

## Supporting Information

### **2,3,9,10,16,17,23,24-Octakis(hexylsulfonyl)phthalocyaninato Metal Complexes with Good *n*-Type Semiconducting Properties. Synthesis, Spectroscopic, and Electrochemical Characteristics**

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**Preparation of 4,5-di(hexylthio)phthalonitrile.** A mixture of 4,5-dichlorophthalonitrile (1.039 g, 5.27 mmol) and hexanethiol (1.418 g, 12 mmol) in DMF (10 mL) was heated to 100°C, then dry K<sub>2</sub>CO<sub>3</sub> (14.57 g) was added in 5 portions over 1 h. The resulting mixture was heated at 100°C under stirring for 12 h. After being cooled to room temperature, the mixture was poured in water (30 mL) and extracted with chloroform (30 mL x 3). The organic phase was combined and dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>. After being evaporated, the purple oil obtained was then applied on a silica gel column with *n*-hexane/chloroform (1:1) as the eluent. Repeated chromatography followed by recrystallization from CHCl<sub>3</sub> and MeOH gave pure target product as yellow-green powder (0.803 g, 65%). Mp: 72°C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 7.42 (s, 2H, arom H), 3.00-3.04 (t, 4H, SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.73-1.77 (m, 4H, SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.33-1.35 (m, 12H, SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 0.92 (t, 6H, SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>). MALDI-TOF MS: an isotopic cluster peaking at *m/z* 361.1, Calcd. for C<sub>20</sub>H<sub>28</sub>N<sub>2</sub>S<sub>2</sub>: [M]<sup>+</sup> 360.5. Anal. Calcd. For C<sub>20</sub>H<sub>28</sub>N<sub>2</sub>S<sub>2</sub>: C, 66.62; H, 7.83; N, 7.77; found: C, 66.77; H, 8.08; N, 7.38.

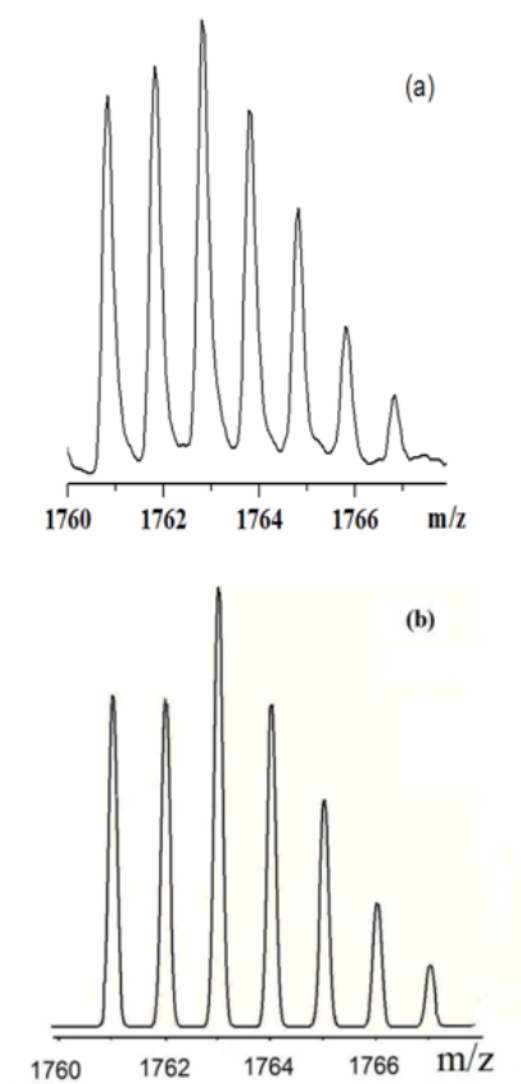
**Preparation of 2,3,9,10,16,17,23,24-octakis(hexylthio)phthalocyanine H<sub>2</sub>Pc(SC<sub>6</sub>H<sub>13</sub>)<sub>8</sub> by cyclic tetramerization of di(hexylthio)phthalonitrile.** A mixture of di(hexylthio)phthalonitrile (59.5 mg, 0.16 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (0.1 mL) in *n*-pentanol (2 mL) was heated to reflux for 5 h under nitrogen. After being cooled to room temperature, the mixture was evaporated to dryness under reduced pressure and the residue was chromatographed on a silica gel column using CHCl<sub>3</sub> as the eluent. A green band containing the target compound was collected. Repeated chromatography followed by recrystallization from CHCl<sub>3</sub> and MeOH gave pure H<sub>2</sub>Pc(SC<sub>6</sub>H<sub>13</sub>)<sub>8</sub> as green powder (7.8 mg, 13.2%).

***Preparation of 2,3,9,10,16,17,23,24-octakis(hexylthio)phthalocyaninato copper complex  $Cu[Pc(SC_6H_{13})_8]$  by cyclic tetramerization of di(hexylthio)phthalonitrile.*** A mixture of di(hexylthio)phthalonitrile (50 mg, 0.14 mmol),  $Cu(CH_3COO)_2 \cdot H_2O$  (15 mg, 0.07 mmol), and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (0.1 mL) in *n*-pentanol (5 mL) was heated at 120°C for 3 h under nitrogen. After being cooled to room temperature, the mixture was evaporated to dryness under reduced pressure and the residue was chromatographed on a silica gel column using  $CHCl_3$  as the eluent. After a small green band containing the metal-free phthalocyanine, the second green band containing the target compound was collected. Repeated chromatography followed by recrystallization from  $CHCl_3$  and MeOH gave blue powder (19.9 mg, 38%).

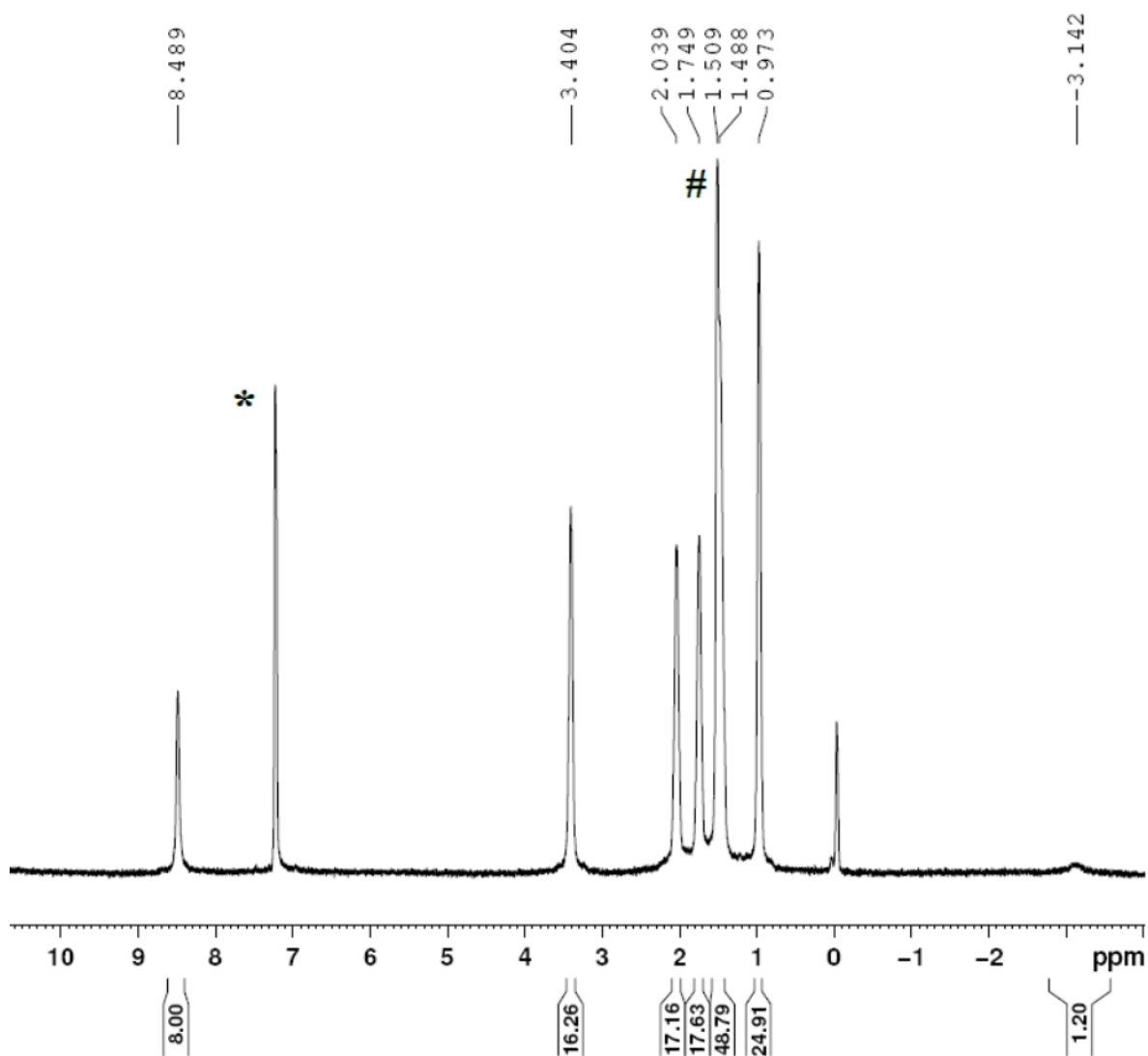
***Preparation of 2,3,9,10,16,17,23,24-octakis(hexylthio)phthalocyaninato zinc complex  $Zn[Pc(SC_6H_{13})_8]$  by cyclic tetramerization of di(hexylthio)phthalonitrile.*** By employing the procedure described above using  $Zn(CH_3COO)_2 \cdot 2H_2O$  (59.2 mg, 0.16 mmol) instead of  $Cu(CH_3COO)_2 \cdot H_2O$  as the starting material, compound  $Cu[Pc(SC_6H_{13})_8]$  was obtained as green powder (25.3 mg, 40%).

***Preparation of 2,3,9,10,16,17,23,24-octakis(hexylthio)phthalocyaninato copper complex  $Cu[Pc(SC_6H_{13})_8]$  by insertion metal ion into  $H_2Pc(SC_6H_{13})_8$ .*** A mixture of  $H_2[Pc(SC_6H_{13})_8]$  (45 mg, 0.03 mmol) and  $Cu(CH_3COO)_2 \cdot H_2O$  (30 mg, 0.16 mmol) in DMF (5 mL) was heated at 150°C for 3 h under nitrogen. After being cooled to room temperature, the mixture was evaporated to dryness under reduced pressure and the residue was chromatographed on a silica gel column using  $CHCl_3$  as the eluent. The dark-green band containing the target compound was collected. Repeated chromatography followed by recrystallization from  $CHCl_3$  and MeOH gave blue powder (20 mg, 42%).

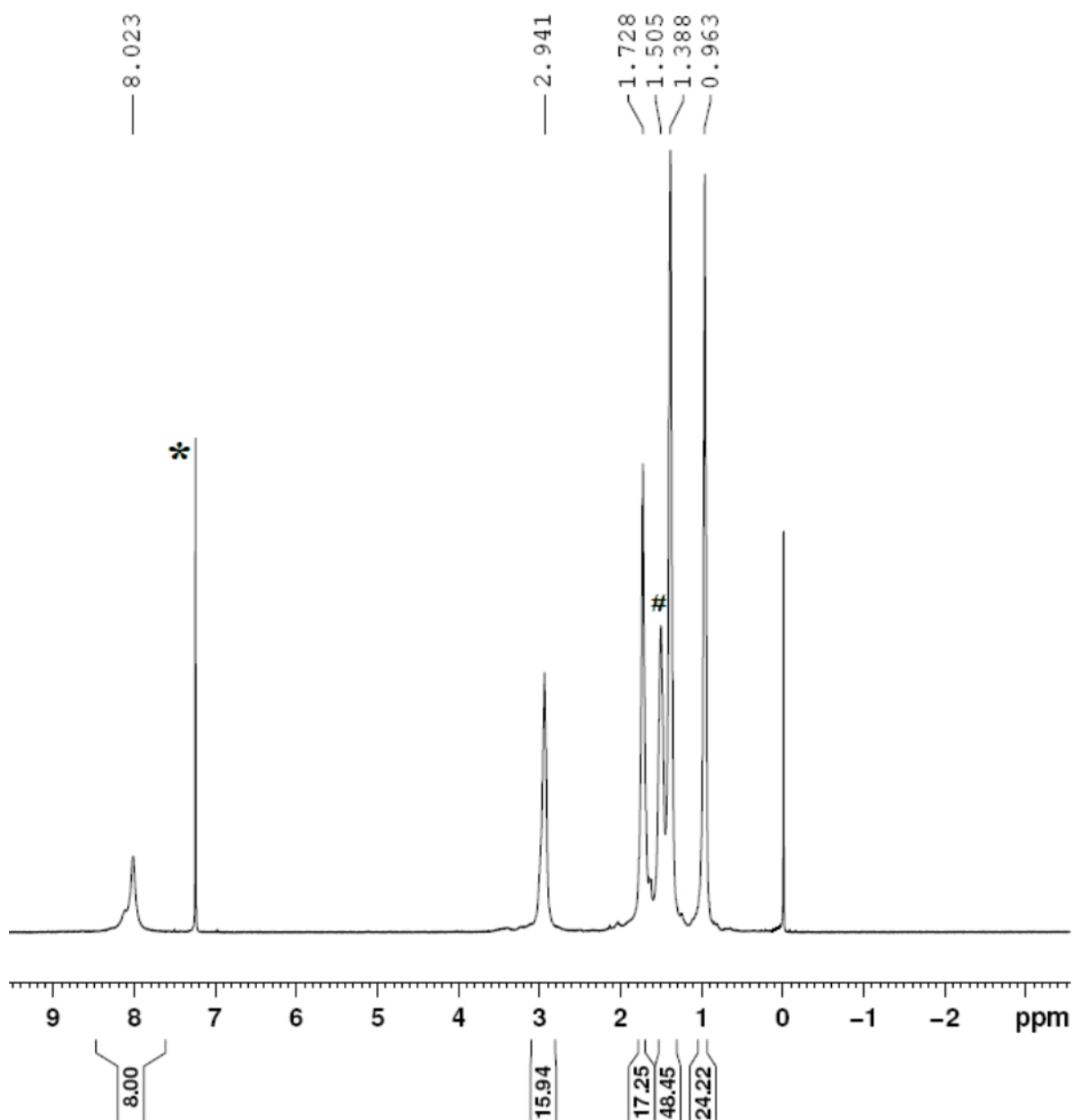
***Preparation of 2,3,9,10,16,17,23,24-octakis(hexylthio)phthalocyaninato zinc complex  $Zn[Pc(SC_6H_{13})_8]$  by insertion metal ion into  $H_2Pc(SC_6H_{13})_8$ .*** By employing the procedure described above using  $Zn(CH_3COO)_2 \cdot 2H_2O$  (35 mg, 0.15 mmol) instead of  $Cu(CH_3COO)_2 \cdot H_2O$  as starting material, compound  $Zn[Pc(SC_6H_{13})_8]$  was obtained as green powder (25 mg, 46.5%).



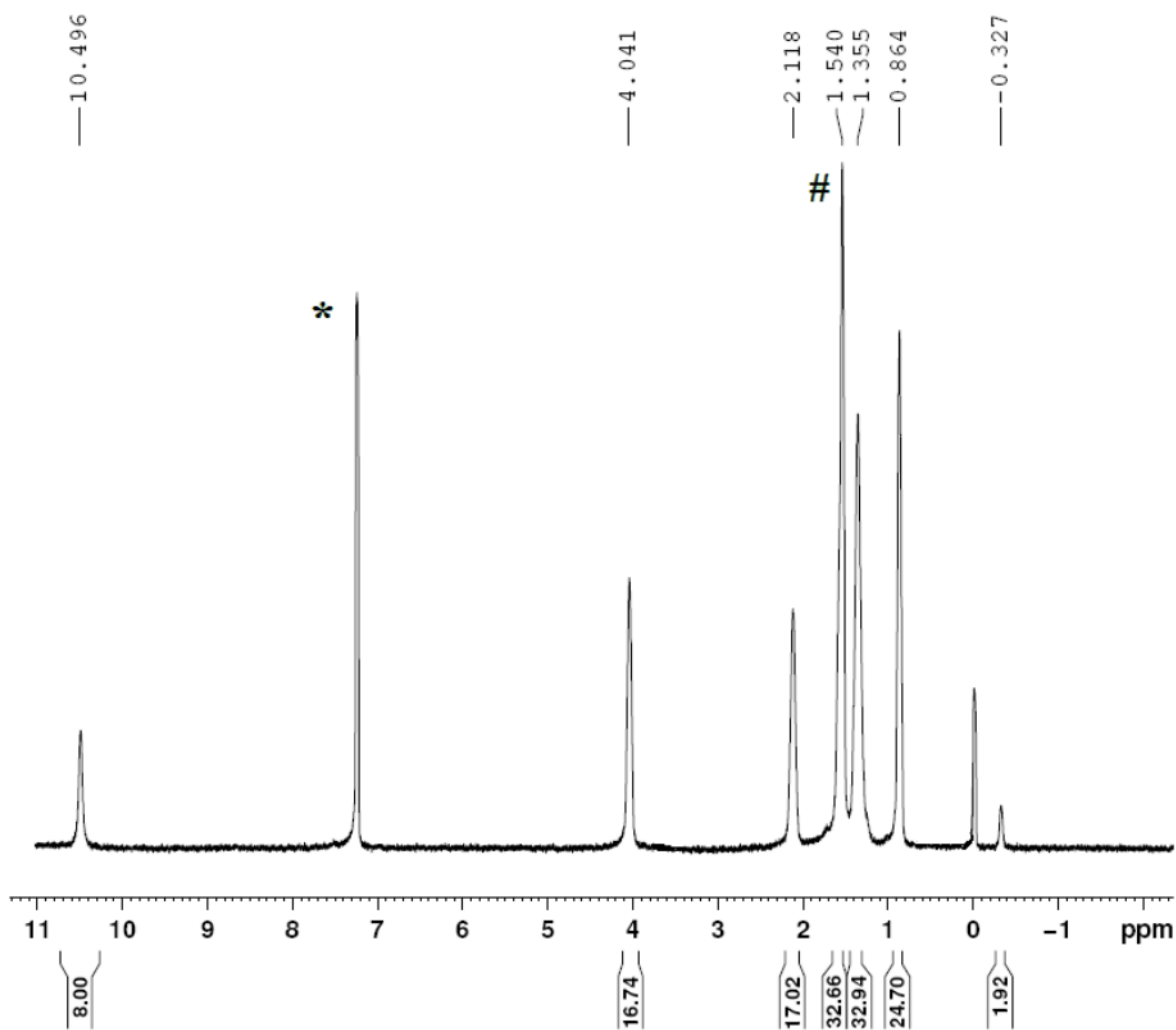
**Figure S1.** (a) Experimental and (b) simulated isotopic pattern for the molecular ion of  $\text{Cu}[\text{Pc}(\text{SO}_2\text{C}_6\text{H}_{13})_8]$  (**2**) shown in the MALDI-TOF mass spectrum.



**Figure S2.**  $^1\text{H}$  NMR spectrum for  $\text{H}_2\text{Pc}(\text{SC}_6\text{H}_{13})_8$  in  $\text{CDCl}_3$ . The signals due to residue  $\text{CHCl}_3$  and  $\text{H}_2\text{O}$  are denoted as \* and #, respectively.

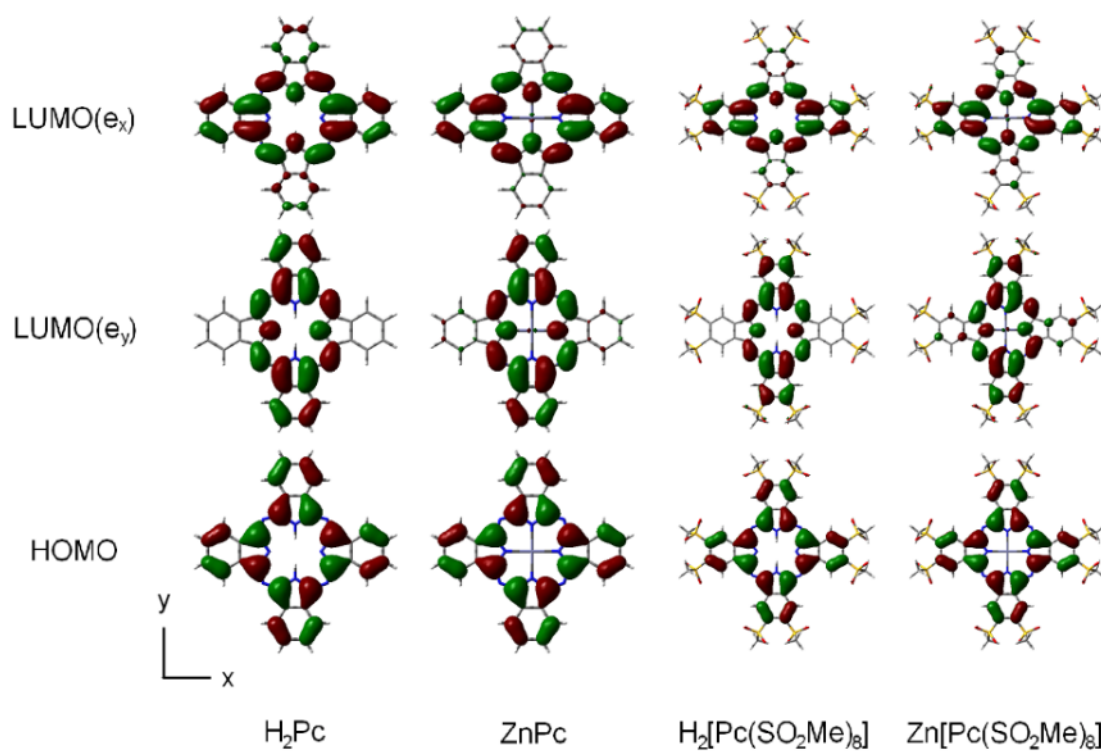


**Figure S3.**  $^1\text{H}$  NMR spectrum for  $\text{Zn}[\text{Pc}(\text{SC}_6\text{H}_{13})_8]$  in  $\text{CDCl}_3$ . The signals due to residue  $\text{CHCl}_3$  and  $\text{H}_2\text{O}$  are denoted as \* and #, respectively.

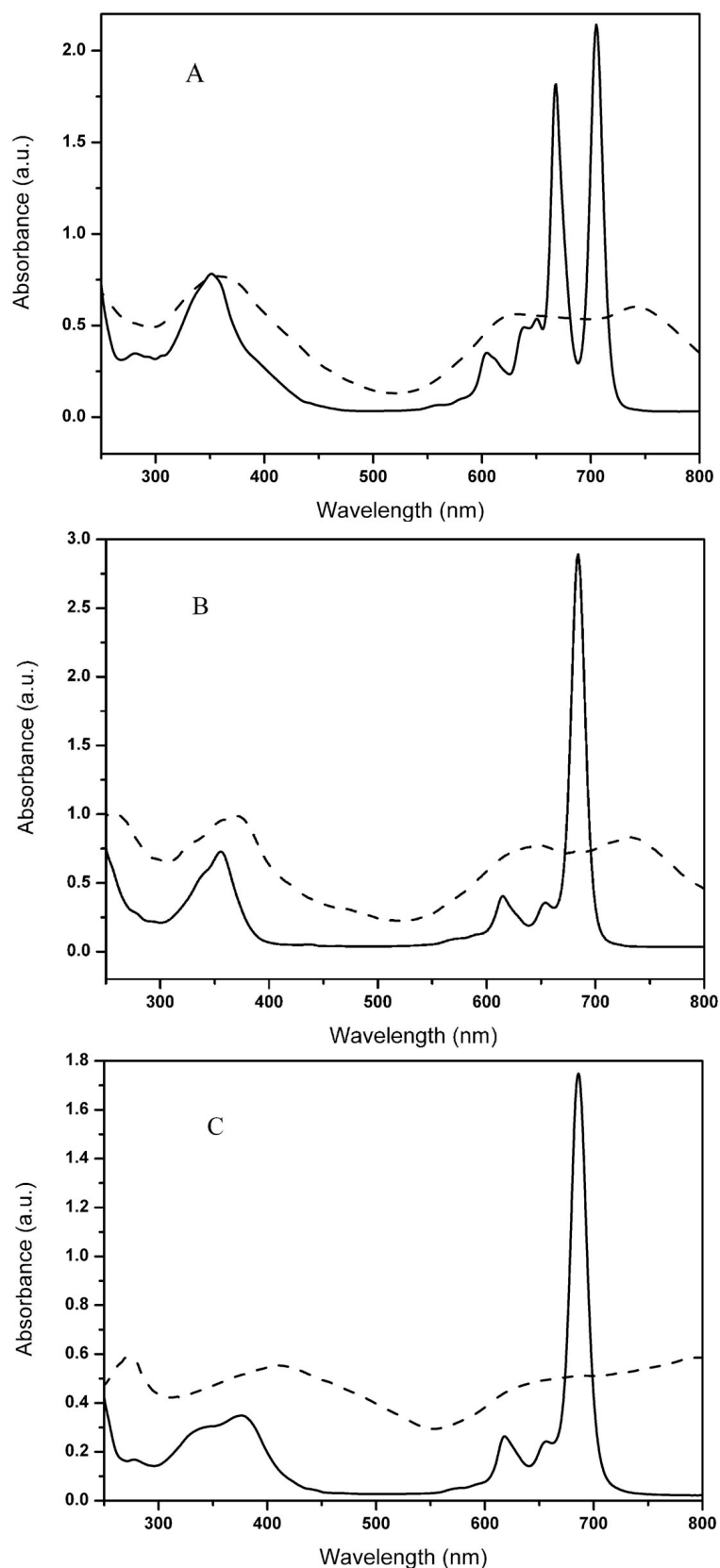


**Figure S4.**  $^1\text{H}$  NMR spectrum for  $\text{H}_2\text{Pc}(\text{SO}_2\text{C}_6\text{H}_{13})_8$  (**1**) in  $\text{CDCl}_3$ . The signals due to residue  $\text{CHCl}_3$  and  $\text{H}_2\text{O}$  are denoted as \* and #, respectively.

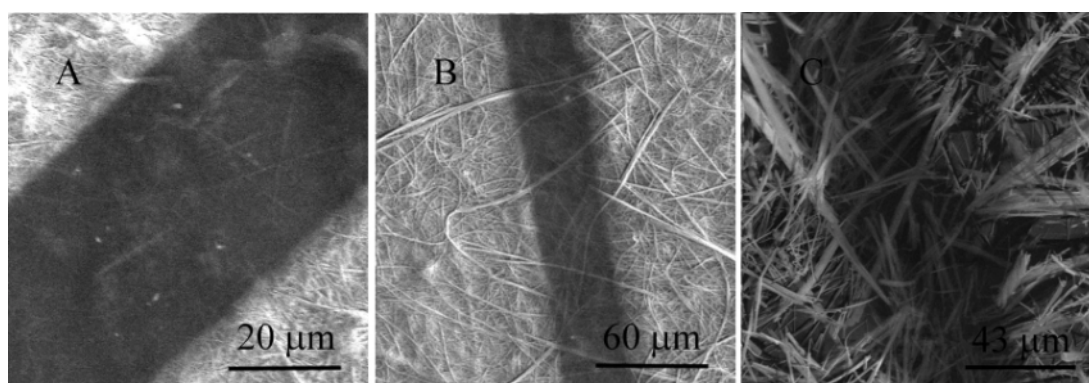




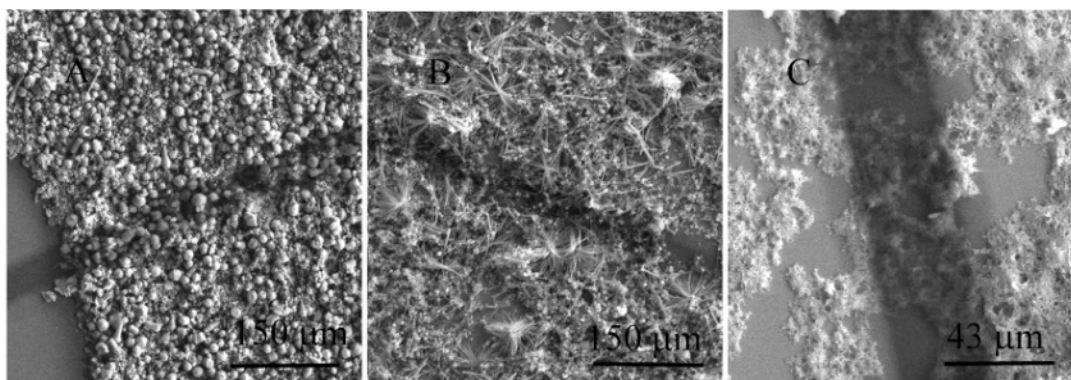
**Figure S5.** Molecular orbital maps of HOMO and LUMO for MPc and  $M[Pc(SO_2CH_3)_8]$  ( $M = 2H, Zn$ ).



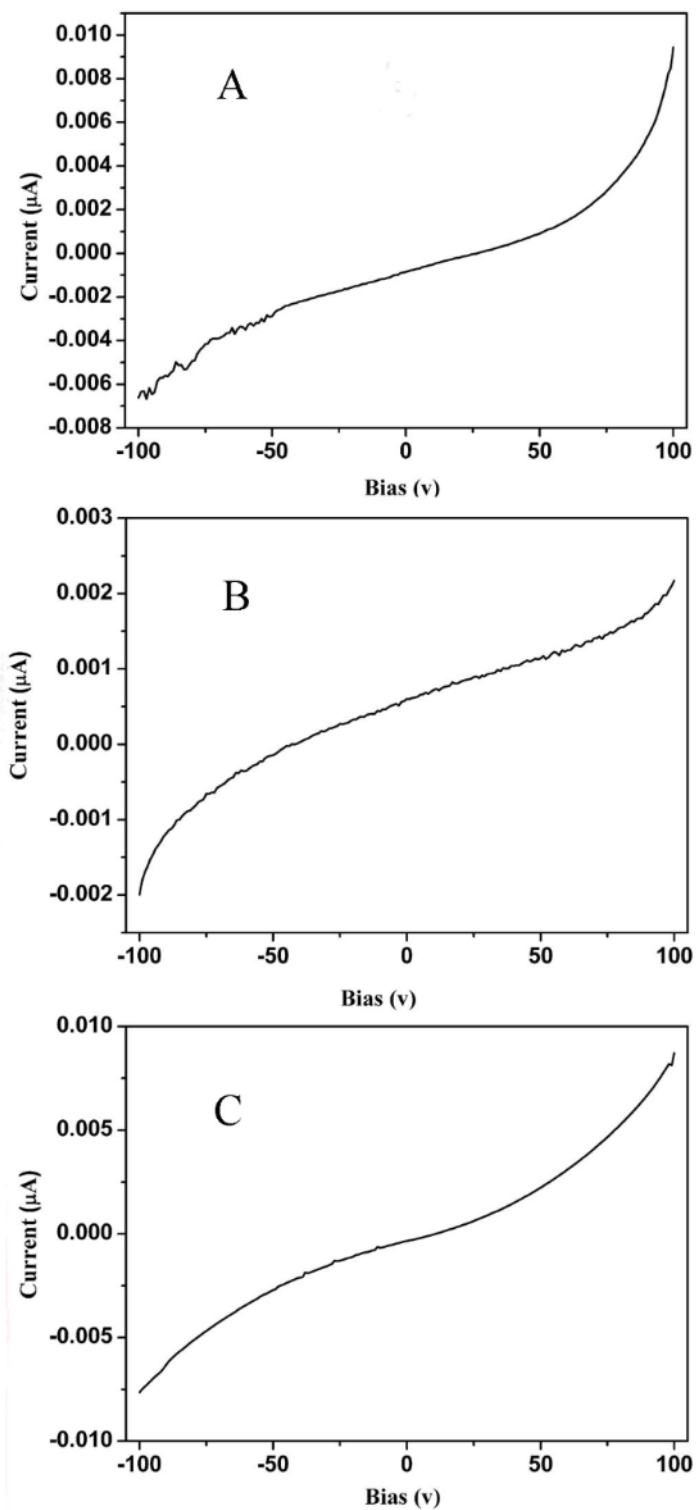
**Figure S6.** Electronic absorption spectra of (A)  $\text{H}_2\text{Pc}(\text{SO}_2\text{C}_6\text{H}_{13})_8$  (**1**) micro-wires (dash line), (B)  $\text{Cu}[\text{Pc}(\text{SO}_2\text{C}_6\text{H}_{13})_8]$  (**2**) micro-wires (dash line), and (C)  $\text{Zn}[\text{Pc}(\text{SO}_2\text{C}_6\text{H}_{13})_8]$  (**3**) micro-wires (dash line) in comparison with those recorded in  $\text{CHCl}_3$  (solid line).



**Figure S7.** SEM images of the two-electrode device fabricated from  $\text{H}_2\text{Pc}(\text{SO}_2\text{C}_6\text{H}_{13})_8$  (**1**) micro-wires (A),  $\text{Cu}[\text{Pc}(\text{SO}_2\text{C}_6\text{H}_{13})_8]$  (**2**) micro-wires (B), and  $\text{Zn}[\text{Pc}(\text{SO}_2\text{C}_6\text{H}_{13})_8]$  (**3**) micro-wires (C) on  $\text{SiO}_2$ .



**Figure S8.** SEM images of the two-electrode devices fabricated from  $\text{H}_2\text{Pc}(\text{SC}_6\text{H}_{13})_8$  micro-spheres (A),  $\text{Cu}[\text{Pc}(\text{SC}_6\text{H}_{13})_8]$  micro-flowers (B), and  $\text{Zn}[\text{Pc}(\text{SC}_6\text{H}_{13})_8]$  three-dimensional network (C) on  $\text{SiO}_2$ .



**Figure S9.**  $I-V$  curves measured on  $\text{CuPc}(\beta\text{-SC}_6\text{H}_{13})_8$  micro-flowers (A),  $\text{H}_2\text{Pc}(\beta\text{-SC}_6\text{H}_{13})_8$  micro-spheres (B) and  $\text{ZnPc}(\beta\text{-SC}_6\text{H}_{13})_8$  three-dimensional network (C).