# **Electronic supplementary information**

## A new class of sandwich rare earth tetrapyrrole complexes

### containing corrole and phthalocyanine macrocycles: synthesis,

# physicochemical characterization and X-ray analysis

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#### **1. Experimental Section**

#### **1.1 Materials and Instrumentation**

*n*-octanol was distilled from sodium under reduced pressure prior to use. All other reagents and solvents were purchased from Sinopharm Chemical Reagent Co. or Aldrich Chemical Co. and used as received. Tetra-*n*-butylammonium perchlorate (TBAP) was purchased from Sigma Chemical or Fluka Chemika Co., recrystallized from ethyl alcohol, and dried under vacuum at 40 °C for at least one week prior to use.

<sup>1</sup>HNMR spectra were recorded in a CDCl<sub>3</sub> solution at 400 MHz using a Bruker Advance 400 spectrometer at 25 °C. Chemical shifts (ppm) were determined with TMS as the internal reference. MALDI-TOF mass spectra were carried out on a Bruker BIFLEX III ultrahigh resolution Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer with  $\alpha$ -cyano-4-hydroxycinnamic acid as matrix. Cyclic voltammetry was carried out at 298 K using a CHI-730C Electrochemical Workstation. A homemade three-electrode cell was used for cyclic voltammetric measurements and consisted of a glassy carbon working electrode, a platinum counter electrode and a homemade saturated calomel reference electrode (SCE). The SCE was separated from the bulk of the solution by a fritted glass bridge of low porosity which contained the solvent/supporting electrolyte mixture. All potentials are referenced to the SCE. High purity N<sub>2</sub> was used to deoxygenate the solution and a stream of nitrogen gas was kept over the solution during each electrochemical experiment.

### 1.2 Titration with base

A series of TBAOH/DMF mixed solvents containing different concentrations of TBAOH was prepared and used as the base-titration reagent. In order to study the *in situ* spectral changes of **1** during the tatration, micro-liter quantities of the above standard solutions were added gradually to a 5.5 mL DMF solution of the triple-

decker in a home-made 1.0 cm cell. After each addition of base, the solution was thoroughly mixed and the spectrum recorded. The changes in spectra were analyzed as a function of the concentration of added base and the Hill equation<sup>1-3</sup> was used to calculate the room temperature equilibrium constant, logK, as described in the literature.

### **1.3 X-ray Crystallography**

Crystal data and details of data collection and structure refinement for 2 are given in Table S3. Data was collected on a Rigaku Saturn 724+ CCD X-ray diffractometer by using monochromated Mo Ka radiation ( $\lambda = 0.71070$  Å) at 120 K. Final unit cell parameters were derived by global refinements and reflections obtained from integration of all the frame data. The collected frames were integrated by using the preliminary cell-orientationmatrix. CrysAlisProAgilent Technologies software was used for collecting frames of data, indexing reflections, and determination of lattice constants; CrysAlisPro Agilent Technologies for integration of intensity of reflections and scaling, SCALE3 ABSPACK for absorption correction, The structures were solved by the direct method (SHELXS-97) and refined by full-matrix leastsquares (SHELXL-97) on  $F^{2,4}$  Anisotropic thermal parameters were used for the nonhydrogen atoms and isotropic parameters for the hydrogen atoms. Hydrogen atoms were added geometrically and refined using ariding model. The 'squeeze' command was used to deal with the disorder of solvent and molecule moiety. CCDC 1021984 for 2, containing the supplementary crystallographic data for this paper can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

1.4 Synthesis of HEu<sub>2</sub>[Pc(R)<sub>8</sub>]<sub>2</sub>[Cor(ClPh)<sub>3</sub>] (1, R=OC<sub>5</sub>H<sub>11</sub>; 2, R=OC<sub>8</sub>H<sub>17</sub>)

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A mixture of Eu(acac)<sub>3</sub>·*n*H<sub>2</sub>O (47 mg, 0.1 mmol), and H<sub>2</sub>[Pc(R)<sub>8</sub>] (where R =  $OC_5H_{11}$  or  $OC_8H_{17}$ ) (ca. 120 mg, 0.1 mmol) in DMF (3 mL) was stirred at 140°C for 1 h under a slow stream of nitrogen, yielding the "half-sandwich" compound Eu[Pc(R)<sub>8</sub>](acac) (where R =  $OC_5H_{11}$  or  $OC_8H_{17}$ ). The resulting blue solution was cooled to room temperature, followed by replacing DMF with *n*-octanol and then being treated with the free-base corrole H<sub>3</sub>[Cor(ClPh)<sub>3</sub>] (63 mg, 0.1 mmol) and DBU (20 mg, 0.13 mmol) at 170°C for another 2 hours under nitrogen. The volatiles were removed under reduced pressure and the residue was chromatographed with CHCl<sub>3</sub> as eluent. A small amount of free-base H<sub>3</sub>[Cor(ClPh)<sub>3</sub>] and the homoleptic double-decker europium phthalocyanine complex Eu[Pc(R)<sub>8</sub>]<sub>2</sub> was collected as the first and second fractions, respectively, and then the target mixed ring triple-decker product as the third fraction. Repeated chromatography followed by recrystallization from CHCl<sub>3</sub> and CH<sub>3</sub>OH gave pure compounds HEu<sub>2</sub>[Pc(OC<sub>5</sub>H<sub>11</sub>)<sub>8</sub>]<sub>2</sub>[Cor(ClPh)<sub>3</sub>] **1** and HEu<sub>2</sub>[Pc(OC<sub>8</sub>H<sub>17</sub>)<sub>8</sub>]<sub>2</sub>[Cor(ClPh)<sub>3</sub>] **2** as grey-green solids.

Data for compound **1** is given in the text. For compound **2**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 5.43 (d, 16 H, OCH<sub>2</sub>), 4.93 (d, 16 H, OCH<sub>2</sub>), 3.74 (b, 12H, C<sub>6</sub>H<sub>4</sub>Cl), 2.57 (s, 32 H, CH<sub>2</sub>), 2.15 (m, 32 H, CH<sub>2</sub>), 1.85 (m, 32 H, CH<sub>2</sub>), 1.73 (m, 32 H, CH<sub>2</sub>), 1.60 (m, 64 H, CH<sub>2</sub>), 1.12 (t, 48 H, CH<sub>3</sub>).



Figure S1. MALDI-TOF mass spectra of a)  $HEu_2[Pc(OC_5H_{11})_8]_2[Cor(ClPh)_3]$  1 and b)  $HEu_2[Pc(OC_8H_{17})_8]_2[Cor(ClPh)_3]$  2.



Figure S2. The packing mode of complex 2 along the direction [1 0 1].



**Figure S3**. <sup>1</sup>H NMR and <sup>1</sup>H-<sup>1</sup>H COSY spectra of  $HEu_2[Pc(OC_5H_{11})_8]_2[Cor(ClPh)_3]$  **1** in CDCl<sub>3</sub>. The asterisk (\*) indicates signals for residual solvent.



**Figure S4**. UV-visible spectral changes of  $HEu_2[Pc(OC_5H_{11})_8]_2[Cor(ClPh)_3]$  **1** during titration with TBAOH in DMF. The insert shows the Hill plot used for calculation of logK.



**Figure S5**. <sup>1</sup>H NMR and <sup>1</sup>H-<sup>1</sup>H COSY spectra of  $HEu_2[Pc(OC_8H_{17})_8]_2[Cor(ClPh)_3]$  **2** in CDCl<sub>3</sub>. The asterisk (\*) indicates signals for residual solvent.



Figure S6. Electronic absorption spectra of 1, 2 and their precursors in CHCl<sub>3</sub>.

complex	$HEu_{2}[Pc(OC_{8}H_{17})_{8}]_{2}[Cor(ClPh)_{3}]$ 2
Formula	C229H309Cl3Eu2N20O16
F.W.	4008.32
system	triclinic
space group	<i>P</i> -1
a	19.854(4)
b	24.158(5)
С	25.212(5)
α	99.59(3)
β	106.63(3)
γ	106.33(3)
Ζ	2
volume	10710(4)
absorption coefficient mm <sup>-1</sup>	0.683
$\theta$ range (deg)	3 to 26
F000	12648
$R_1  [I \!\!>\! 2  heta]^{\mathrm{a}}$	0.1208
$R_2[I \!\!>\! 2 heta]^{\mathrm{b}}$	0.3465
$R_{\rm int}$ all	0.1522
$R_{\rm w2}$ all	0.3804
GOF on F <sup>2</sup>	1.242

**Table S1.**Crystal data and structure refinement of  $HEu_2[Pc(OC_8H_{17})_8]_2[(ClPh)_3Cor]$  **2**.

 ${}^{a}R_{1} = \Sigma |F_{o}|F_{c}| / \Sigma |F_{o}|, \ {}^{b}R_{w2} = [\Sigma w (F_{o}^{2} - F_{c}^{2})^{2} / \Sigma w (F_{o}^{2})^{2}]^{1/2}.$ 

distance							
Eu1-N1	2.370(7)	Eu1-N9	2.549(8)	Eu2-N13	2.369(7)	Eu2-N9	2.571(7)
Eu1-N3	2.401(7)	Eu1-N10	2.585(7)	Eu2-N17	2.395(7)	Eu2-N12	2.577(7)
Eu1-N5	2.411(7)	Eu1-N11	2.597(7)	Eu2-N19	2.396(7)	Eu2-N11	2.581(7)
Eu1-N7	2.424(6)	Eu1-N12	2.599(7)	Eu2-N15	2.398(7)	Eu2 N10	2.631(6)
angle							
N1-Eu1-N3	71.4(2)	N9-Eu1-N10	62.2(2)	N13-Eu2-N17	111.1(2)	N9-Eu2-N12	91.9(2)
N1-Eu1-N5	110.7(2)	N1-Eu1-N11	104.5(2)	N13-Eu2-N19	70.2(3)	N13-Eu2-N11	101.3(2)
N3-Eu1-N5	70.9(2)	N3-Eu1-N1	1 78.0(2)	N17-Eu2-N19	71.0(2)	N17-Eu2-N11	125.1(2)
N1-Eu1-N7	70.7(2)	N5-Eu1-N11	121.2(2)	N13-Eu2-N15	72.7(2)	N19-Eu2-N11	80.4(2)
N3-Eu1-N7	110.4(2)	N7-Eu1-N11	167.3(2)	N17-Eu2-N15	71.5(2)	N15-Eu2-N11	163.0(2)
N5-Eu1-N7	71.3(2)	N9-Eu1-N11	57.8(2)	N19-Eu2-N15	111.3(2)	N9-Eu2-N11	57.7(2)
N1-Eu1-N9	162.3(2)	N10-Eu1-N11	93.3(2)	N13-Eu2-N9	79.7(2)	N12-Eu2-N11	61.6(2)
N3-Eu1-N9	102.0(2)	N1-Eu1-N12	78.1(2)	N17-Eu2-N9	166.4(2)	N13-Eu2-N10	121.9(2)
N5-Eu1-N9	81.4(2)	N3-Eu1-N12	119.8(2)	N19-Eu2-N9	121.7(2)	N17-Eu2-N10	105.2(2)
N7-Eu1-N9	126.6(2)	N5-Eu1-N12	168.6(2)	N15-Eu2-N9	105.3(2)	N19-Eu2-N10	167.3(2)
N1-Eu1-N10	124.1(2)	N7-Eu1-N12	106.2(2)	N13-Eu2-N12	162.7(2)	N15-Eu2-N10	78.0(2)
N3-Eu1-N10	164.2(2)	N9-Eu1-N12	91.9(2)	N17-Eu2-N12	79.9(2)	N9-Eu2-N10	61.3(2)
N5-Eu1-N10	103.5(2)	N10-Eu1-N12	65.2(2)	N19-Eu2-N12	102.4(2)	N12-Eu2-N10	64.8(2)
N7-Eu1-N10	80.5(2)	N11-Eu1-N12	61.1(2)	N15-Eu2-N12	124.4(2)	N11-Eu2-N10	92.6(2)
Eu1-N9-Eu2	88.6(2)	Eu1-N10-Eu2	86.52(19)	Eu2-N11-Eu1	87.3(2)	Eu2-N12-Eu1	87.3(2)

**Table S2**. Selected bond distances (Å) and angles (°) for  $HEu_2[Pc(OC_8H_{17})_8]_2[(ClPh)_3Cor]$  **2**.

Comment		$\lambda_{\rm max}$ / nm						
Compound	1	2	3	4	5	Kel.		
H <sub>3</sub> [(ClPh) <sub>3</sub> Cor]		416	572	616	650	5		
$Eu[Pc(OC_5H_{11})_8](acac)$	361			613	680	tw		
Eu[Pc(OC <sub>8</sub> H <sub>17</sub> ) <sub>8</sub> ](acac)	361			614	681	tw		
$HEu_{2}[Pc(OC_{5}H_{11})_{8}]_{2}[(ClPh)_{3}Cor]$ 1	351	420	537		680	tw		
HEu <sub>2</sub> [Pc(OC <sub>8</sub> H <sub>17</sub> ) <sub>8</sub> ] <sub>2</sub> [(ClPh) <sub>3</sub> Cor] <b>2</b>	352	421	537		681	tw		

Table S3. Electronic absorption data for each sandwich and their precursors in CHCl<sub>3</sub>.

tw =this work

Compound	oxidation					rec	luction			
Compound	5th	4th	3rd	2nd	1st	1st	2nd	3rd	$E_{1/2}(\text{ox}_1\text{-}\text{red}_1)$	$E_{1/2}(\operatorname{red}_2\operatorname{-red}_1)$
$HEu_2[Pc(OC_5H_{11})_8]_2[Cor(PhCl)_3] (1)$	1.39	1.25	1.05	0.70	0.33	-0.08	-1.27	-1.45	0.41	1.19
$HEu_{2}[Pc(OC_{8}H_{17})_{8}]_{2}[Cor(ClPh)_{3}]$ (2)	1.37	1.25	1.06	0.72	0.34	-0.09	-1.29	-1.51	0.43	1.20

**Table S4.** Half-wave potentials ( $E_{1/2}$ , V vs SCE) of each sandwich in CH<sub>2</sub>Cl<sub>2</sub>, 0.1 M TBAP.

### Notes and references

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