

## Supporting Information for

### **Sandwich-type tetrakis(phthalocyaninato) europium-cadmium quadruple-decker: structure, spectroscopic, OFET and gas sensor**

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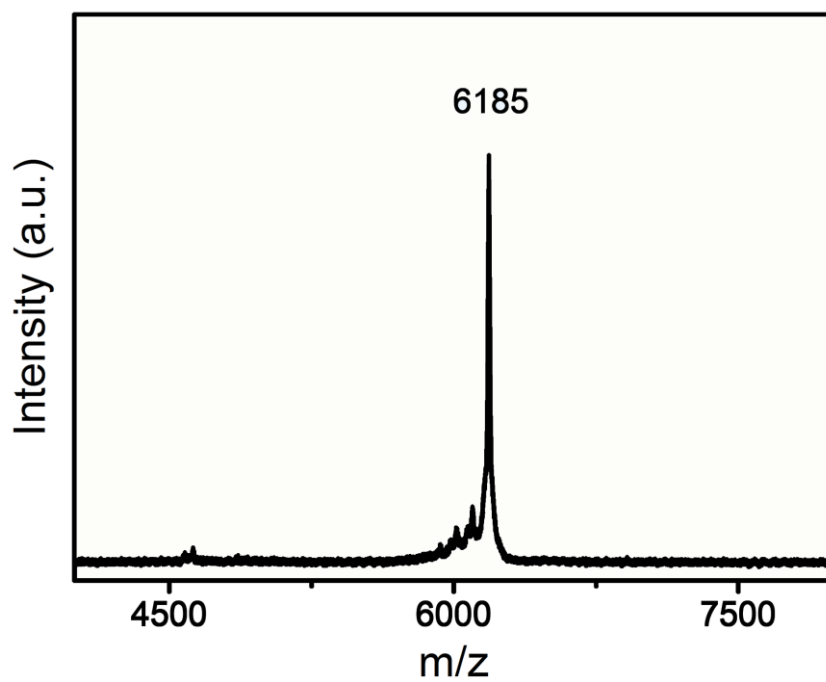
## Experimental Section

*Measurements.* Electronic absorption spectra were recorded with a Hitachi U-4100 spectrophotometer.  $^1\text{H}$  NMR spectra were recorded on a Bruker DPX 400 spectrometer in  $\text{CDCl}_3$ . Spectra were referenced internally using the residual solvent resonance ( $\delta = 7.26$  for  $^1\text{H}$  NMR) relative to  $\text{SiMe}_4$ . MALDI-TOF mass spectra were taken on a Bruker BIFLEX III ultra-high-resolution. Elemental analyses were performed on an Elementar Vavio El III. Electrochemical measurement was carried out with a BAS CV-50W voltammetric analyzer. The cell comprised inlets for a glassy-carbon-disk working electrode with a diameter of 2.0 mm in diameter and a silver-ware counter electrode. The reference electrode was  $\text{Ag}^+/\text{Ag}$  (a solution of 0.01 M  $\text{AgNO}_3$  and 0.1 M TBAP in acetonitrile), 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 ( $\text{Fc}^+/\text{Fc}$ ) couple [ $E_{1/2}(\text{Fc}^+/\text{Fc}) = 0.501$  V vs. SCE]. Typically, a 0.1 M solution of  $[\text{NBu}_4][\text{ClO}_4]$  in  $\text{CH}_2\text{Cl}_2$  containing 1 mM of sample was purged with nitrogen for 10 min, and then the voltammogram was recorded at ambient temperature. The scan rate was  $20 \text{ mV s}^{-1}$  for the CV measurement. X-ray diffraction experiment was carried out on a Bruker AXS D8 ADVANCE X-ray diffractometer. AFM images were collected in air under ambient conditions using the tapping mode with a NanoscopeIII/Bioscope scanning probe microscope from Digital instruments. The sensor property was measured by Keysight 1912A under  $\text{N}_2$  gas, and OFET property was measured by HP 4140B in the air.

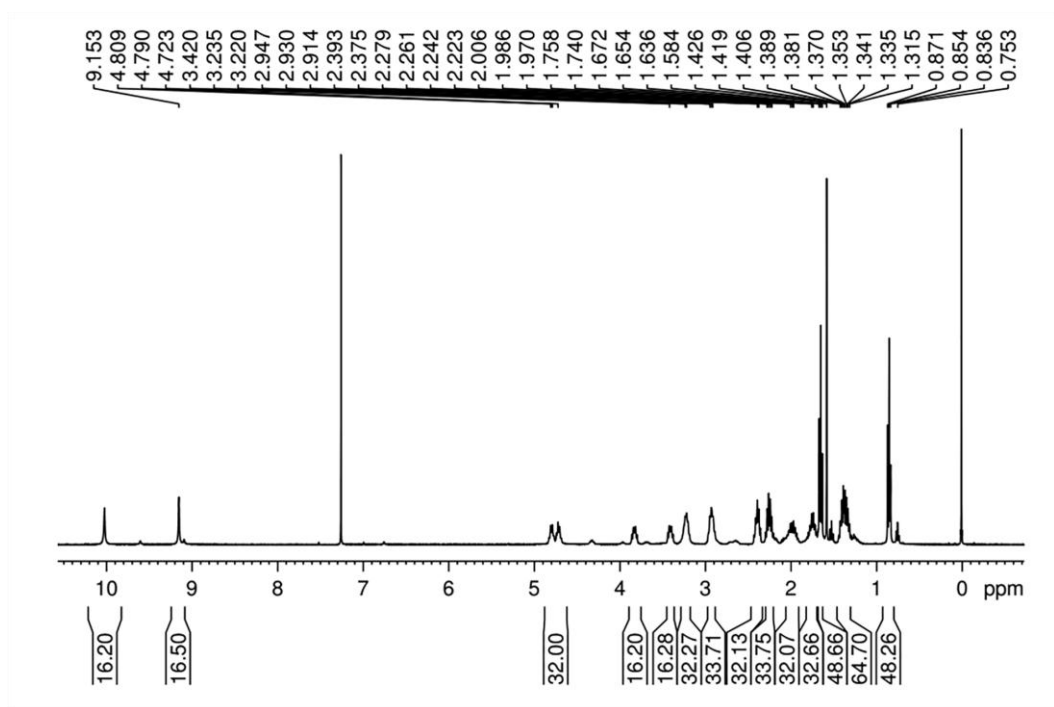
*Chemicals.* Anhydrous 1,2,4-trichlorobenzene (TCB) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) were purchased from Aldrich. Dichloromethane for voltammetric studies was freshly distilled from  $\text{CaH}_2$  under an atmosphere of nitrogen. Column chromatography was carried out on silica gel (Merck, Kieselgel 60, 70-230 mesh) with the indicated eluents. All other reagents and solvents were used as received. The

compounds of  $\text{Eu}(\text{acac})_3 \cdot n\text{H}_2\text{O}$  and  $\text{Eu}[\text{Pc}(\text{SC}_6\text{H}_{13})_8]_2$  were prepared according to the literature methods.<sup>1-2</sup>

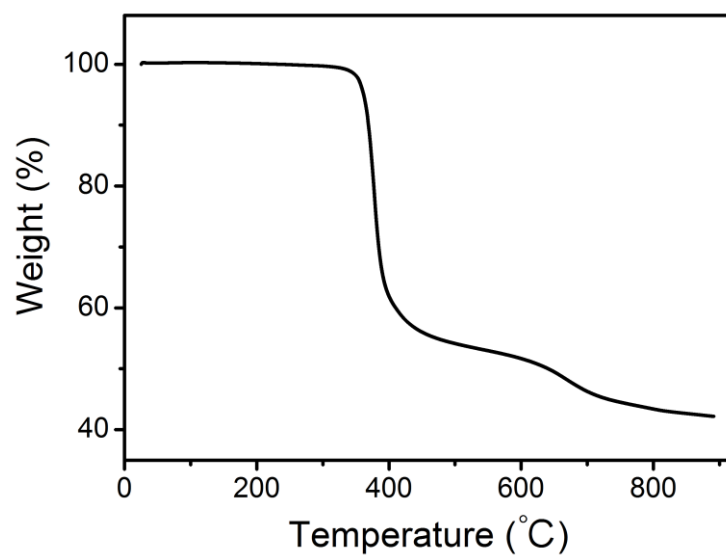
*Synthesis of  $\{[\text{Pc}(\text{SC}_6\text{H}_{13})_8]\text{Eu}[\text{Pc}(\text{SC}_6\text{H}_{13})_8]\text{Cd}[\text{Pc}(\text{SC}_6\text{H}_{13})_8]\text{Eu}[\text{Pc}(\text{SC}_6\text{H}_{13})_8]\}$  (I).* In a Schlenk flask, the mixture of  $\text{Eu}[\text{Pc}(\text{SC}_6\text{H}_{13})_8]_2$  (91 mg, 0.03 mmol) and  $\text{Cd}(\text{OAc})_2 \cdot \text{H}_2\text{O}$  (7.7 mg, 0.03 mmol) in TCB (2 mL) was heated to reflux under nitrogen for 6 h, and then the solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel eluting with  $\text{CHCl}_3$  and *n*-hexane (1:1, v/v), then the solvent was removed under reduced pressure. Repeated chromatography followed by recrystallization from  $\text{CHCl}_3$  and *n*-hexane gave pure compound as a dark powder. Yield: 80 mg (84 %).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 10.02 (s, 16 H, Pc- $\alpha$ -H), 9.15 (s, 16 H, Por- $\alpha$ -H), 4.80 (m, 16 H,  $-\text{SCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 4.72 (m, 16 H,  $-\text{SCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 3.84 (m, 16 H,  $-\text{SCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 3.39 (m, 16 H,  $-\text{SCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 3.22 (m, 32 H,  $-\text{SCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 2.94 (m, 32 H,  $-\text{SCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 2.37 (m, 32 H,  $-\text{SCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 2.26 (m, 32 H,  $-\text{SCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 2.00 (m, 32 H,  $-\text{SCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 1.75 (m, 32 H,  $-\text{SCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 1.38 (m, 64 H,  $-\text{SCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 1.65 (m, 48 H,  $-\text{SCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 0.85 (m, 48 H,  $-\text{SCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), Figure S3 (Supporting Information). MALDI-TOF MS: an isotopic cluster peaking at  $m/z$  6185,  $[\text{M}]^+$ , 6185, Figure S2 (Supporting Information). Anal. Calc. Anal. Calc. For  $\text{C}_{320}\text{H}_{448}\text{CdEu}_2\text{N}_{32}\text{S}_{32}$ : C, 62.14%; H, 7.30%; N, 7.25%. Found: C, 61.92%; H, 7.30%; N, 7.28%.



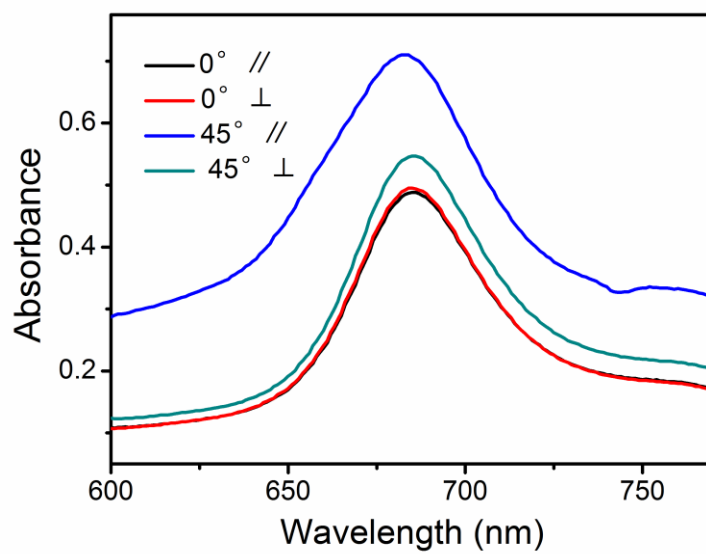
**Fig. S1.** Experimental isotopic pattern for the molecular ion of compound **1** shown in the MALDI-TOF mass spectrum.



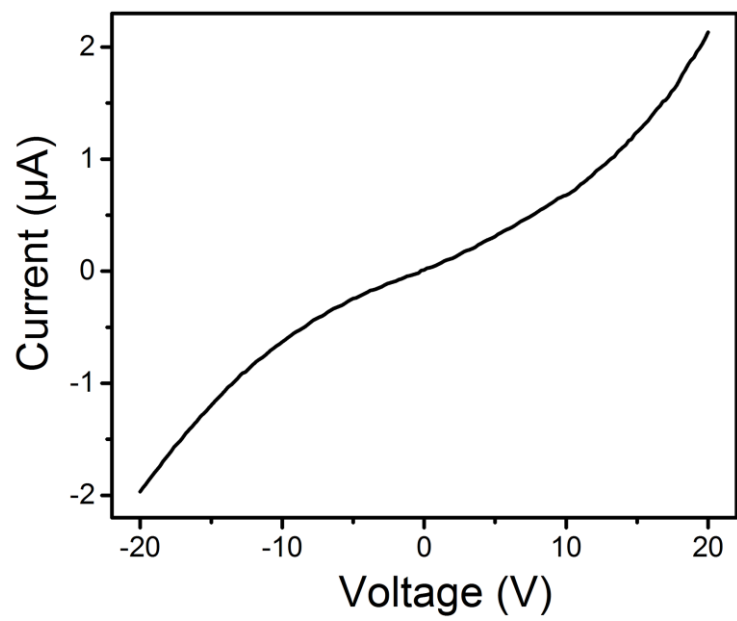
**Fig. S2.** <sup>1</sup>H NMR spectrum of compound **1** in CDCl<sub>3</sub>.



**Fig. S3.** Thermogravimetric analysis of complex **1**.



**Fig. S4.** Polarized UV-vis spectra for QLS film of **1**.



**Fig. S5.** I-V curve of the QLS film of **1**.



**Table S1.** Half-wave redox potentials (V vs SCE) in CH<sub>2</sub>Cl<sub>2</sub> containing 0.1 mol dm<sup>-3</sup> [Bu<sub>4</sub>N][ClO<sub>4</sub>] together with the HOMO and LUMO levels of **1**.

Compound	Oxd <sub>3</sub> /V	Oxd <sub>2</sub> /V	Oxd <sub>1</sub> /V	Red <sub>1</sub> /V	E <sub>HOMO</sub> /eV <sup>[b]</sup>	E <sub>LUMO</sub> /eV <sup>[c]</sup>	ΔE <sup>o</sup> <sub>1/2</sub> /V <sup>[a]</sup>
<b>(1)</b>	1.00	0.65	0.37	-0.59	-4.81	-3.85	0.97

<sup>[a]</sup> ΔE<sup>o</sup><sub>1/2</sub> = Oxd<sub>1</sub> - Red<sub>1</sub>, *i.e.* the HOMO-LUMO gap of corresponding molecule;

<sup>[b]</sup> calculated from empirical formula of HOMO = -(Oxd<sub>1</sub> + 4.44 eV);

<sup>[c]</sup> LUMO = -(Red<sub>1</sub> + 4.44 eV).

**Table S2.** The orientation angle of the phthalocyanine ring determined from polarized UV-vis absorbance of the films of of Compound **1**.

Compound	$A_{\parallel 0^\circ}$	$A_{\perp 0^\circ}$	$D_{0^\circ}$	$A_{\parallel 45^\circ}$	$A_{\perp 45^\circ}$	$D_{45^\circ}$	$\theta^\circ$
<b>1</b>	0.490	0.498	0.984	0.713	0.548	1.301	32.8°

**Table S3.** Comparison between the present study and the literatures about OFET property.

OFET materials	$\mu_e$ (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )	$\mu_h$ (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )	Ref.
diketopyrrolopyrrole	$4.4 \times 10^{-4}$	$8.6 \times 10^{-4}$	3
Eu <sub>2</sub> [Pc(OC <sub>8</sub> H <sub>17</sub> ) <sub>8</sub> ] <sub>2</sub> [Pc(OCH <sub>2</sub> CF <sub>3</sub> ) <sub>8</sub> ]	$2.14 \times 10^{-4}$	$2.72 \times 10^{-2}$	4
Eu <sub>2</sub> {Pc[(OC <sub>2</sub> H <sub>4</sub> ) <sub>3</sub> OCH <sub>3</sub> ] <sub>8</sub> } <sub>2</sub> [Pc(OCH <sub>2</sub> CF <sub>3</sub> ) <sub>8</sub> ]	$5.83 \times 10^{-4}$	$1.3 \times 10^{-2}$	4
DbT-TTAR/DTTQ-11	0.83	0.37	5
naphthalene diimide (NDI)-benzothiadiazole	$2.4 \times 10^{-3}$	0.258	6
diketopyrrolopyrrole	0.1	$2 \times 10^{-3}$	7
This work	$5.6 \times 10^{-3}$	$1.2 \times 10^{-3}$	

**Table S4.** Comparison between the present study and the literatures about gas sensors for NO<sub>2</sub> detection.

Sensing materials	NO <sub>2</sub> (ppm)	Operating temperature	Ref.
Cu/ graphene	1	room-temperature	8
H <sub>2</sub> [Pc(OCH <sub>2</sub> (CF <sub>2</sub> ) <sub>6</sub> CF <sub>3</sub> ) <sub>4</sub> ]	0.1	room-temperature	9
silver-polypyrrole	5	room-temperature	10
TIPS-pentacene	0.25	room-temperature	11
LuPc <sub>2</sub>	0.75	room-temperature	12
This work	0.25	room-temperature	

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