

*Electronic Supplementary Information (ESI) for*

**Single crystal microsheet field effect transistors of a novel dimeric  
phthalocyanine-involved triple-decker**

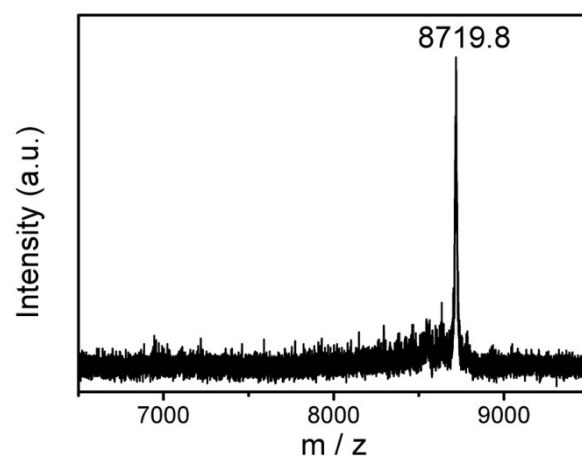
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***Experimental Section***

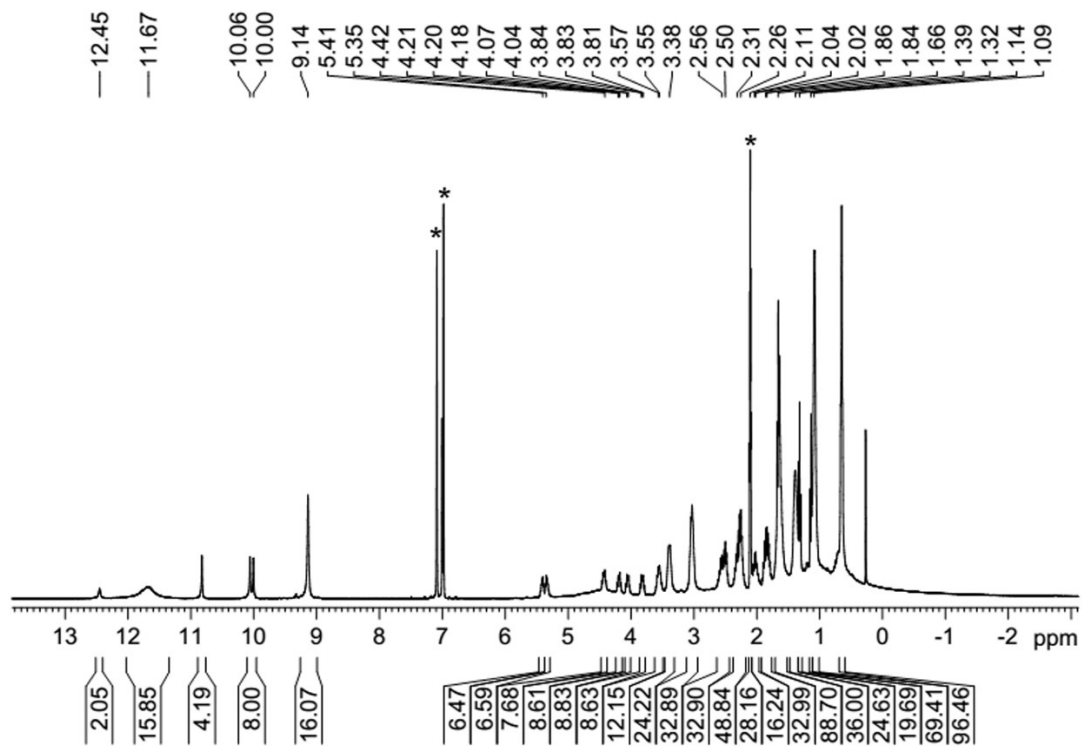
**Chemicals and Synthesis:** The  $[\text{Pc}(\text{SC}_6\text{H}_{13})_8]\text{Eu}[\text{BiPc}(\text{SC}_6\text{H}_{13})_{12}]\text{Eu}[\text{Pc}(\text{SC}_6\text{H}_{13})_8]$  { $\text{Pc}(\text{SC}_6\text{H}_{13})_8$ = 2,3,9,10,16,17,23,24-octakis (hexylthio)-phthalocyaninate,  $\text{BiPc}(\text{SC}_6\text{H}_{13})_{12}$ = bis[7,8,12,13,17,18-hexakis(hexylthio)tribenzo [g, l, q]-5,10,15,20-tetraazaporphyrinate[b, e]benzene-linked binuclear phthalocyanate]} was synthesized by the self-cyclic tetramerization of phthalonitriles in the presence of metal salts according to the previously published procedures. The  $[\{\text{Pc}(\text{SC}_6\text{H}_{13})_8\}\text{Eu}\{\text{BiPc}(\text{SC}_6\text{H}_{13})_{12}\}\text{Eu}(\text{SC}_6\text{H}_{13})_8]$  and  $\text{Pc}(\text{SC}_6\text{H}_{13})_8$  were synthesized according to the published procedure,<sup>1-2</sup> which reacted with  $[\text{Eu}(\text{acac})_3]\cdot n\text{H}_2\text{O}$  in TCB for 8 hours. The solvent was removed under reduced pressure and the residue left was chromatographed on a silica gel column with  $\text{CHCl}_3$  as eluent. Repeated chromatography followed by recrystallization from  $\text{CHCl}_3$  and methanol gave pure compound as a green powder. All other reagents and solvents were of reagent grade and used as received. <sup>1</sup>H NMR (400 MHz, Toluene- $\text{D}_8$ , 343K) for **1**,  $\delta$ : 12.45 (s, 2, *Pc- $\alpha$ -H*), 11.67 (s, 16, *Pc- $\alpha$ -H*), 10.82 (s, 4, *Pc- $\alpha$ -H*), 10.07 (d, 8, *Pc- $\alpha$ -H*), 9.14 (s, 16, *Pc- $\alpha$ -H*), 5.41 (m, 12,  $\text{SCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 4.42 (m, 8,  $\text{SCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 4.18 (m, 8,  $\text{SCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 4.07 (m, 8,  $\text{SCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 3.82 (m, 8,  $\text{SCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 3.55 (m, 12,  $\text{SCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 3.03, (m, 32,  $\text{SCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 3.38, (m, 24,  $\text{SCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 2.50, (m, 32,  $\text{SCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 1.84 (m, 32,  $\text{SCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 2.26 (m, 48,  $\text{SCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 2.02 (m, 16,  $\text{SCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 1.32 (m, 24,  $\text{SCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 1.66 (m, 88,

SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.09 (m, 19, SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.08 (m, 69, SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.39 (m, 36, SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 0.65 (m, 96, SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>); <sup>13</sup>C NMR (400MHz, Toluene-D<sub>8</sub>, 273K): δ= 141.35, 140.75, 140.13, 139.73, 138.46, 137.18, 119.44, 118.50, 85.22, 37.44, 35.72, 35.59, 34.75, 34.02, 32.73, 32.46, 31.83, 31.31, 30.64, 30.02, 29.95, 29.81, 29.77, 29.09, 29.03, 24.33, 23.55, 23.34, 22.78, 15.31, 14.79, 14.57, 14.05 ppm; MALDI-TOF MS: an isotopic cluster peaking at m/z 8719.8 [MH]<sup>+</sup>, Anal. Calc. For C<sub>450</sub>H<sub>618</sub>Eu<sub>4</sub>N<sub>48</sub>S<sub>44</sub>: C, 61.99%; H, 7.14%; N, 7.71%. Found: C, 61.74%; H, 7.09%; N, 7.68%. Figure S1-S3 (Supporting Information).

*Measurements:* Electrochemical measurement was carried out with a CHI760D voltammetric analyzer. The cell comprised inlets for a glassy carbon disk working electrode of 3.0 mm in diameter and a silver-wire counter electrode. The reference electrode was Ag/Ag<sup>+</sup> (0.01 mol dm<sup>-3</sup>), 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 (Fc<sup>+</sup>/Fc) couple [*E*<sub>1/2</sub>(Fc<sup>+</sup>/Fc) = 0.50 V vs. SCE]. Typically, a 0.1 mol dm<sup>-3</sup> solution of [Bu<sub>4</sub>N][ClO<sub>4</sub>] in CH<sub>2</sub>Cl<sub>2</sub> containing 0.5 mmol dm<sup>-3</sup> of sample was purged with nitrogen for 5 min, then the voltammogram was recorded at ambient temperature. Crystal data for **1** was determined by X-ray diffraction analysis at 150 K using Oxford Diffraction Gemini E system with Cu<sub>Kα</sub> radiation λ = 1.5418 Å, and details of the structure refinement are given in Table S1 (Supporting Information). X-ray diffraction experiment was carried out on a Bruker AXS D8 ADVANCE X-ray diffractometer. Scanning electron microscopy (SEM) images were obtained using a JEOL JSM-6700F field-emission scanning electron microscopy. For SEM imaging, C (1~2 nm) was sputtered onto the substrate to prevent charging effects and to improve the image clarity. Transmission electron microscopy (TEM) images were obtained using a JEM-2100F field-emission transmission electron microscopy.



**Fig. S1** MALDI-TOF mass spectrum for the molecular ion of compound **1**.



**Fig. S2**  $^1\text{H}$  NMR spectrum of compound **1**.

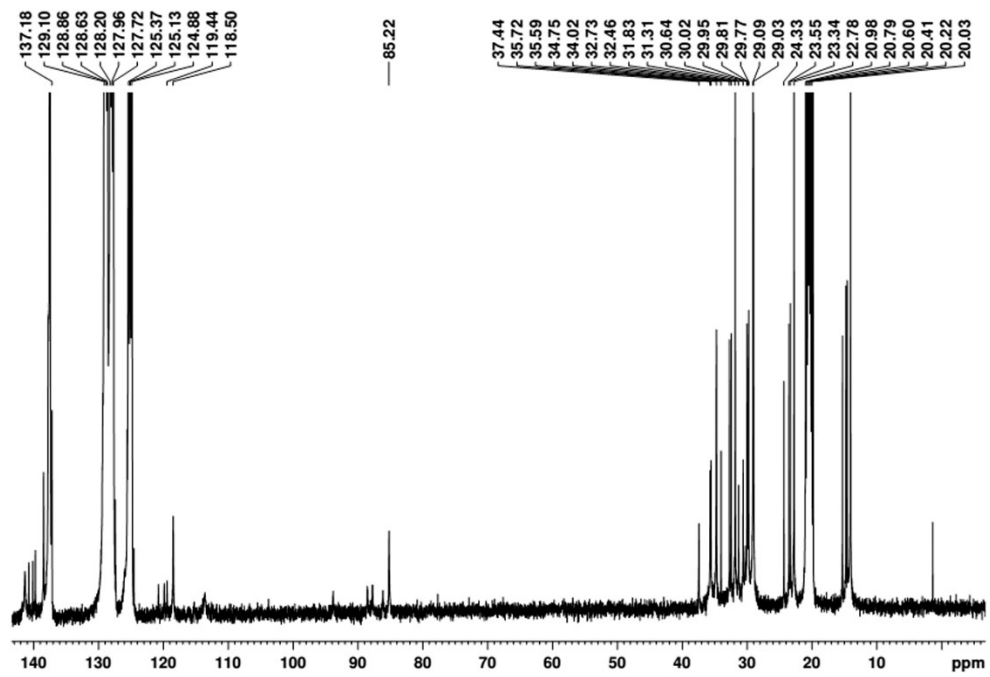
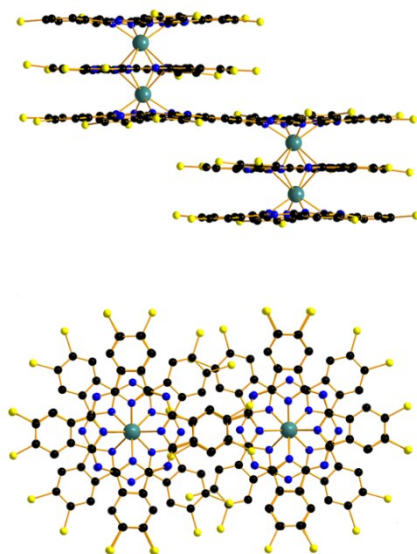
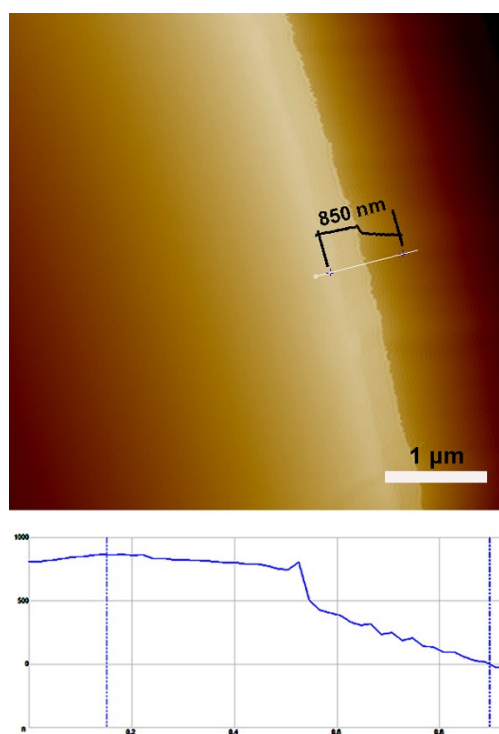


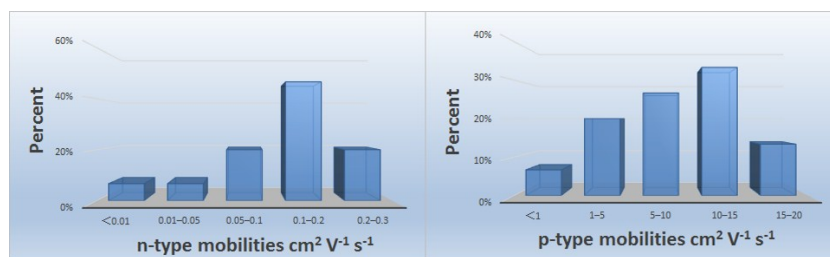
Fig. S3  $^{13}\text{C}$  NMR spectrum of compound 1.



**Fig. S4.** Molecular structure of **1** in side view (top) and top view (bottom) with all hydrogen atoms and *n*-hexyl chains omitted for clarity [Eu(III) green, C black, S yellow and N blue].



**Fig. S5** AFM image of microsheets edge.



**Fig. S6** The distribution diagram of device mobilities.



**Table S1.** The crystallographic data of compound **1**.

Compound	<b>1</b>
formula	C <sub>450</sub> H <sub>618</sub> Eu <sub>4</sub> N <sub>48</sub> S <sub>44</sub>
fw	8718.40
Crystal system	triclinic
a	18.4066(3)
b	26.4212(6)
c	27.4788(6)
$\alpha$	106.338(2)
$\beta$	108.689(2)
$\gamma$	102.171(2)
V	11462.6(4)
Z	1
F(000)	4604
R <sub>1</sub> (I>2 $\theta$ )	0.0781
R <sub>w2</sub> (I>2 $\theta$ )	0.2055
R <sub>w2</sub> for all	0.2378
GOF on F <sup>2</sup>	0.967
CCDC number	1509684

**Table S2.** Half-wave redox potentials (V vs SCE) in CH<sub>2</sub>Cl<sub>2</sub> containing 0.1 M [Bu<sub>4</sub>N][ClO<sub>4</sub>] together with the HOMO and LUMO levels of [Pc(SC<sub>6</sub>H<sub>13</sub>)<sub>8</sub>]Eu[BiPc(SC<sub>6</sub>H<sub>13</sub>)<sub>12</sub>]Eu[Pc(SC<sub>6</sub>H<sub>13</sub>)<sub>8</sub>] (**1**).

Compound	Oxd <sub>4</sub> /V	Oxd <sub>3</sub> /V	Oxd <sub>2</sub> /V	Oxd <sub>1</sub> /V	Red <sub>1</sub> /V	Red <sub>2</sub> /V	Red <sub>3</sub> /V	Red <sub>4</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>	1.22	1.04	0.78	0.59	-0.34	-0.44	-0.59	-0.76	-5.03	-4.10	0.93

<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).

**References:**

- (1) K. Wang, D. Qi, H. Wang, W. Cao, W. Li, T. Liu, C. Duan and J. Jiang, *Chem.–Eur. J.*, 2013, **19**, 11162-11166.
- (2) C. Huang, Y. Zhang, J. Sun, Y. Bian and D. P. Arnold, *J. Porphyrins Phthalocyanines*, 2013, **17**, 679-681.