

## Supporting Information

### **Mixed (Phthalocyaninato)(porphyrinato) Heterometal Complexes with Sandwich Quadruple-decker Molecular Structure**

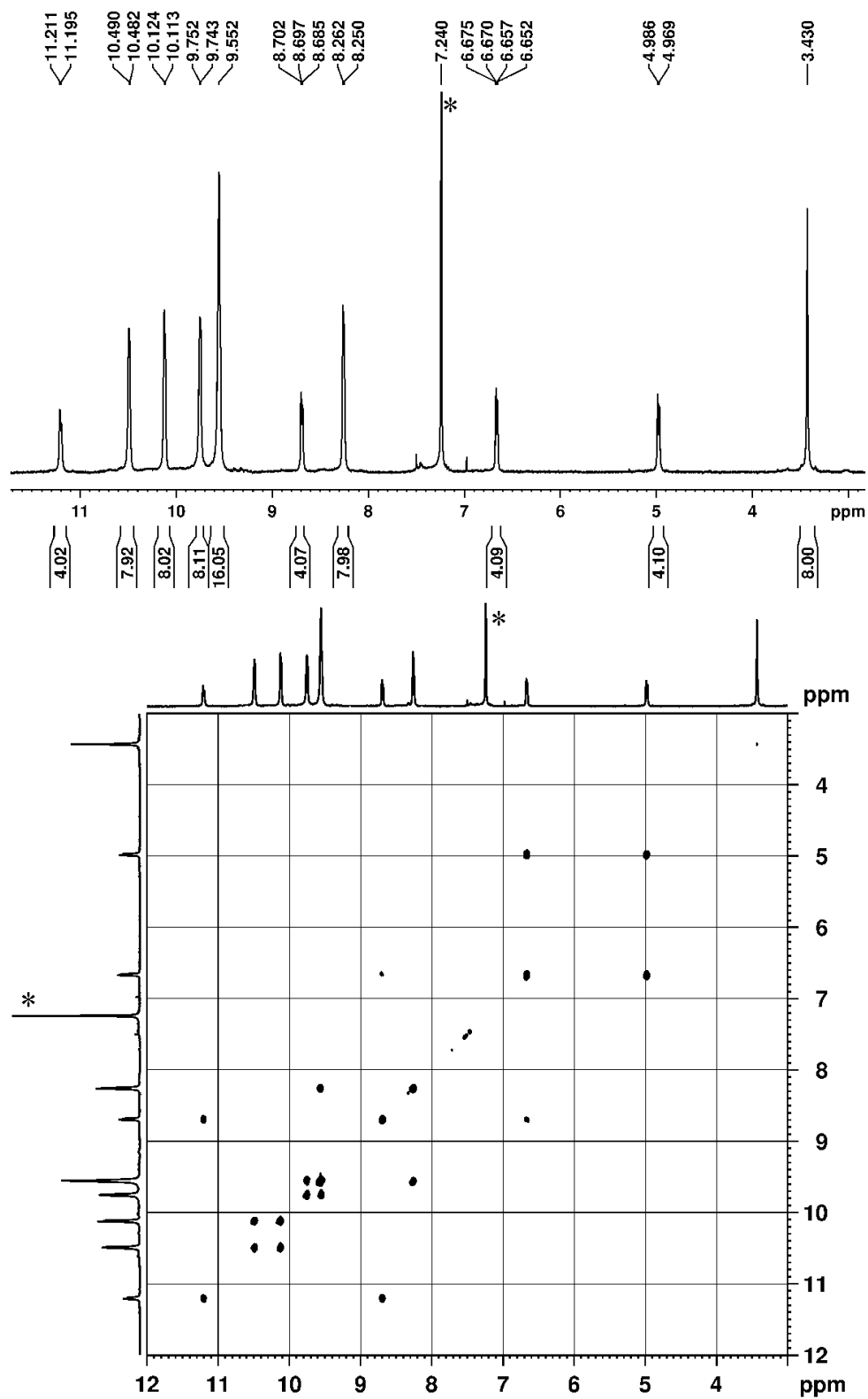
Hailong Wang,<sup>a</sup> Kang Wang,<sup>a</sup> Yongzhong Bian,<sup>a</sup> Jianzhuang Jiang<sup>\*a</sup> and Nagao  
Kobayashi<sup>\*b</sup>

## Experimental Section

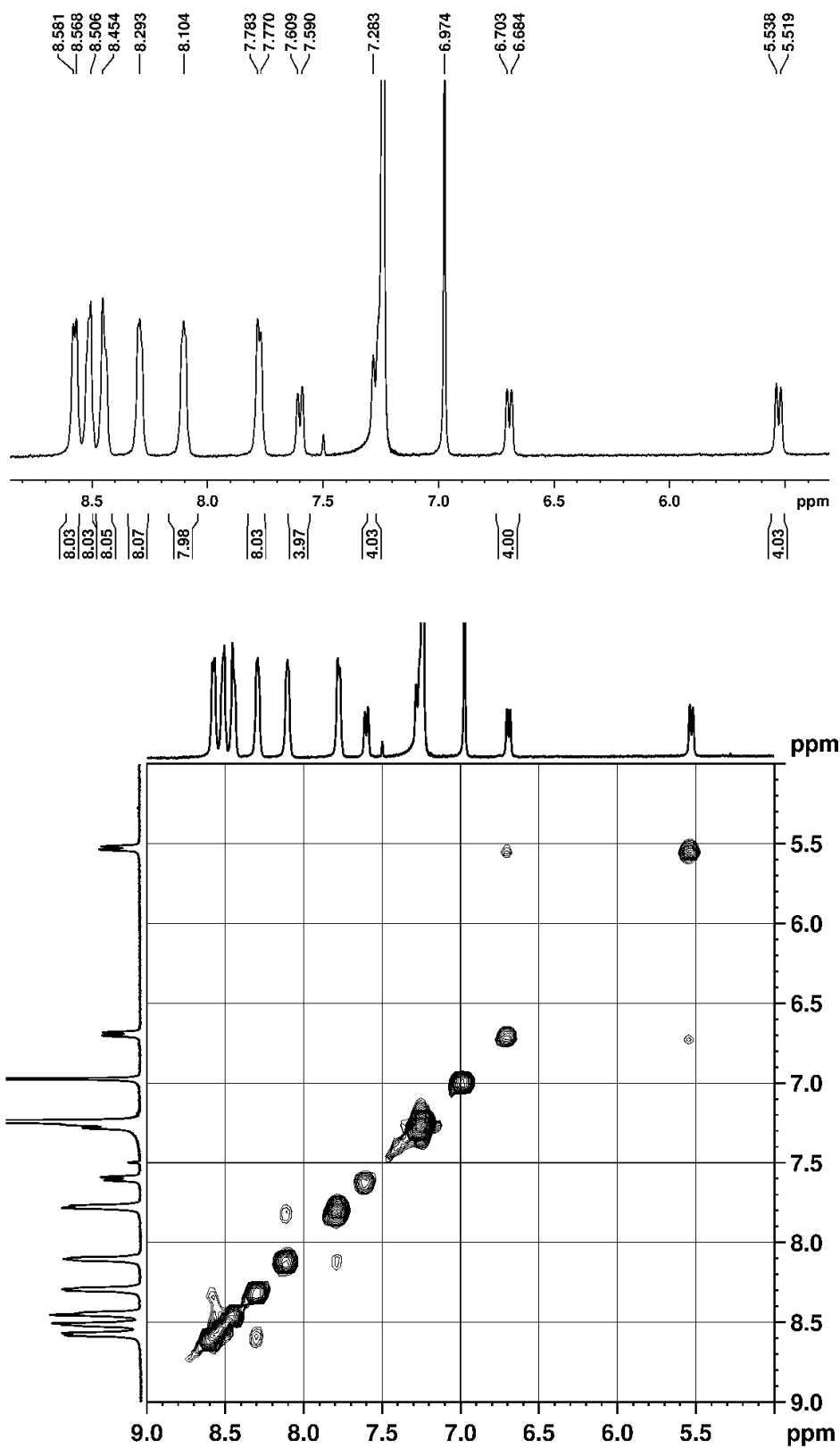
**The synthesis of [(TCIPP)M(III)(Pc)Cd(II)(Pc)M(III)(Pc)] (M = Eu, Y) (1, 2):** A mixture of Cd(OAc)<sub>2</sub>·2H<sub>2</sub>O (5.3 mg, 0.02 mmol), neutral mixed ring rare earth double-decker [(TCIPP)M(Pc)] (0.01 mmol), and neutral bis(phthalocyaninato) rare earth compound [(Pc)M(III)(Pc)] (M = Eu, Y) (0.01 mmol) in TCB (4 mL) was heated to reflux under nitrogen for 5 h. After being cooled to room temperature, the volatiles were removed under reduced pressure. The residue was chromatographed on a silica gel column using CHCl<sub>3</sub> as the eluent to give a purple band, which contained mainly the unreacted mixed ring rare earth double-decker [(TCIPP)M(Pc)] and a small amount of the quadruple-decker [(Por)M(III)(Pc)Cd(II)(Pc)M(III)(Por)]. Further elution with CHCl<sub>3</sub> gave a blue band containing the unreacted homoleptic bis(phthalocyaninato) rare earth double-decker [M(Pc)<sub>2</sub>], which was followed by two blue bands containing the target quadruple-decker complexes [(Por)M(III)(Pc)Cd(II)(Pc)M(III)(Pc)] and [(Pc)M(III)(Pc)Cd(II)(Pc)M(III)(Pc)], respectively. The symmetrical mixed ring quadruple-decker compound [(Por)M(III)(Pc)Cd(II)(Pc)M(III)(Por)] could not be isolated due to its poor stability which decomposed into mixed ring rare earth double-decker [(TCIPP)M(Pc)]. Repeated chromatography followed by recrystallization from chloroform and methanol gave the pure sandwich-type mixed (phthalocyaninato)(porphyrinato) 4d-4f heterometal quadruple-decker complexes [(Por)M(III)(Pc)Cd(II)(Pc)M(III)(Pc)] (M = Eu, Y) (1, 2) in the yield of 9-14% together with small amount of

$[(Pc)M(III)(Pc)Cd(II)(Pc)M(III)(Pc)]$  (M = Eu, Y), 3-5%.

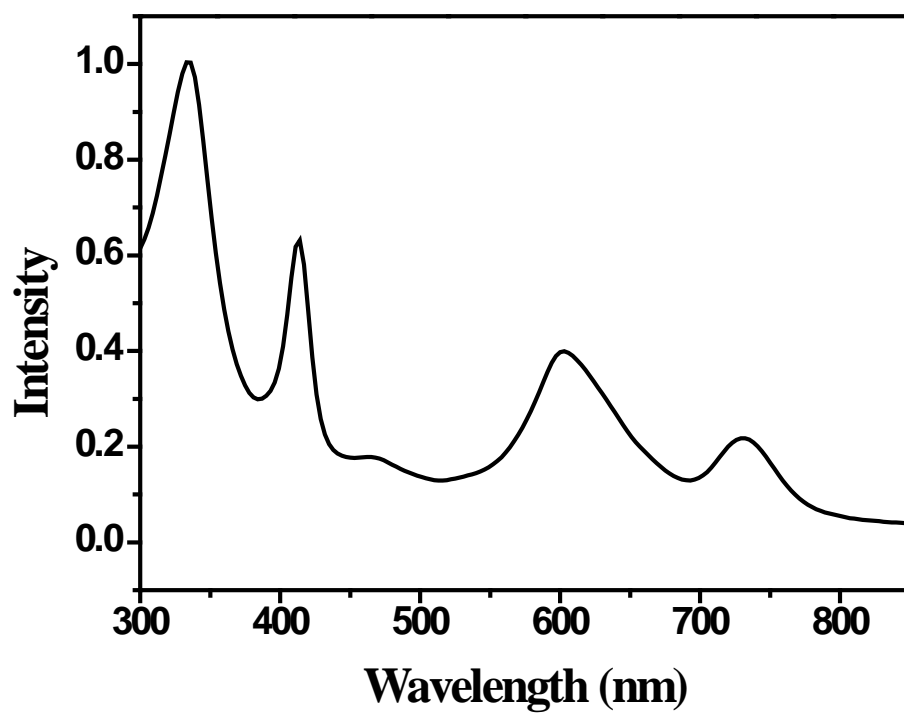
Single crystals of quadruple-decker compound **1** suitable for X-ray diffraction analysis have been obtained by diffusion of the methanol into a solution of this complex in chloroform. The crystallographical data of **1** has been determined by X-ray diffraction analysis at 100 K using Oxford Diffraction Gemini E system. MS (MALDI-TOF) for **1**: an isotopic cluster peaking at  $m/z$  2704.71 (Calcd. for  $M^+$  2704.41). Anal. Calcd. for  $C_{140}H_{74}CdCl_4Eu_2N_{28} \cdot 2H_2O \cdot CH_3OH$ : C 61.08, H 2.91, N 14.15; Found: C 60.87, H 3.02, N 13.73. MS (MALDI-TOF) for **2**: an isotopic cluster peaking at  $m/z$  2578.73 (Calcd. for  $M^+$  2578.29). Anal. Calcd. for  $C_{140}H_{74}CdCl_4Y_2N_{28} \cdot H_2O \cdot CHCl_3$ : C 62.36, H 2.78, N 14.44; Found: C 62.36, H 3.10, N 14.72.



**Figure S1.**  $^1H$  NMR and  $^1H$ - $^1H$  COSY spectra of  $[(TCIPP)Eu(III)(Pc)Cd(II)(Pc)Eu(III)(Pc)]$  (**1**) in  $CDCl_3$ .



**Figure S2.** <sup>1</sup>H NMR and <sup>1</sup>H-<sup>1</sup>H COSY spectra of [(TCIPP)Y(III)(Pc)Cd(II)(Pc)Y(III)(Pc)] (**2**) in CDCl<sub>3</sub>.



**Figure S3.** Electronic absorption spectrum of [(TCIPP)Y(III)(Pc)Cd(II)(Pc)Y(III)(Pc)] (**2**) in CHCl<sub>3</sub>.

**Table S1.**  $^1\text{H}$  NMR data ( $\delta$ ) and assignments of the sandwich-type mixed (phthalocyaninato)(porphyrinato) quadruple-decker complexes with rare earth and cadmium  $[(\text{TCIPP}^{2-})\text{M}(\text{III})(\text{Pc}^{2-})\text{Cd}(\text{II})(\text{Pc}^{2-})\text{M}(\text{III})(\text{Pc}^{2-})]$  ( $\text{M} = \text{Eu}, \text{Y}$ ) (**1**, **2**) in  $\text{CDCl}_3$ .

Compound	Pc1		Pc2		Pc3	
	$\text{H}^\alpha$	$\text{H}^\beta$	$\text{H}^\alpha$	$\text{H}^\beta$	$\text{H}^\alpha$	$\text{H}^\beta$
<b>1</b>	10.49 (d)	10.12 (d)	9.75 (d)	9.55 (m) <sup>a</sup>	9.55 (m)	8.26 (d)
<b>2</b>	8.58 (d)	8.51 (d)	8.45 (d)	8.29 (d)	8.10 (d)	7.78 (d)

Compound	TCIPP				
	$\text{H}^{\text{endo-ortho}}$	$\text{H}^{\text{endo-meta}}$	$\text{H}^{\text{exo-ortho}}$	$\text{H}^{\text{exo-meta}}$	$\text{H}^{\beta\text{-pyrrole}}$
<b>1</b>	11.21 (d)	8.70 (m)	6.68 (m)	4.99 (d)	3.43 (s)
<b>2</b>	7.61 (d)	7.28 (d) <sup>b</sup>	6.70 (d)	5.54 (d)	6.97 (s)

[a] Overlapped signal between the  $\text{H}^\beta$  of the Pc2 ring and  $\text{H}^\alpha$  of the Pc3 ring.

[b] Obscured by the strong residual  $\text{CHCl}_3$  signal at  $\delta 7.24$ .

**Table S2.** Comparison in the electronic absorption bands for the mixed (phthalocyaninato)(porphyrinato) rare earth and cadmium quadruple-decker complexes **1** and **2** with their double-decker precursors in CHCl<sub>3</sub>.

Compound	abs, $\lambda_{\max}$ /nm			
<b>1</b>	337	416	613	718
[(TCIPP <sup>2-</sup> )Eu(Pc <sup>•-</sup> )]	330	409	473	728
[(Pc <sup>2-</sup> )Eu(Pc <sup>•-</sup> )]	322	459	605	671
<b>2</b>	334	412	603	731
[(TCIPP <sup>2-</sup> )Y(Pc <sup>•-</sup> )]	332	401	470	732
[(Pc <sup>2-</sup> )Y(Pc <sup>•-</sup> )]	319	458	598	663



**Table S3.** Comparison in the half-wave redox potentials of the mixed (phthalocyaninato)(porphyrinato) rare earth and cadmium quadruple-decker complexes **1** and **2** with their double-decker precursors (V vs SCE) in CH<sub>2</sub>Cl<sub>2</sub> containing 0.1 M TBAP.

Compound	Oxd <sub>4</sub>	Oxd <sub>3</sub>	Oxd <sub>2</sub>	Oxd <sub>1</sub>	Red <sub>1</sub>	Red <sub>2</sub>	Red <sub>3</sub>	$\Delta E^{\circ}_{1/2}$
<b>1</b>	+1.36	+1.18	+0.70	+0.36	-0.66	-1.02	-1.33	1.02
[(TCIPP <sup>2-</sup> )Eu(Pc <sup>•-</sup> )]		+1.69 <sup>a</sup>	+1.39	+0.72	+0.21	-1.28	-1.66 <sup>a</sup>	0.51
[(Pc <sup>2-</sup> )Eu(Pc <sup>•-</sup> )]			+1.59	+0.55	+0.12	-1.07	-1.29	0.43
<b>2</b>	+1.39	+1.13	+0.68	+0.31	-0.64	-0.98	-1.34	0.95
[(TCIPP <sup>2-</sup> )Y(Pc <sup>•-</sup> )]		+1.74	+1.41	+0.69	+0.18	-1.28	-1.69 <sup>a</sup>	0.51
[(Pc <sup>2-</sup> )Y(Pc <sup>•-</sup> )]			+1.61	+0.47	+0.06	-1.11	-1.35	0.41

<sup>a</sup> By differential pulse voltammetry with a scan rate of 10 mV s<sup>-1</sup>.