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ARTICLE TYPE

A new class of rare earth tetrapyrrole sandwich complexes containing corrole and phthalocyanine macrocycles: synthesis, physicochemical characterization and X-ray analysis

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The first europium triple-decker tetrapyrrole with mixed corrole and phthalocyanine macrocycles was synthesized and characterized by spectroscopic and electrochemical methods. The molecular structure was characterized by single-crystal X-ray diffraction and showed the corrole to be in the middle of the sandwich with phthalocyanine macrocycles on each extreme.

Rare earth tetrapyrrole double- and triple-decker derivatives have received increasing attention in recent years due to their unique spectroscopic, electronic and redox properties that cannot be realized by their mono-metallic macrocycle counterparts.¹⁻⁴ All tetrapyrrole sandwich complexes characterized to date have contained only porphyrin or phthalocyanine macrocycles, both of which are in a -2 valence state. Another well known class of tetrapyrrole macrocycles are the trinegatively charged corroles⁵⁻¹¹ (Chart 1) which have also received a great deal of attention because of their possible applications in the fields of catalysis, sensors, solar cells and photodynamic therapy.⁵⁻⁹ However, there have been no reports of double- or triple-decker tetrapyrrole complexes containing a corrole macrocycle. In addition there is only one report in the literature about a mono-macrocylic lanthanide corrole.¹²

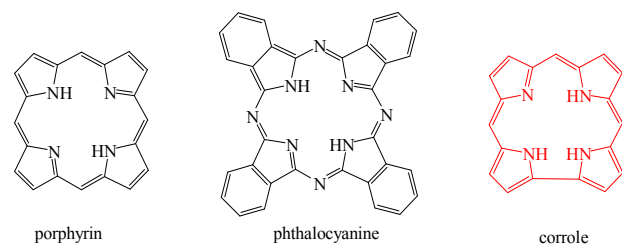
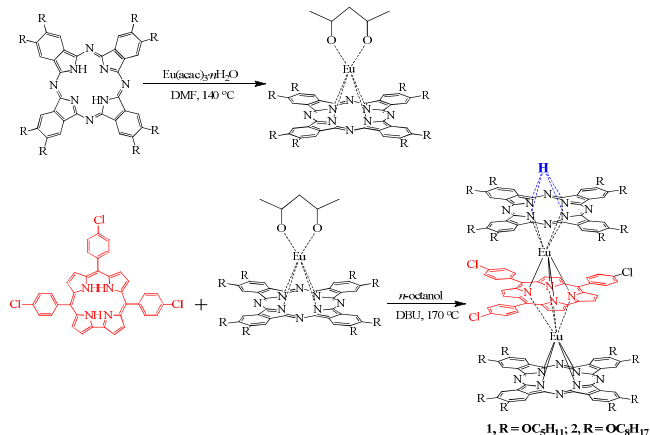


Chart 1. Schematic structures of building blocks for sandwich rare earth complexes.

One major difference between corroles, porphyrins and phthalocyanines is that corroles have a somewhat more condensed N4 coordination core and a much more electron-rich π system; they also act as trianionic, rather than dianionic ligands and are of lower symmetry.^{10,11} These structural differences are associated with different chemical and physical properties of the macrocycles, and it is of interest to know how the properties of a

tetrapyrrole sandwich complex might change by the presence of one or more corrole macrocycles in the structure.

This is addressed in the present manuscript where we describe the first synthesis and characterization of a new class of triple-decker rare earth compounds which contains one corrole and two phthalocyanine macrocycles. The reported sandwich compounds are represented as $\text{HEu}_2[\text{Pc}(\text{R})_8]_2[\text{Cor}(\text{CIPh})_3]$, where $\text{R} = \text{OC}_5\text{H}_{11}$ (**1**) or OC_8H_{17} (**2**), Pc = the dianion of phthalocyanine and Cor = the trianion of corrole. The molecular structure of $\text{HEu}_2[\text{Pc}(\text{OC}_8\text{H}_{17})_8]_2[\text{Cor}(\text{CIPh})_3]$ was characterized by single-crystal X-ray diffraction and is the first example of a tetrapyrrole sandwich complex containing a corrole macrocycle.



Scheme 1. Synthesis of sandwich complexes **1** and **2**.

A detailed synthetic procedure for the synthesis of **1** and **2** is given in Electronic supplementary information (ESI) and involves prior generation of the “half-sandwich” phthalocyanine complex $\text{Eu}[\text{Pc}(\text{R})_8](\text{acac})$ from $\text{Eu}(\text{acac})_3 \cdot n\text{H}_2\text{O}$ ¹³ and $\text{H}_2[\text{Pc}(\text{R})_8]$,¹⁴ followed by treatment with the free-base corrole $\text{H}_3[\text{Cor}(\text{CIPh})_3]$ ¹⁵ in *n*-octanol containing DBU as shown in the Scheme 1. The most likely role of DBU is to generate the corrole anion,^{7,16,17} which then reacts with the europium monophthalocyanine to give the desired triple-decker products.

Repeated chromatography followed by recrystallization from CHCl_3 and CH_3OH gave pure compounds **1** (16% yield) and **2** (15% yield) as grey-green solids. MALDI-TOF MS showed a

strong signal at $m/z = 3333.08$ and 4006.09 for compounds **1** and **2**, respectively (Figure S1, ESI†), these values corresponding exactly to the molecular weights of a triple-decker complex containing two europium ions, one corrole and two phthalocyanine macrocycles having the formulas given above. Elemental analysis calcd (%) for **1** ($\frac{1}{2}\text{CHCl}_3$): C 64.22, H 6.34, N 8.25; found: C 64.18, H 6.52, N 8.04, and for **2**: C, 68.62; H, 7.77; N, 6.99. Found (%): C, 68.31; H, 8.10; N, 6.75.

Single crystals of **2** suitable for X-ray diffraction analysis were obtained by diffusion of methanol into a solution of the complex in chloroform. Compound **2** crystallizes in the triclinic system with a $P\bar{1}$ space group. The sandwich triple-decker structure is clearly revealed by the single crystal X-ray diffraction analysis. The molecular structure of **2** is illustrated in Figure 1; the full crystallographic data can be obtained from the Cambridge Crystallographic Data Centre and is summarized in Tables S1 and S2 (ESI†).

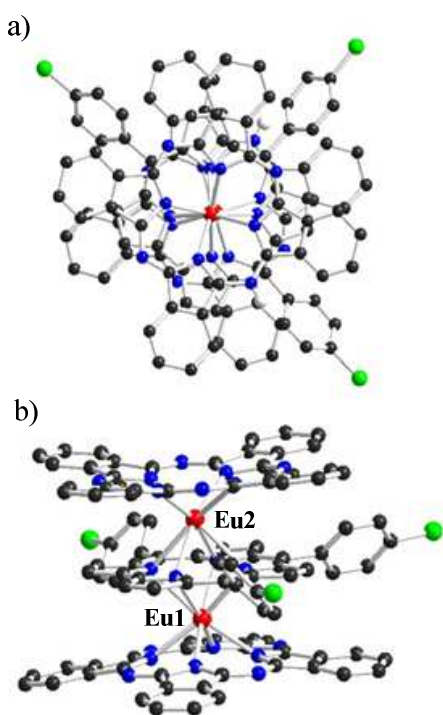


Figure 1. Molecular structure of $\text{HEu}_2[\text{Pc}(\text{OC}_8\text{H}_{17})_8]_2[\text{Cor}(\text{CIPh})_3]$ **2** in two perspective views: a) top view and b) side view. The side chains and hydrogen atoms are omitted for clarity [Eu(III) red, C black, N blue, and Cl green].

There are two crystallographically independent europium ions in compound **2**. Each europium center is octa-coordinated by the isoindole and pyrrole nitrogen atoms of an outer $\text{Pc}(\text{OC}_8\text{H}_{17})_8$ ring and the central $\text{Cor}(\text{CIPh})_3$ macrocycle, confirming the arrangement of ligands as $[\text{Pc}(\text{OC}_8\text{H}_{17})_8]\text{Eu}[\text{Cor}(\text{CIPh})_3]\text{Eu}[\text{Pc}(\text{OC}_8\text{H}_{17})_8]$. The Eu1 atom adopts a slightly distorted square antiprism geometry, while the Eu2 atom exhibits a slightly distorted square prism coordination conformation. Both europium centers lie closer to the outer $[\text{Pc}(\text{OC}_8\text{H}_{17})_8]^{2-}$ ring than to the plane of the central $[\text{Cor}(\text{CIPh})_3]^{3-}$ ligand; the distances of the two Eu ions from the

corresponding N4 planes of the phthalocyanine macrocycles are significantly shorter than the distance to the planes of the central corrole ligand, these values being 1.368 vs. 1.781 Å for Eu1 and 1.350 vs. 1.793 Å for Eu2. Similar results have been reported for other structurally characterized lanthanide homo- and heteroleptic tetrapyrrole triple-decker complexes¹⁸⁻²¹ where the distance between each metal ion and the outer macrocycle is significantly shorter than that between the same metal and the plane of the central macrocycle. This is true independent of the type of macrocycle, porphyrin or phthalocyanine.

The Eu1-Eu2 separation is 3.5743 Å in compound **2**. The inner corrole ring is almost planar with the average dihedral angle of the individual pyrrole ring with respect to the corresponding N4 mean plane (ϕ 1.7°), while the two $\text{Pc}(\text{OC}_8\text{H}_{17})_8$ rings are slightly domed toward the metal centers, with the average dihedral angle of the individual isoindole ring being 8.6° with respect to the N4 mean plane. The average Eu1-N $[\text{Pc}(\text{OC}_8\text{H}_{17})_8]$ bond length (2.402 Å) is significantly shorter than the average Eu1-N $[\text{Cor}(\text{CIPh})_3]$ distance (2.583 Å). The Eu2-N $[\text{Pc}(\text{OC}_8\text{H}_{17})_8]$ bond length (2.390 Å) is also shorter than Eu2-N $[\text{Cor}(\text{CIPh})_3]$ (2.590 Å). The adjacent triple-decker molecules are arranged in a staggered packing mode along the direction [1 0 1], Figure S2 (ESI†).

The structures of **1** and **2** in solution were confirmed by $^1\text{H-NMR}$ in CDCl_3 . Figure S3a (ESI†) shows the $^1\text{H-NMR}$ spectrum of $\text{HEu}_2[\text{Pc}(\text{OC}_5\text{H}_{11})_8]_2[\text{Cor}(\text{CIPh})_3]$ **1** in CDCl_3 . On the basis of the integration, the two broad bands at δ 3.77-3.42 are assigned to the $\text{C}_6\text{H}_4\text{Cl}$ ring protons of the corrole, while protons in the OC_5H_{11} groups of the two phthalocyanine macrocycles exhibit two single resonances at δ 5.42 and 4.95 (OCH_2), three multiplets at δ 2.58 (CH_2), 2.13 (CH_2), 1.92 (CH_2) and one triplet at 1.34 (CH_3). Unlike heteroleptic (phthalocyaninato)(porphyrinato) europium triple-decker complexes,²²⁻²⁴ signals are not observed for the α protons on the corrole or phthalocyanine macrocycles. It is likely that the triple-decker compounds are slightly paramagnetic with the α protons close to the metal centers.²⁵ As seen in Figure S3a (ESI†), compound **1** has a single resonance at δ -1.26 in the high field region of the spectrum, which is assigned to an N-H proton,²⁶ thus providing evidence in support of a proton associated with one of the two phthalocyanine macrocycles (see the Scheme 1). The presence of a single extra proton in **1** is also proven by UV-visible monitored titrations of **1** with TBAOH in DMF. Examples of the spectral changes which show the loss of one proton from this compound during the titration are illustrated in Figure S4 (ESI†).

A $^1\text{H-}^1\text{H}$ COSY experiment in CDCl_3 was also run for compound **1** (Figure S3b, ESI†). Only connectivities between protons of the $-\text{CH}_3$ and $-\text{CH}_2$ groups are observed. Compound **2** exhibits a similar NMR spectrum as shown in Figure S5 (ESI†).

Electronic absorption spectra of the triple-decker complexes **1** and **2** and their precursors were recorded in CHCl_3 . Examples of the spectra are shown in Figure S6 (ESI†) and the data are summarized in Table S3 (ESI†). The free base corrole $\text{H}_3[(\text{CIPh})_3\text{Cor}]$ reactant is characterized by a Soret band at 416 nm and three Q bands at 572, 616 and 650 nm while the two “half-sandwich” $\text{Eu}[\text{Pc}(\text{R})_8](\text{acac})$ complexes have an intense Q band at 680/681 nm with a weak absorbance at 613/614 nm. In contrast, both sandwich products are characterized by a relatively

strong Soret band at 351 nm along with a weak satellite at 420/421 nm in addition to broad Q-bands at 537 nm and 681 nm. Neither **1** nor **2** exhibits a near-infrared absorption band which is seen for most neutral tetrapyrrole double-decker complexes with rare earth metals and is diagnostic of a π -cation radical.²⁷⁻³⁰ Thus, the UV-vis spectrum of **1** and **2** differs not only from spectra of the starting materials (see Figure S6, ESI†) but also from UV-visible spectra of previously characterized double- and triple-decker phthalocyanine complexes, all of which exhibit weak absorptions in the Soret region and intense Q bands at 644-686 nm.²⁷⁻³¹

The electrochemistry of **1** and **2** were examined in CH₂Cl₂ containing 0.1 M TBAP. Examples of cyclic voltammograms for the two complexes are shown in Figure 2 and the measured half-wave potentials are listed in Table S4 (ESI†).

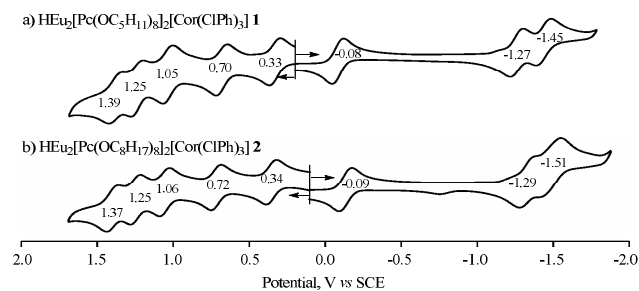


Figure 2. Cyclic voltammograms of a) **1** and b) **2** in CH₂Cl₂ containing 0.1 M TBAP.

Compounds **1** and **2** exhibit five reversible, one-electron oxidations and three reversible, one-electron reductions, all of which can be attributed to ligand-based redox processes. The half-wave potentials **1** and **2** for oxidation and reduction are given in Table S4 (ESI†). It should be noted that the $\Delta E_{1/2}$ values between the first oxidation and the first reduction of the newly synthesized triple-decker complexes spans a relatively narrow range of potentials, 0.41-0.43 V. The separation in $E_{1/2}$ values was also calculated between the first and second reductions of **1** and **2** and ranged 1.19 to 1.23 V.

In conclusion, the first (phthalocyaninato)(corrolato) europium triple-decker species was synthesized and characterized in both solution and the solid state. The molecular structure of this novel triple-decker tetrapyrrole was unambiguously revealed by single crystal X-ray analysis, which showed the corrole macrocycle to be at the central position of the sandwich. The newly synthesized compounds are not only extremely stable in air, but they are also extremely stable under an N₂ atmosphere after the addition of three electrons or the abstraction of five electrons to give $\{\text{HEu}_2[\text{Pc}(\text{R})_8]_2[\text{Cor}(\text{CIPh})_3]\}^n$, where n varies from -3 to +5. To our knowledge, compounds **1** and **2** are the only triple-decker tetrapyrrole complexes to show eight reversible redox processes with no evidence for decomposition or reaction with the solvent over the range of nine different oxidation states on the cyclic voltammetry time scale.

It is envisaged that other highly stable heteroleptic sandwich corrole compounds can also be synthesized by the above described method and further investigations in this direction are currently under way.

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- † Electronic supplementary information (ESI) available: Experimental details, MALDI-TOF mass spectra, ¹H NMR and ¹H-¹H COSY spectra in CDCl₃, Electronic absorption data and spectra, Half-wave potentials. CCDC 1021984. See DOI: 10.1039/b000000x/
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