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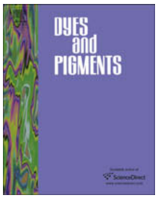

The synthesis, spectroscopy, electrochemistry and photophysical properties of novel, sandwich europium(III) complexes with a porphyrin ligand bearing four pyrenyl groups in meso-positions

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ABSTRACT

Novel, metal free porphyrins containing four pyrenyl groups in the meso-positions were used to provide novel, sandwich-type mixed tetrapyrrole europium double- and triple-deck complexes. The sandwich-type complexes together with the metal free porphyrin were characterized using electronic absorption, IR and ^{1}H NMR spectroscopy in addition to elemental analysis. The electrochemical behaviour of the sandwich complexes was investigated by cyclic voltammetry and differential pulse voltammetry in CH_2Cl_2, their photophysical properties were studied in comparison to those of the metal free porphyrin ligand. Fluorescence quenching observed was tentatively attributed to efficient and rapid energy transfer from the pyrenyl groups to porphyrin followed by electron transfer from porphyrin to phthalocyanine.

1. Introduction

Owing to their unique optical, electrical and magnetic properties associated with the intriguing inter-ring π–π interactions, sandwich-type bis(phthalocyaninato) rare earth complexes have been intensively studied over the past several decades as prospective molecular electronic, molecular magnetic, electrochemical display, and non-linear optical materials [1,2]. Since early 1980s, bis(porphyrinato) rare earth analogues with the same sandwich molecular structures have also been synthesized and put forward as structural and spectroscopic models for the “special pair” found in the reaction centre of photosynthetic bacteria [3]. Recently, mixed (phthalocyaninato)(porphyrinato) rare earth analogues have received increasing attention partly because the individual chromophores display very different optical and redox properties which facilitate the study of the π–π interactions and the extent of hole delocalization. The mixed ring triple-decker complexes are also attractive for their potential use in information storage due to their large number of redox states, reversible electrochemistry, and relatively low oxidation potentials [4,5].

Due to the lack of fluorescence of most of the sandwich tetrapyrrole metal complexes, few researches have been conducted on the photophysics of sandwich complexes [6–11]. Since late 1980s, Holten and co-workers have investigated the photophysics of a series of bis- and tris(octaethylporphyrinato) rare earth complexes [6–11], among which fluorescence quenching has been observed for some compounds. Recently, Jiang reported the photophysics of mixed (naphthalocyaninato)(porphyrinato) rare earth double-decker compounds M^{III}(Nc)(OEP) (M = La, Eu, Lu; Nc = 2,3-naphthalocyaninae; OEP = 2,3,7,8,12,13,17,18-octaethylporphyrinate), in which the central metal ions were found to add influence on the properties of sandwich complexes as revealed by both absorption and emission spectra through tuning the ring-to-ring separation and thus ring-to-ring interaction [12–16]. To the best of our knowledge, the luminescence properties of mixed (phthalocyaninato)(porphyrinato) rare earth complexes have not yet been reported.

It is well known that to tune the performance of the sandwich compounds, a good method is to introduce effective substituents onto porphyrin or phthalocyanine ring. In this paper, we devised and synthesized a novel porphyrin ligand with four pyrenyl groups at the meso-positions H_2TPYRP (**1**), with which the mixed (phthalocyaninato)(porphyrinato) europium double- and triple-decker complexes Eu(Pc)(TPYRP) (**2**) and $Eu_2(Pc)_2$(TPYRP) (**3**) were prepared according to published procedure (Fig. 1) [17,24]. To the

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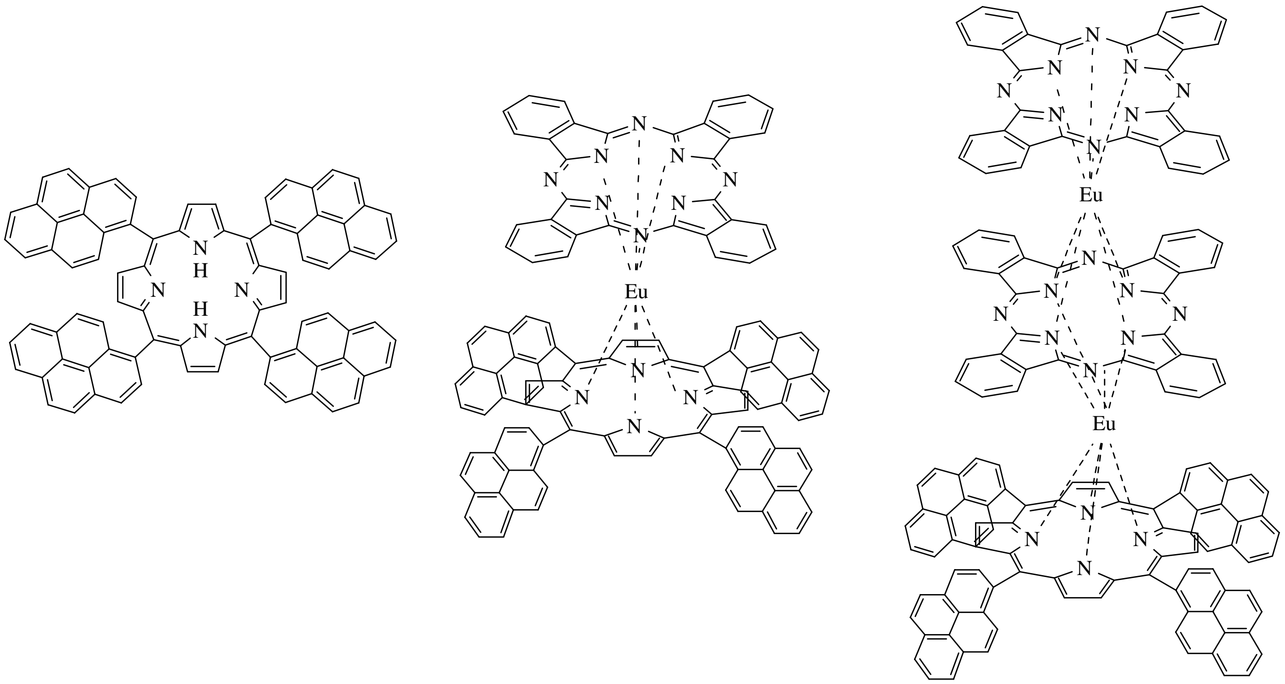

H_2TPYRP (1) **Eu(Pc)(TPYRP) (2)** **Eu(Pc)$_2$(TPYRP) (3)**

Fig. 1. Schematic molecular structures of the free porphyrin and sandwich compounds fused with pyrenyl groups.

best of our knowledge, these represent the first example of sandwich tetrapyrrole rare earth complexes attached directly with the excellent pyrenyl fluorophores. As a result, their photophysical properties were comparatively studied together with that of the monomeric metal free porphyrin H_2TPYRP (**1**).

2. Results and discussion

2.1. Synthesis

Both the double- and triple-decker complexes Eu(Pc)(TPYRP) (**2**) and $Eu_2(Pc)_2$(TPYRP) (**3**) were prepared by a raise-by-one-story procedure [17–20]. The synthesis of the former compound involves prior generation of the half-sandwich complexes Eu(TPYRP)(acac) from $Eu(acac)_3$ and H_2TPYRP (**1**), followed by treatment with excessive Li_2Pc at 200 °C in *n*-octanol. The later one was obtained by a similar method using $Eu(Pc)_2$ instead of Li_2Pc as starting material in refluxed TCB [21,22].

Both the newly prepared complexes together with the metal free porphyrin gave satisfactory elemental analysis results as given in Table 1. The sandwich nature for the double- and triple-decker complexes was further unambiguously confirmed by various spectroscopic methods. The MALDI-TOF spectra of complexes showed the molecular ion $(M)^+$ signals with correct isotopic pattern (Table 1).

2.2. Electronic absorption spectra

The electronic absorption spectra of the metal free porphyrin substituted by four pyrenyl groups at the meso-positions H_2TPYRP (**1**) and the mixed ring europium double- and triple-decker complexes **2** and **3** in the region of 300–800 nm recorded in $CHCl_3$ are shown in Fig. 2. Due to the four pyrene groups attached to the meso-position of porphyrin, H_2TPYRP (**1**) shows different spectrum from common metal free tetra(aryl)porphyrins. Compared with H_2TPP, significant red-shift takes place on both the broadened Soret (by 16 nm) and the Q (by 5–7 nm) absorption bands of H_2TPYRP (**1**). Actually, H_2TPYRP (**1**) looks like red brown instead of mauve when dissolved in organic solvent.

However, except for some more or less shift in corresponding absorption bands associated with the tetra(pyrenyl)porphyrin ligand, sandwich compounds **2** and **3** display very much similar electronic absorption spectra to other counterparts composed of tetra(aryl)porphyrin ligand, which can therefore be assigned in a similar manner (Fig. 2) [17–24]. The electronic absorption data of these compounds are organized in Table 2. In addition to the normal absorption bands assigned mainly to the Soret and Q bands of phthalocyanine and porphyrin, respectively, observation of the absorptions at 965 nm due to electronic transitions involving the semi-occupied orbital and at 1330 nm with a shoulder at 1715 nm attributed to the ring-to-ring charge transfer transition (RRCT) in the spectrum of compound **2** confirms the presence of a hole in one of the two macrocyclic ligands, actually phthalocyanine ring of this compound [20]. It must be pointed out that in line with that observed in the electronic absorption spectrum of metal free porphyrin **1**, both double- and triple-decker complexes **2** and **3** show a relatively intensive absorption band at about 300–320 nm attributed to the pyrenyl groups.

Table 1
Analytical and mass spectroscopic data for the newly prepared H_2TPYRP (**1**), Eu(Pc)(TPYRP) (**2**) and $Eu_2(Pc)_2$(TPYRP) (**3**).[a]

Compound	M^+ (*m*/*z*)[b]	Analysis (%)		
		C	H	N
H_2TPYRP·$0.25CHCl_3$ (**1**)	1111.3 (1112.4)	88.28 (88.67)	4.34 (4.09)	5.11 (4.91)
Eu(Pc)(TPYRP)·$0.75CHCl_3$ (**2**)	1773.8 (1775.4)	74.84 (75.26)	8.74 (9.02)	3.51 (3.29)
$Eu_2(Pc)_2$(TPYRP)·$0.5CHCl_3$ (**3**)	2438.3 (2438.7)	71.31 (71.40)	3.47 (3.09)	11.11 (11.21)

[a] Calculated values given in parentheses.

[b] By MALDI-TOF mass spectrometry.

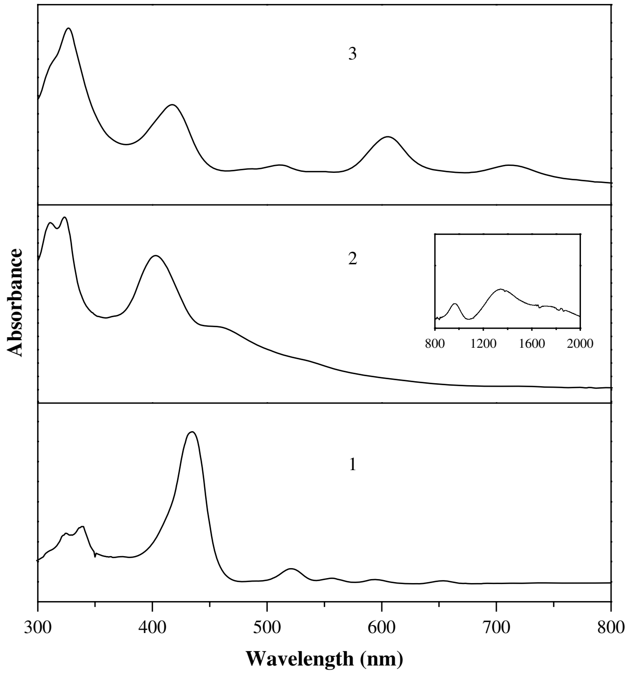

Fig. 2. The electronic absorption spectra of H_2TPYRP (**1**), Eu(Pc)(TPYRP) (**2**), and $Eu_2(Pc)_2$(TPYRP) (**3**) in $CHCl_3$. Inset is the near-IR region spectrum of Eu(Pc)(TPYRP) (**2**).

2.3. IR spectra

IR spectroscopy has been one of the most versatile techniques used to probe the extent of hole delocalization in sandwich compounds. Both the sandwich and metal free compounds showed strong bands at 1590–1740 cm^{-1} which is assigned as the benzene stretchings of the pyrene attached on porphyrin. By analogy with the IR spectra of M(Pc)(TPP) [17,24], the strong band at 1315 cm^{-1} in the IR spectrum of Eu(Pc)(TPYRP) (**2**) is assigned as the characteristic IR marker band of phthalocyanine monoanion radical. However, the marker band of porphyrin monoanion radical $TPYRP^-$ at 1270–1300 cm^{-1} was not seen for **2**. These results suggest that the electron hole in this double-decker compound is localized mainly at the phthalocyanine ring. Observation of the peak at 1330 cm^{-1} for $Eu_2(Pc)_2$(TPYRP) demonstrates the dianion nature of phthalocyanine in complex **3**.

2.4. ^1H NMR spectra

In line with the previous results of mixed (phthalocyaninato)(porphyrinato) rare earth double-decker complexes [25,26], satisfactory ^1H NMR spectrum could not be recorded for double-decker compound **2** in $CDCl_3$ due to the unpaired electron in the HOMO of this compound. Upon addition of hydrazine hydrate, which reduced the neutral double-decker into the corresponding monoanion form $[Eu^{III}(Pc)(TPYRP)]^-$ [25,26], satisfactory ^1H NMR spectrum could then be obtained. Fig. 3 shows the ^1H NMR spectra of the double-decker **2** recorded in $CDCl_3/DMSO-d_6$ (1:1) with the addition of ca. 1% hydrazine hydrate and triple-decker **3** recorded in $CDCl_3$. The data are collected in Table 3. The AA′BB′ multiplet at δ 10.52 in the spectrum of **2** is attributed to the Pc α-protons, while the signal for the correlated Pc β-protons is at δ 8.77. The TPYRP β-protons resonate as a sharp singlet at δ 6.62. As a result of restricted rotation about the C(meso)–C(ipso) bond in the TPYRP ligand, eight sets of pyrenyl proton signals at δ 5.40, 7.16, 7.66, 8.16, 8.42, 8.92, 9.56, and 11.64 were observed for the pyrenyl protons.

For compound **3**, due to the paramagnetic effect of the Eu(III) centres, the inner phthalocyanine ring protons are significantly downfield shifted, the signal appears at δ 13.15 (Pc-Hα), δ 10.95 (Pc-Hβ). The outer phthalocyanine ring protons, being influenced by only one Eu(III) centre, resonate at δ 10.25 (Pc-Hα) and δ 8.88 (Pc-Hβ). The TPYRP β-protons resonate as a sharp singlet at δ 2.76. Eight sets of pyrenyl proton signals at δ 5.0, 6.89, 7.47, 8.13, 8.53, 9.26, 10.59 and 14.52 are observed for compound **3**.

2.5. Electrochemical properties

The electrochemical behaviour of the sandwich complexes **2** and **3** was investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in CH_2Cl_2. It is worth noting that satisfactory CV and DPV curves for metal free porphyrin H_2TPYRP (**1**) were not obtained due to the poor reversibility of redox process. The results for **2** and **3** are summarized in Table 4. Fig. 4 shows the cyclic voltammogram of compound **3**. The separation between the reduction and oxidation peak potentials for all the processes lies between 65 and 90 mV, showing their reversible nature. All these processes can be attributed to successive removal from or addition of one electron to the ligand-based orbitals. Compound **2** displayed a one-electron oxidation labeled as Oxd. 1 and up to three one-electron reductions labeled as Red. 1–Red. 3 within the electrochemical window of CH_2Cl_2. The potential difference between $E_{1/2}$(Oxd. 1) and $E_{1/2}$(Red. 1) ($\Delta E^{\circ}{}_{1/2}$) for the double-decker **2** (0.52 eV) corresponds well with that for Eu(Pc)(TPP) (0.45 eV) [27] and Eu(Pc)(TClPP) (0.51 eV) [20]. It seems that pyrenyl groups attached onto the meso-position of the porphyrin does not affect the energy of semi-occupied orbital. For the triple-decker **3**, the first oxidation occurs at 0.51 eV, which is higher than that for $Eu_2(Pc)_2$(TPP) and $Eu_2(Pc)_2$(TClPP) at 0.30 eV [24] and 0.34 eV [24], respectively. However, the gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) as revealed by the difference between $E_{1/2}$(Oxd. 1) and $E_{1/2}$(Red. 1) for compound **3** remains similar to their analogues $Eu_2(Pc)_2$(TPP) and $Eu_2(Pc)_2$(TClPP), Table 4, due to the increased LUMO of this compound as revealed by $E_{1/2}$(Red. 1) of −0.62 eV.

2.6. Fluorescence

The fluorescence spectra of compound **1** when porphyrin was selectively excited at 450 nm are shown in Fig. 5. An intense emission band at about 650 nm was observed with a fluorescence quantum yield of 18% and a fluorescence lifetime of 9.0 ns. Both the emission wavelength and the fluorescence lifetime suggest the porphyrin origin of this emission band [28]. The large steric hindrance due to the introduction of four bulky pyrenyl groups to porphyrin in **1** makes the molecule much more rigid and reduces the non-radioactive decay of the excited states efficiently. Therefore the fluorescence quantum yield of compound **1** is larger than that of metal free tetra(phenyl)porphyrin H_2TTP (11%) [28].

Table 2
Electronic absorption data for the H_2TPYRP (**1**), Eu(Pc)(TPYRP) (**2**), and $Eu_2(Pc)_2$(TPYRP) (**3**) in $CHCl_3$.

Compound	λ_{max}/nm (log ε)								
1	266 (5.14)	276 (5.30)	325 (5.08)	339 (5.14)	435 (5.57)	521 (4.51)	557 (3.92)	594 (3.73)	654 (3.35)
2	311 (5.08)	323 (5.11)	403 (4.48)	455 (sh)	965 (3.60)	1330 (3.79)	1715 (2.55)		
3	327 (5.06)	417 (5.05)	511 (4.45)	546 (4.32)	605 (4.48)	711 (4.41)			

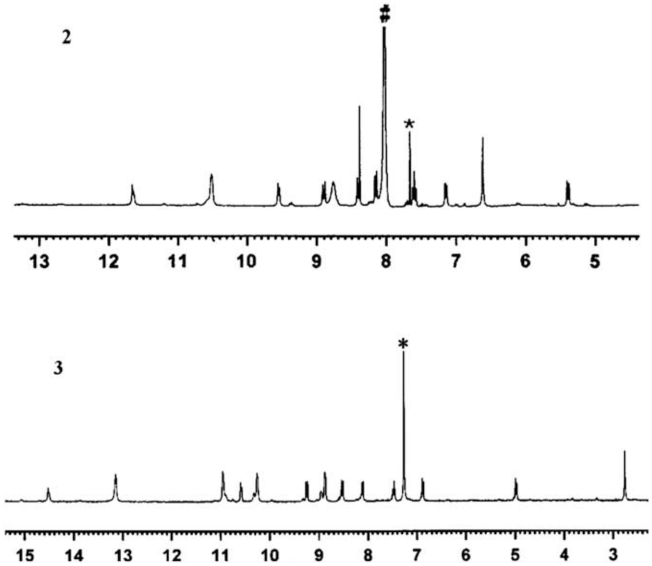

Fig. 3. The ^1H NMR spectrum of **3** in $CDCl_3$ and ^1H NMR spectrum of **2** in $CDCl_3$/DMSO-d_6 (1:1) with the addition of ca. 1% (by volume) hydrazine hydrate.

When the pyrenyl units in compound **1** were selectively excited at 270 nm, the emission spectrum of compound **1** is identical to that of porphyrin (Fig. 6). The fluorescence of pyrene, which was normally observed at 380 nm [29], was completely quenched. The excitation spectrum of compound **1** shows obviously contributions of the pyrenyl absorption to the fluorescence of porphyrin, indicating the presence of singlet–singlet energy transfer from pyrenyl groups to porphyrin ring. The energy transfer efficiency (Φ_{ent}) estimated from the fluorescence quenching efficiency is 100% probably due to the very short distance between pyrenyl groups and porphyrin ring and also due to the good overlap between the emission of pyrenyl groups and the absorption of porphyrin.

When phthalocyanine was appended to porphyrin by metal coordination to yield Eu(Pc)(TPYRP) (**2**), the fluorescence of porphyrin was quenched dramatically. This fluorescence quenching is also observed for other similar sandwich tetrapyrrole double-decker compounds such as Eu(Pc)(TPP) and Eu(Pc)(TClPP) due to the ultra-fast electron transfer between the face-to-face stacked porphyrin and phthalocyanine, which is a prevalent property for face-to-face stacked aromatic dimeric compounds [30]. When the pyrenyl units in compound **2** were selectively excited at 270 nm, the fluorescence of pyrene is quenched completely as that in compound **1**. Because of the very fast fluorescence quenching, it is hard to measure the dynamics and detect the product of this fluorescence quenching. As a result, the inbeing of the fluorescence quenching in compound **2** cannot be determined experimentally at this stage. However, theoretical calculation on the free energy change of electron transfer following Rehm–Weller equation indicates that the electron transfer from pyrenyl groups to phthalocyanine ring is a thermodynamically unfavorable process. The poor overlapping between the emission of pyrenyl and the absorption of phthalocyanine excludes the energy transfer from pyrenyl groups to phthalocyanine ring. Accordingly, the most possible procedure for the fluorescence quenching in compound **2** is an efficient and quick energy transfer from pyrenyl groups to porphyrin followed by electron transfer from porphyrin to phthalocyanine. Similar fluorescence quenching was also observed for compound **3** and analogical photophysical process is expected.

Table 4
Electrochemical data for the double- and triple-decker complexes Eu(Pc)(TPYRP) (**2**) and $Eu_2(Pc)_2$(TPYRP) (**3**).[a]

Compound	O_2	O_1	R_1	R_2	R_3	$\Delta E^o{}_{1/2}$	$\Delta E^{o'}{}_{1/2}$
2		+0.71	+0.19	−0.85	−1.29	0.52	1.04
3	+0.97	+0.51	−0.62	−1.01		1.13	0.39

[a] Recorded with $[Bu_4N][ClO_4]$ as electrolyte in CH_2Cl_2 (0.1 M) at ambient temperature. Potentials were obtained by cyclic voltammetry with a scan rate of 20 mV s^{-1}.

3. Experimental section

3.1. General remarks

1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) and phthalonitrile were purchased from Aldrich. *n*-Pentanol and anhydrous 1,2,4-trichlorobenzene (TCB) were freshly distilled from Na and CaH_2, respectively, under nitrogen. Column chromatography was carried out on silica gel (Merck, Kieselgel 60, 200–300 mesh) with the indicated eluents. All other reagents and solvents were used as-received. The compounds $Eu(acac)_3 \cdot H_2O$ [31] and pyrene-3-aldehyde [32,33] were prepared according to the published procedures.

^1H NMR spectra were recorded on a Bruker DPX 300 spectrometer (300 MHz) in $CDCl_3$ or $CDCl_3$/DMSO-d_6 (1:1) with the addition of ca. 1% hydrazine hydrate. Spectra were referenced internally by using the residual solvent resonance ($\delta = 2.49$ for DMSO-d_6) relative to $SiMe_4$. Electronic absorption spectra were recorded on a Hitachi U-4100 spectrophotometer. Fluorescence spectra and the fluorescence lifetime were measured on a Multi-frequency Phase and Modulation Fluorometer with the excitation at 410 nm. The fluorescence lifetimes were measured with multi-frequency phase modulation method with a scattering sample as standard [34,35]. The fluorescence quantum yields are calculated with compound H_2TPP as standard [28]. MALDI-TOF mass spectra were taken on a Bruker BIFLEX III ultra-high resolution 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-50 W voltammetric analyzer. The cell comprise 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 $[Bu_4N][ClO_4]$ in DMF containing 0.5 mmol dm^{-3} of sample was

Table 3
^1H NMR data (δ) for the reduced form of the double-decker compound Eu(Pc) (TPYRP) (**2**) and the triple-decker compound $Eu_2(Pc)_2$(TPYRP) (**3**).

Compound	Pc-H_α	Pc-H_β	TPYRP H_β	Pyrenyl-H
2[a]	10.52 (br s, 8H)	8.77 (br s, 8H)	6.62 (s, 8H)	5.40 (d, 4H), 7.16 (d, 4H), 7.66 (t, 4H), 8.16 (d, 4H), 8.42 (d, 8H), 8.92 (d, 4H), 9.56 (d, 4H), 11.64 (d, 4H)
3[b]	inner 13.15 (br s, 8H); outer 10.25 (br s, 8H)	inner 10.95 (br s, 8H); outer 8.88 (br s, 8H)	2.76 (s, 8H)	5.0 (d, 4H), 6.89 (d, 4H), 7.47 (t, 4H), 8.13 (d, 8H), 8.53 (d, 4H), 9.26 (d, 4H), 10.59 (d, 4H), 14.52 (d, 4H)

[a] Recorded in DMSO-d_6/$CDCl_3$ (1:1) with the addition of ca. 10% (by volume) hydrazine hydrate on a 300 MHz spectrometer.

[b] Recorded in $CDCl_3$ on a 300 MHz spectrometer.

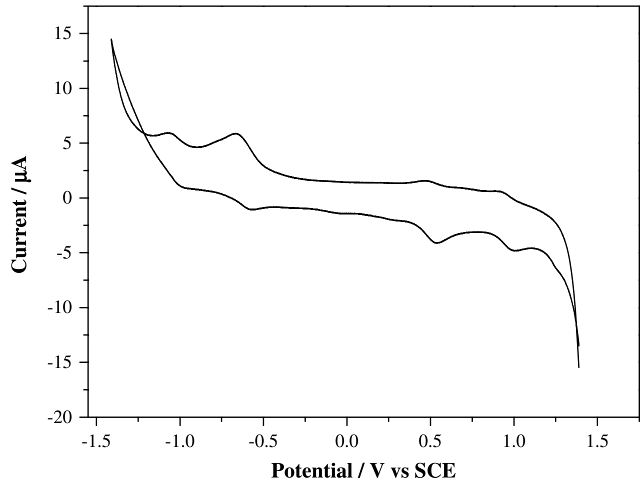

Fig. 4. Cyclic voltammogram of $Eu_2(Pc)_2(TPYRP)$ (**3**) in CH_2Cl_2 containing 0.1 M $[Bu_4N][ClO_4]$ at a scan rate of 20 mV s^{-1}.

purged with nitrogen for 10 min, then the voltammograms were recorded at ambient temperature. The scan rate was 20 and 10 mV s^{-1} for CV and DPV, respectively.

3.2. Preparation of H_2TPYRP (**1**)

H_2TPYRP (**1**) was synthesized by the Adler–Longo method [36]. A mixture of pyrene-3-aldehyde (1.15 g, 5 mmol) and pyrrole (0.34 g, 5 mmol) in propyl acid (60 mL) was refluxed for 2 h under a slow stream of nitrogen, CH_3OH (100 mL) was added into the reaction solution after being cooled to room temperature. The precipitate was filtered and washed with CH_3OH, then subjected to chromatography on a silica gel column with $CHCl_3$ and petroleum ether (7:3) as eluent. After removing the solvent in vacuo, the residue was re-chromatographed under similar condition followed by recrystallisation from $CHCl_3/CH_3OH$ to give the target compound H_2TPYRP (**1**) (1.38 g, 25%). MS: $(M+H)^+$ 1111.3 [calcd. for $C_{84}H_{46}N_4$ (M^+) 1112.4].

3.3. Preparation of Eu(Pc)(TPYRP) (**2**)

A mixture of $Eu(acac)_3 \cdot H_2O$ (95 mg, 0.2 mmol) and H_2TPYRP (**1**) (56 mg, 0.05 mmol) in *n*-octanol (5 mL) was stirred at 200 °C for 4 h under a slow stream of nitrogen. The resulting darkish-yellow solution was cooled to room temperature, then mixed with Li_2Pc (27 mg, 0.05 mmol), the mixture was then heated at ca. 160 °C for a further 12 h under nitrogen. The residue left after removing the volatiles in vacuo was chromatographed on a silica gel column with $CHCl_3$ and petroleum ether as eluent. A small amount of unreacted H_2TPYRP was eluted first with $CHCl_3$/petroleum ether (7:3), then $CHCl_3$ was used to develop the second fraction containing yellowish-brown Eu(Pc)(TPYRP) (**2**). This target compound was further purified by repeated chromatography followed by recrystallisation from $CHCl_3$ and CH_3OH, giving a brown powder (15 mg, 16%). MS: $(M+H)^+$ 1775.4 [calcd. for $C_{116}H_{60}N_{12}Eu$ (M^+) 1773.8].

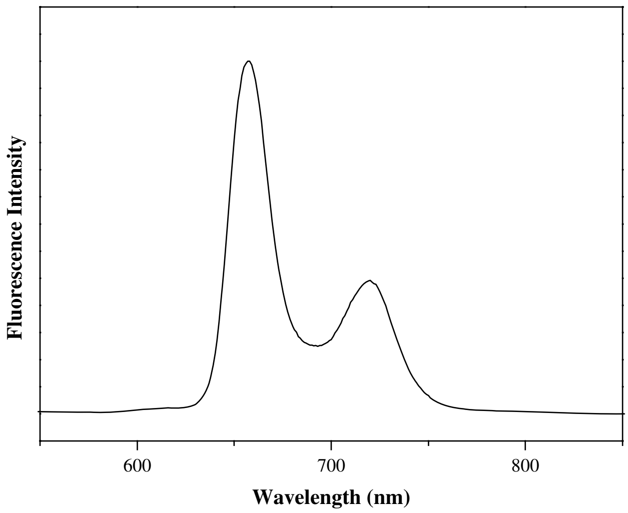

Fig. 5. The normalized fluorescence spectrum of compound H_2TPYRP (**1**) in chloroform with excitation at 450 nm.

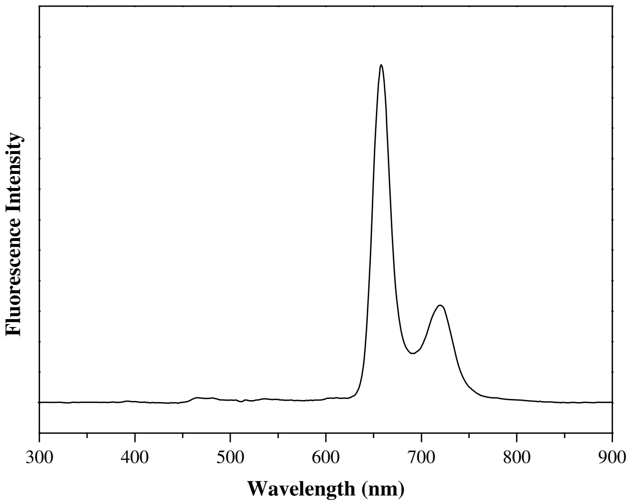

Fig. 6. The normalized fluorescence spectrum of compound H_2TPYRP (**1**) in chloroform with excitation at 270 nm.

3.4. Preparation of $Eu_2(Pc)_2$(TPYRP) (**3**)

A mixture of $Eu(acac)_3 \cdot H_2O$ (95 mg, ca. 0.2 mmol) and H_2TPYRP (56 mg, 0.05 mmol) in TCB (5 mL) was stirred at 210 °C for 4 h under a slow stream of nitrogen. After being cooled to room temperature, $Eu(Pc)_2$ (60 mg, 0.05 mmol) was added and the mixture was then refluxed for a further 3 h under nitrogen. The residue left after removing the volatiles in vacuo was chromatographed on a silica gel column with $CHCl_3$ and petroleum ether as eluent. Unreacted H_2TPYRP was eluted with $CHCl_3$/petroleum ether (7:3), $CHCl_3$ was then used to develop an olive-green fraction containing the target triple-decker **3**. Repeated chromatography followed by recrystallisation from $CHCl_3$ and CH_3OH gave pure **3** as a darkish-blue powder (22 mg, 18%). MS: $(M+H)^+$ 2438.7 [calcd. for $C_{148}H_{76}N_{20}Eu_2$ (M^+) 2438.3].

4. Conclusions

In summary, we have prepared two new sandwich mixed tetrapyrrole europium complexes using a newly designed and synthesized porphyrin bearing four pyrenyl groups at the meso-positions. In addition to common elemental analysis and spectroscopic characterizations, the photophysical properties of these sandwich complexes were comparatively studied in comparison with the metal free porphyrin ligand. The fluorescence quenching observed in compound **2** is tentatively attributed to an efficient and quick energy transfer from pyrenyl groups to porphyrin followed by electron transfer from porphyrin to phthalocyanine.

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