl groups) to the phthalocyanine rings induced changes in the spectroscopic and electrochemical properties. Although the excited states of the homoleptic double- and triple-decker complexes usually are considered to lack fluorescence, in these cases, the homoleptic bis(phthalocyaninato) erbium(III) complexes $Er[Pc(\beta\text{-}OR/R)_4]_2$ displayed intense fluorescence compared with the half-sandwich phthalocyaninato erbium(III) complexes $(acac)Er[Pc(\beta\text{-}OR/R)_4]$. For the two kinds of phthalocyaninato erbium(III) complexes, the pentyloxy-substituted complexes gave relatively intense emission compared with the *tert*-butyl-substituted complexes. These differences in the electronic ground state absorptions and in the excited state properties correlate with observations made from electrochemical measurements.

Keywords: Lanthanide complexes; Phthalocyanines; Erbium; Acetylacetone; Sandwich

1. Introduction

Phthalocyanines are of lasting importance not only for fundamental interest but also for their promising applications in many areas [1,2]. Among their total functional systems, sandwich and half-sandwich phthalocyaninato rare earth complexes constitute an essential and useful class of advanced materials [3,4]. For the specific photoluminescent rare earth metal ions such as Er^{3+}, sandwich-type and acetylacetonate-ligated half-sandwich phthalocyaninato moieties are expected as excellent models to protect these luminescent ions from the environments and to achieve energy transfer from chromophores to the central rare earth ions [5,6].

The properties of phthalocyaninato metal complexes depend strongly on the substituents bound to the phthalocyanine ring and the ligands ligated to central metal ion [7–9]. In order to enhance the performance of the material, one way is to introduce different kinds of substituents onto the phthalocyanine ring so that the properties of phthalocyanines can be significantly altered [10]. In this paper, we present two homoleptic bis(phthalocyaninato) erbium(III) complexes and two half-sandwich phthalocyaninato erbium(III) complexes with *n*-pentyloxy or *tert*-butyl substituents which are highly soluble in common organic solvents. These complexes show rather different spectral and electrochemical properties.

2. Experimental

2.1. Materials and methods

n-Pentanol was distilled from sodium; dichlorobenzene was distilled and used. Column chromatography was carried out using silica gel columns; the electrolyte $[Bu_4N][ClO_4]$ was recrystallized from tetrahydrofuran. All other reagents and

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solvents were used as received. 4-Pentyloxy-phthalonitrile [11], 4-*tert*-butyl-phthalonitrile [12] and H_2(tBu$_4$-Pc) [13] were prepared according to published procedures.

^{1}H NMR spectra were recorded on a Bruker DPX 300 spectrometer (300 MHz) in $CDCl_3$. Electronic absorption spectra were recorded on a V-570 UV/VIS/NIR Spectrophotometer. Fluorescence emission spectra were recorded on a Hitachi F-4500 Spectrophotometer and MALDI-TOF mass spectra were taken on a Bruker BIFLEX III ultrahigh-resolution Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer.

Electrochemical measurements were carried out using a Shanghai ChenHua voltammetric analyzer. The cell comprised of a glassy carbon disk working electrode and a Pt wire counter electrode. The reference electrode was Ag/AgCl. Typically, a 0.1 M solution of $[Bu_4N][ClO_4]$ in CH_2Cl_2 containing 0.5 mM of sample was purged with nitrogen for 10 min. The scan rates were 20 mV s^{-1} for CV.

The synthetic route to (phthalocyaninato) erbium complexes (**1**–**4**) are given in Scheme 1.

2.2. Synthesis of 4-pentyloxy phthalonitrile

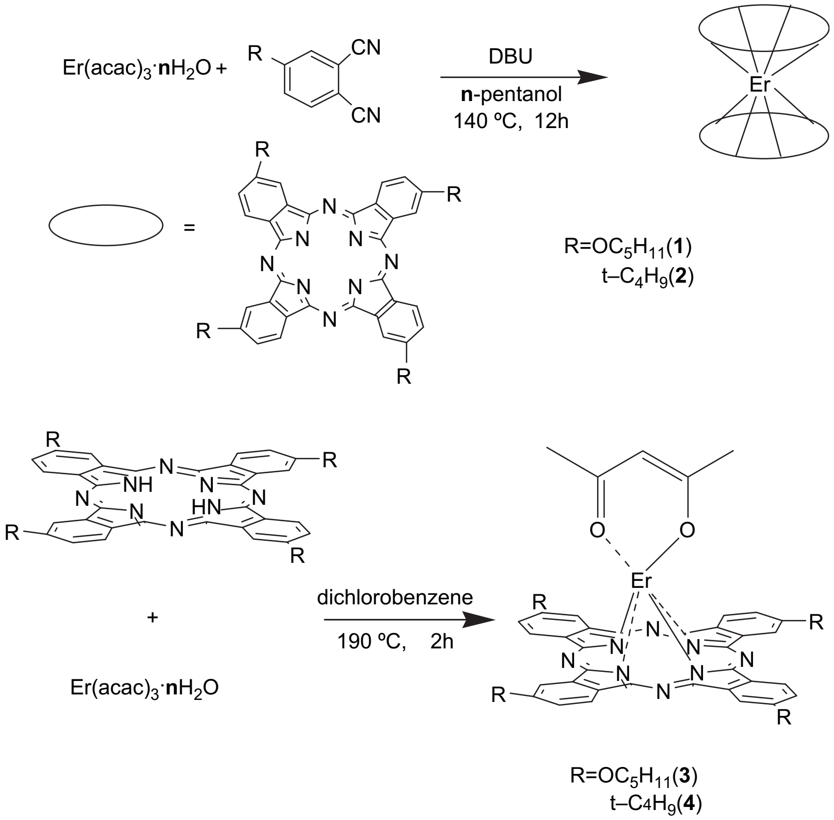
A mixture of 4-nitrophthalonitrile (2 g, 11 mmol), 8 ml *n*-pentanol and anhydrous K_2CO_3 (2 g, 14 mmol) in dry DMF (60 ml) was stirred at room temperature for 72 h and then poured into 200 ml of cool water. The suspension was extracted with $CHCl_3$ three times. The organic layer was evaporated to dryness. The crude product was purified by column chromatography over SiO_2 (hexane:acetone = 7:1) to afford the pure product in 63% yield. MS (EI-MS) *m/z*: 214 (M^+). ^{1}H NMR ($CDCl_3$): δ (300 MHz, $CDCl_3$): 7.70 (d, 1H); 7.25 (m, 1H); 7.18 (m, 1H); 3.94 (t, 2H); 1.73 (m, 2H); 1.29–1.33 (m, 4H); 0.96 (t, 3H).

2.3. Synthesis of $H_2Pc(\beta\text{-}C_4H_9)_4$

To 25 ml of dry octanol was added lithium (82 mg, 12 mmol) under a slow stream of dry nitrogen. After complete reaction, *tert*-butyl-phthalonitrile (2.2 g, 10 mmol) was added and the ensuing solution was heated to 180 °C at which point the solution turned green after a few minutes, and was heated for two more hours. After the reaction was complete, octanol was partially removed under reduced pressure and the remaining blue paste was poured into acetic acid/acetone and left under agitation overnight. The crude product was precipitated in methanol, filtered, and rinsed with methanol. Chromatography on silica gel using $CHCl_3$ as eluent gave the product in 71% yield. The product is characteristic of metal-free phthalocyanines as indicated by UV/vis spectroscopy.

2.4. Synthesis of $Er[Pc(\beta\text{-}OR/R)_4]_2$ ($R = OC_5H_{11}, C_4H_9$) (**1** and **2**)

A mixture of $Er(acac)_3 \cdot nH_2O$ (25.9 mg), 1,8-diazobicyclo [5.4.0]undec-7-ene (DBU) (40 mg, 0.26 mmol) and substituted



Scheme 1. Synthesis of (phthalocyaninato) erbium complexes (**1**–**4**).

phthalonitrile (0.6 mmol) in *n*-pentanol (3 ml) was heated at 140 °C under nitrogen for 12 h. After cooling to room temperature, the mixture was filtered and the residue washed with *n*-pentanol (3 ml). The combined filtrates were concentrated under reduced pressure and then subjected to chromatography over SiO_2 (chloroform:hexane = 2.5:1). After eluting out the residual metal-free phthalocyanine, a dark blue solution containing the sandwich compound was collected and rotary-evaporated. The crude product was further purified by recrystallization from a mixture of $CHCl_3$ and MeOH. Yield: 30% for **1** and 24% for **2**. The two products are characterized by UV/vis spectroscopy and MALDI-TOF mass spectrometry.

2.5. Synthesis of (acac)Er[Pc(β-OR/R)$_4$] (R = OC_5H_{11}, C_4H_9) (3 and 4)

In a three port glass vessel equipped with an nitrogen inlet, a condenser and a septum port, anhydrous dichlorobenzene (20 ml) and H_2[Pc(β-OR/R)] (0.5 mmol) was added and the system degassed for 1 h. Er(acac)·$n$$H_2O$ (1 g) was added, and the mixture was heated to reflux for 2 h. Formation of the complex was monitored using thin layer chromatography and UV/vis absorption spectroscopy. After the reaction was complete, the mixture was submitted to chromatography over SiO_2. Dichlorobenzene was first eluted using hexane. $CHCl_3$ was used to elute metal-free phthalocyanine. Finally, the eluent (acetone:chloroform = 1:1) was used to afford pure products. Yield: 61% for **3** and 59% for **4**. The complexes are characterized using UV/vis spectroscopy and MALDI-TOF mass spectrometry.

3. Results and discussion

3.1. Synthesis and characterization

Over the past decade, a substantial number of rare earth(III) double-decker complexes with mixed phthalocyaninato ligands have been synthesized. This work describes the treatment of substituted phthalonitriles with Er(acac)$_3$·$n$$H_2O$ in the presence of DBU. This pathway is convenient and efficient for increasing reaction yields and the products are easily purified without using HPLC [14]. Meanwhile, we prepared (acac)Er[Pc(β-R)$_4$] by the reaction of H_2[Pc(β-R)$_4$] with Er(acac)$_3$·$n$$H_2O$ in dichlorobenzene.

To acquire satisfactory characterization results for the four (phthalocyaninato) erbium complexes **1**–**4** by using MALDI-TOF mass spectrometry, α-cyano-4-hydroxycinnamic acid was used as a matrix for **1** and**2** and β-carboline for **3** and **4**. The MALDI-TOF mass spectra of these compounds clearly showed intense signals for the molecular ion M^+ or the protonated molecular ion $[M+H]^+$. Fig. 1 presents the spectrum of **2**, in which the peak at *m/z* 1639.6 appears. Experimental and simulated isotopic patterns of the molecular ion for **2** were also given. Pattern (a) did not fully resemble pattern (b). It seems that (a) is the mixed signal of MH^+ and M^+, but (b) is only the signal of M^+. Table 1 summarizes the analytical mass spectroscopic data of other compounds.

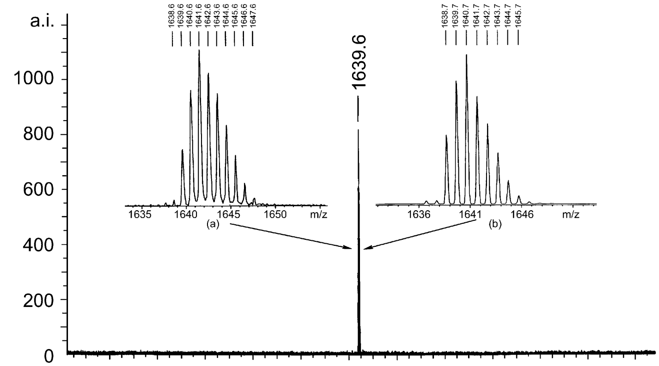


Fig. 1. MALDI-TOF spectrum of Er[Pc(β-C_4H_9)$_4$]$_2$. (a) Experimental and (b) simulated isotopic patterns for this molecule.

Table 1
MALDI-TOF mass spectroscopic data for compounds **1**–**4**

Compound	M^+ or $[MH]^+$ [*m/z*][a]
[Er{Pc(β-OC_5H_{11})$_4$}$_2$]	1879.5(1879.8)[b]
[Er{Pc(β-C_4H_9)$_4$}$_2$]	1639.6(1639.7)[b]
[(acac)Er{Pc(β-OC_5H_{11})$_4$}]	1178.5[c](1178.5)[b]
[(acac)Er{Pc(β-C_4H_9)$_4$}]	1003.8(1003.4)[b]

[a] By MALDI-TOF mass spectrometry.
[b] Mass according to the most intense isotopic peak of M^+.
[c] Mass from [(acac)Er{Pc(β-OC_5H_{11})$_4$}]·$3H_2O$.

3.2. Spectroscopic properties

3.2.1. Electronic ground state absorption

Double-deckers **1** and **2** can be regarded as single-hole complexes in which an unpaired electron is present in one of the macrocyclic ligands [3,15]. However, complexes **3** and **4** have no unpaired electron in the ligands.

The electronic ground state absorption spectra of these complexes are presented in Fig. 2 and the absorption data are collected in Table 2. From the spectra, the complexes **1**–**4** show a typical Soret band (B band) absorption at

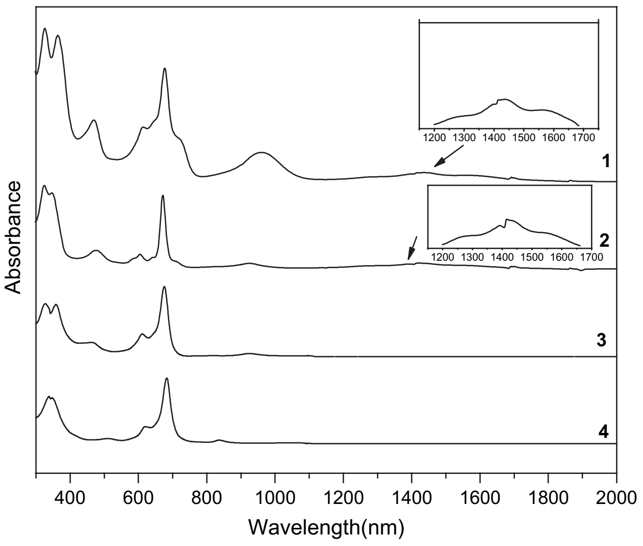


Fig. 2. Electronic absorption spectra of all compounds (2×10^{-5} mol/l) in $CHCl_3$.

Table 2
Electronic absorption data for compounds **1**–**4** in $CHCl_3$

Compound	λ_{max} [nm] (logε)						
1	310(5.13)	360(5.10)	450(4.74)	600(4.63)	678(4.99)	955(4.40)	1450(3.87)
2	309(4.86)	338(4.81)	475(4.24)	600(4.10)	675(4.81)	925(3.80)	1420(3.81)
3	320(4.65)	350(4.64)	450(4.10)	605(4.30)	675(4.78)	920(3.54)	–
4	330(4.62)	335(4.59)	452(3.70)	615(4.18)	670(7.45)	845(3.60)	–

approximately 340–360 nm. A distinct feature of these UV/vis spectra was the extent of B band splitting. Obvious splitting of B band was observed for complexes **1** and **3**, while complexes **2** and **4** almost showed a single B band, indicating that these complexes **1**–**4** can take on different molecular symmetry [16]. The Q band which appears around 670 nm as a strong absorption with a weak vibronic band around 600 nm, is responsible for the color of the compound [17]. For homoleptic bis(phthalocyaninato) erbium(III) complexes **1** and **2**, two weak π-radical-anion bands at 450–475 and 920–955 nm are also seen. The broad near-IR band at 1430–1450 nm is highly characteristic for rare earth(III) double-deckers which contain a hole in one of the ligands [15]. For half-sandwich phthalocyaninato erbium(III) complexes **3** and **4**, the absorption at 920 nm for **3** and the absorption at 845 nm for **4** can be attributed to the electronic transitions involving the semi-occupied molecular orbital (SOMO) [15,17]. The weak absorption at 450 nm for **3** is common for alkoxy-substituted phthalocyanines, which may be attributed to an n–π* transition [9].

A simplified molecular orbital diagram of [$Er\{Pc(\beta\text{-}OC_5H_{11})_4\}_2$] and [$Er\{Pc(\beta\text{-}C_4H_9)_4\}_2$] constructed from the a_{1u} and e_g orbitals of the two ligands is given in Fig. 3. Due to the more electron-rich $Pc(\beta\text{-}OC_5H_{11})_4$ and $Pc(\beta\text{-}C_4H_9)_4$ with respect to Pc, both the a_{1u} and e_g orbitals of compounds **1** and **2** are higher than those of Pc. The former two similar absorptions at 450–465 and 920–950 nm are observed in the spectra of unsubstituted bis(phthalocyaninato)rare earth(III) complexes [$M(Pc)_2$] [18,19] and are assigned to the transitions from the fourth-occupied HOMO to the SOMO and from the SOMO to the LUMO, respectively [20]. The latter band at 1430–1450 nm is the transition between the second-highest occupied orbital and the semi-occupied orbital [21].

3.2.2. Fluorescence behavior

The fluorescence emission spectra of complexes **1**–**4** are presented in Fig. 4. The excitation wavelengths at 670, 680, 660 and 650 nm corresponded to the most intense Q-band absorption, respectively. The emissions are within the 700–710 nm region with a red shift of about 10 nm compared with that for the unsubstituted phthalocyanine metal complexes [22], since the induction of substituent enlarges the conjugated system and decreases the energy gap between HOMO and LUMO. Although the excited states of the homoleptic double- and triple-decker complexes usually are considered to be lacking fluorescence [23], in these cases, the homoleptic bis(phthalocyaninato) erbium(III) complexes $Er[Pc(\beta\text{-}OR/R)_4]_2$ show intense fluorescence compared with the half-sandwich phthalocyaninato erbium(III) complexes $(acac)Er[Pc(\beta\text{-}OR/R)_4]$. For the two kinds of phthalocyaninato erbium(III) complexes, the pentyloxy-substituted complexes give relatively intense emission compared with the *tert*-butyl-substituted complexes.

The reason for these differences of emission intensity may arise from two aspects. One is that the half-sandwich phthalocyaninato erbium(III) complexes $(acac)Er[Pc(\beta\text{-}OR/R)_4]$, encountered intermolecular π–π interaction to induce the photoexcited state, decay more strongly than did the homoleptic bis(phthalocyaninato) erbium(III) complexes $Er[Pc(\beta\text{-}OR/R)_4]_2$ [8]. The other reason is that in contrast to *n*-pentoxy substituent, the bulky *tert*-butyl is near to phthalocyanine ring and easily quenches the fluorescence. In addition, the heavy atom

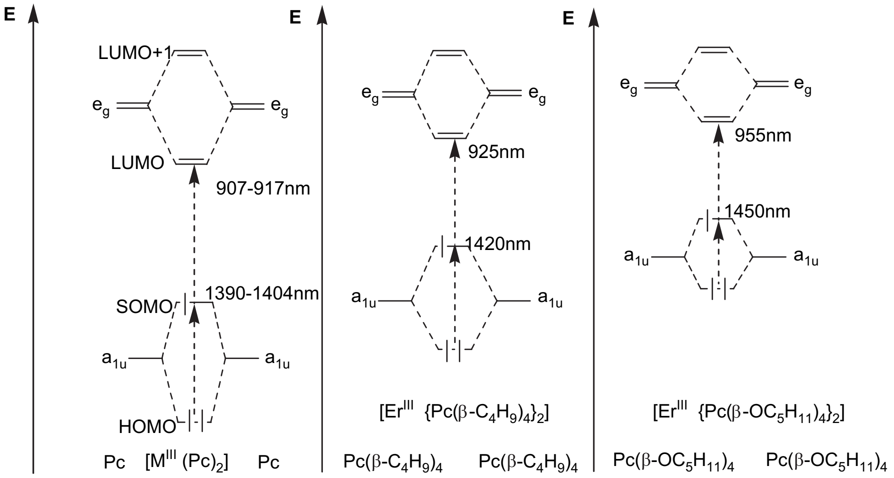


Fig. 3. Simplified molecular orbital diagrams for [$M^{III}(Pc)_2$], [$Er^{III}\{Pc(\beta\text{-}C_4H_9)_4\}_2$] and [$Er^{III}\{Pc(\beta\text{-}OC_5H_{11})_4\}_2$].

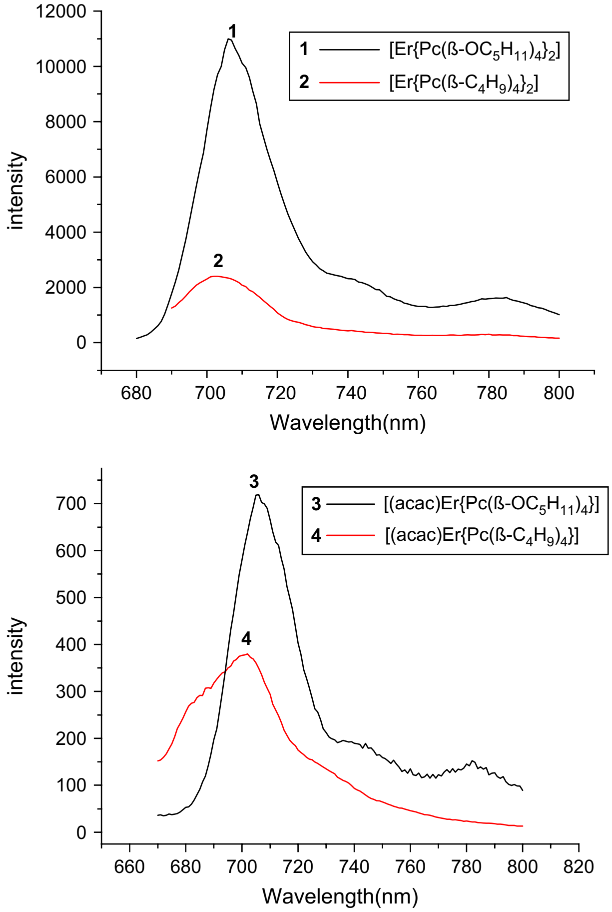


Fig. 4. Fluorescence emission spectra of complexes **1–4** (2×10^{-5} mol/l) in $CHCl_3$.

effect of erbium may also be a common factor for the decay of the photoexcited state [23].

3.3. Electrochemical properties

The redox behaviors of the complexes **1–4** were studied by cylic voltammetry (CV) in CH_2Cl_2 (Fig. 5). Complexes **1** and **2** show three quasi-reversible one-electron oxidations and three quasi-reversible one-electron reductions, while complexes **3** and **4** show two oxidations and two reductions. Since the oxidation state of the central trivalent rare earth ion does not change, these processes are due to successive removal or addition of electrons from or to the ligand-based orbitals.

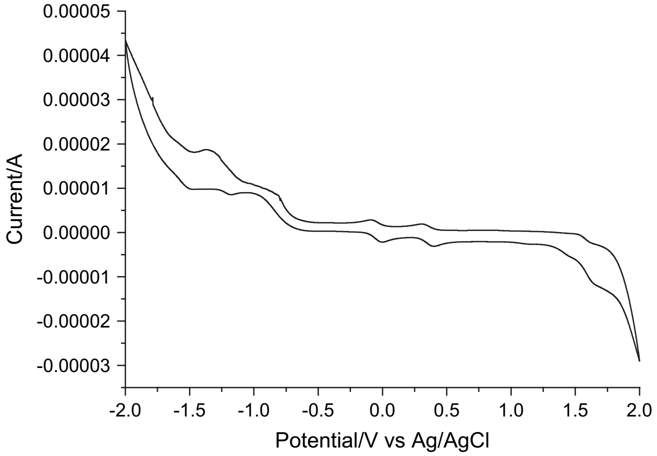


Fig. 5. Cyclic voltammetry of $[Er\{Pc(\beta\text{-}OC_5H_{11})_4\}_2]$ in CH_2Cl_2 containing 0.1 M $[Bu_4N][ClO_4]$ at a scan rate of 20 mV s^{-1}.

Compared with the unsubstituted analogues, the incorporation of the four electron-donating *n*-pentyloxy or *tert*-butyl groups onto each phthalocyanine ring makes the complexes easier to oxide and harder to reduce. This is well demonstrated by the lower oxidation and reduction half-wave potentials of the corresponding redox processes of $Er[Pc(\beta\text{-}OR/R)_4]_2$ compared with those of $Er(Pc)_2$ [23].

Like many other series of double-deckers, complexes **1** and **2** have the similar electrochemistry characters. As shown in Table 3, the potential difference between R_1 and R_2 ($\Delta E''_{1/2}$) represents the HOMO–LUMO gap, and reflects the energy necessary for the transition of an electron from the HOMO to LUMO, therefore correlates with the lowest energy optical transition in the electronic absorption spectrum whereas the gap between O_2 and O_1 ($\Delta E'_{1/2}$) reflects the energy separation between the semi-occupied orbital and the second-highest HOMO and also shows whether the π–π interaction is weak or strong. These values should be related to the position of the corresponding electronic transitions (the absorptions at 920–955 and 1430–1450 nm, respectively).

As shown in Table 3, the potential difference between O_1 and R_1 ($\Delta E_{1/2}$) are related to the energy level of the semi-occupied molecular orbital. The potentials of both O_2 and O_3 involve the second-highest occupied orbital. The remaining reduction processes R_2 and R_3 are related to the energy level of the LUMO (as well as the unoccupied orbitals). It is noteworthy that compared with complexes **1** and **3** containing *n*-pentoxy

Table 3
Electrochemical data for complexes **1–4**

Compound	Oxd_3	Oxd_2	Oxd_1	Red_1	Red_2	Red_3	$\Delta E_{1/2}$[a]	$\Delta E'_{1/2}$[b]	$\Delta E''_{1/2}$[c]
1	+1.68	+1.43	+0.44	−0.03	−1.50	−1.77	0.47	0.99	1.47
2	+1.60	+1.41	+0.41	−0.01	−1.42	−1.70	0.42	1.00	1.41
3		+1.62	+0.42	−0.03	−1.46		0.45	1.20	1.43
4		+1.60	+0.40	−0.01	−1.40		0.41	1.20	1.39

[a] $\Delta E_{1/2} = Oxd_1 - Red_1$.
[b] $\Delta E'_{1/2} = Oxd_2 - Oxd_1$.
[c] $\Delta E''_{1/2} = Red_1 - Red_2$.

bound to phthalocyanine ring, complexes **2** and **4** with *tert*-butyl give smaller $\Delta E_{1/2}$ and $\Delta E''_{1/2}$ values, which may be correlated with their relatively weak fluorescence emissions.

For complexes **3** and **4**, the reduction and oxidation may be related to the interaction between the Pc ring and the central metal ion. The LUMO of mono(metallophthalocyanines) is doubly degenerated (e_g) and can accept up to four electrons. Hence, a tentative mechanism for electrochemical reaction can be given as follows:

$$(\mathrm{acac})\mathrm{ErPc}(0) \overset{\mathrm{Oxd}_1}{\rightleftarrows} (\mathrm{acac})\mathrm{ErPc}(-1) \overset{\mathrm{Oxd}_2}{\rightleftarrows} (\mathrm{acac})\mathrm{ErPc}(-2)$$
$$\overset{\mathrm{Rxd}_1}{\rightleftarrows} (\mathrm{acac})\mathrm{ErPc}(-3) \overset{\mathrm{Rxd}_2}{\rightleftarrows} (\mathrm{acac})\mathrm{ErPc}(-4)$$

4. Conclusion

In summery, we prepared two homoleptic bis(phthalocyaninato) erbium(III) complexes $\mathrm{Er[Pc(\beta\text{-}OR/R)_4]_2}$ and two half-sandwich phthalocyaninato erbium(III) complexes (acac) $\mathrm{Er[Pc(\beta\text{-}OR/R)_4]}$. The compounds were fully characterized with various spectroscopic and electrochemical methods. Introduction of different substituents (alkoxy or alkyl groups) to the phthalocyanine rings induce obvious changes in the spectroscopic and electrochemical properties.

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