

## Supporting Information for

### Significant photoelectric conversion properties of multilayer films formed by a cationic zinc phthalocyanine complex and graphene oxide

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#### Preparation of 2(3),9(10),16(17),23(24)-Tetrakis{2-[N'-(N-methyl imidazole)]ethoxy phthalocyaninato}zinc(II) chloride (ImZnPc).

The synthetic route is shown in Scheme S1.

#### Preparation of 4-(2-Chloroethoxy)phthalonitrile (1)

2-chloroethanol (1.6 g, 20 mmol) and 4-nitrophthalonitrile (1.73 g, 10 mmol) were dissolved in dry DMF (50 mL). After stirring for 1 h at room temperature, anhydrous potassium carbonate (2.76 g, 20 mmol) was added portionwise over a period of 2 h. The mixture was stirred continuously for 36 h at room temperature under nitrogen atmosphere. Then it was poured into ice-water and the precipitate was filtered off. The crude product was purified by silica column chromatography with CH<sub>2</sub>Cl<sub>2</sub> as eluent and a pale yellow solid was obtained and dried under vacuum. Yield: 1.29 g (63 %). m.p. 88~90 °C. FT-IR  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3104, 3073 (Ar-H), 2927, 2855 (Aliph. C-H), 2229 (C≡N), 1597, 1556, 1486, 1424, 1294, 1239, 1101, 1026, 975, 884, 839, 677. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>):  $\delta$  8.07 (d, 1H, Ar-H), 7.82 (d, 1H, Ar-H), 7.50 (dd, 1H, Ar-H), 4.46 (t, 2H), 4.01 (t, 2H); Anal. Calcd. for C<sub>10</sub>H<sub>7</sub>ClN<sub>2</sub>O: C, 58.13; H, 3.41; N, 13.56 %. Found: C, 58.25; H, 3.35; N, 13.27 %. FAB-MS (m/z): 207 [M+H]<sup>+</sup>.

#### Preparation of N-methyl-N-(3,4-dicyanophenoxyethyl)imidazolium chloride (2)

N-methylimidazole (0.492 g, 6 mmol) and compound 1 (1.03 g, 5 mmol) were refluxed for 3 h. Then the mixture was washed with ethyl acetate and monitored by TLC until no reactants was left. A white solid was given and dried under vacuum. Yield: 1.35 g (94 %). m.p. 229~230 °C. FT-IR  $\nu_{\text{max}}/\text{cm}^{-1}$ : 3154, 3103, 3022 (Ar-H), 2977, 2927, 2856 (Aliph. C-H), 2229 (C≡N), 1592, 1496, 1415, 1314, 1258, 1162, 1086, 1041, 960, 910, 853, 728. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>):  $\delta$  9.25 (s, 1H, Imidazole-H), 8.11 (d, 1H, Ar-H), 7.85 (d, 1H,

Ar-H), 7.83 (t, 1H, Imidazole-H), 7.74 (t, 1H, Imidazole-H), 7.52 (dd, 1H, Ar-H), 4.66 (t, 2H, CH<sub>2</sub>), 4.54 (t, 2H, CH<sub>2</sub>), 3.88 (s, 3H, CH<sub>3</sub>). Anal. Calcd. for C<sub>14</sub>H<sub>13</sub>ClN<sub>4</sub>O: C, 58.24; H, 4.54; N, 19.40 %. Found: C, 58.48; H, 4.71; N, 19.16 %. FAB-MS (m/z): 253 [M-Cl]<sup>+</sup>.

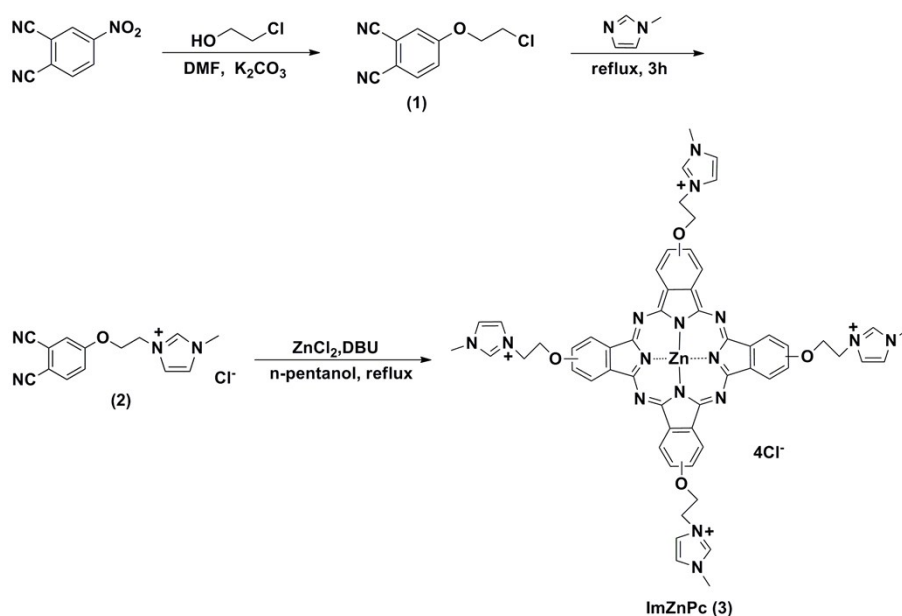
### **Preparation of 2(3),9(10),16(17),23(24)-Tetrakis{2-[N'-(N-methylimidazole)]ethoxy phthalocyaninato} zinc(II) chloride (ImZnPc) (3)**

A mixture of compound **2** (1.16 g, 4 mmol), ZnCl<sub>2</sub> (136 mg, 1 mmol), n-pentanol (8 mL) and 1,8-diazabicyclo[5.4.0]undec-7-ene(DBU) (0.9 mL, 6 mmol) was stirred at 120 °C for 24 h under nitrogen atmosphere. The solvents were removed in vacuo and the residue was dissolved in methanol, the product was separated by filtration and the filtrate was concentrated in vacuo. After concentrating, a dark green product was washed with ethyl acetate, CH<sub>2</sub>Cl<sub>2</sub>, acetone and then dried. Yield: 260 mg (21 %). m.p. >300 °C. FT-IR (ν<sub>max</sub>/cm<sup>-1</sup>): 3154, 3094 (Ar-CH), 2974, 2924, 2869 (Aliph. CH), 1610, 1490, 1390, 1336, 1236, 1090, 1041, 881, 746. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>): δ 9.47 (m, 4H, Imidazole-H), 9.29 (m, 4H, Imidazole-H), 8.90 (d, 4H, Imidazole-H), 8.08 (s, 4H, Ar-H), 7.85 (s, 8H, Ar-H), 4.96 (d, 16H, CH<sub>2</sub>CH<sub>2</sub>), 3.99 (s, 12H, CH<sub>3</sub>). Anal. Calcd. for C<sub>56</sub>H<sub>52</sub>Cl<sub>4</sub>ZnN<sub>16</sub>O<sub>4</sub>: C, 55.12; H, 4.30; N, 18.36 %. Found: C, 55.62; H, 4.02; N, 18.12 %. TOF MS ES<sup>+</sup> (m/z): 573.9 [(M-2Cl)/2]<sup>+</sup>, 370.9 [(M-3Cl)/3]<sup>+</sup>, 269.5 [(M-4Cl)/4]<sup>+</sup>. UV-Vis (CH<sub>3</sub>OH): λ<sub>max</sub>, nm (log ε), 674 (5.19), 608 (4.50), 348 (4.90).

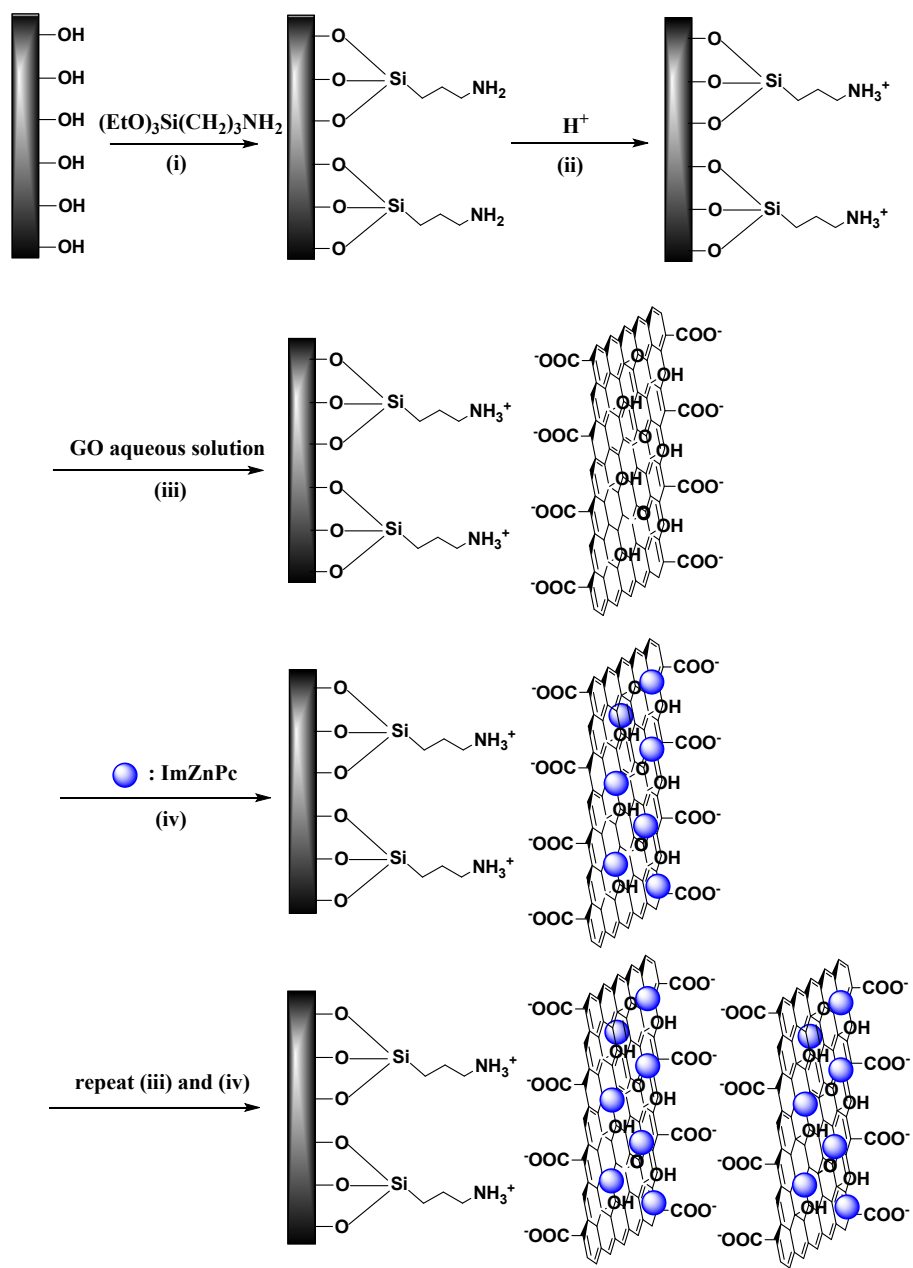
### **Preparation of Graphite oxide (GO)**

The graphite powder (4 g) and NaNO<sub>3</sub> (3.2 g) were introduced to concentrated H<sub>2</sub>SO<sub>4</sub> (98%, 135 mL) in an ice-bath. KMnO<sub>4</sub> (18 g) was added gradually with stirring, so that the temperature of the suspension was controlled below 20 °C. After removing the ice-bath, the suspension was stirred at 35 °C for 30 min and then maintained at room temperature for 5 days. After oxidation, the suspension was diluted to 700 mL with stirring by adding hot deionized water. The reaction was terminated by adding H<sub>2</sub>O<sub>2</sub> (3 wt % aqueous solution) dropwise while stirring at room temperature until the suspension turned bright yellow. In order to remove the ions of oxidant and other inorganic impurity, the resultant suspension was purified by repeating of the following procedure cycle many times: centrifugation, remove the supernatant liquid, addition of 500 mL of warm water,

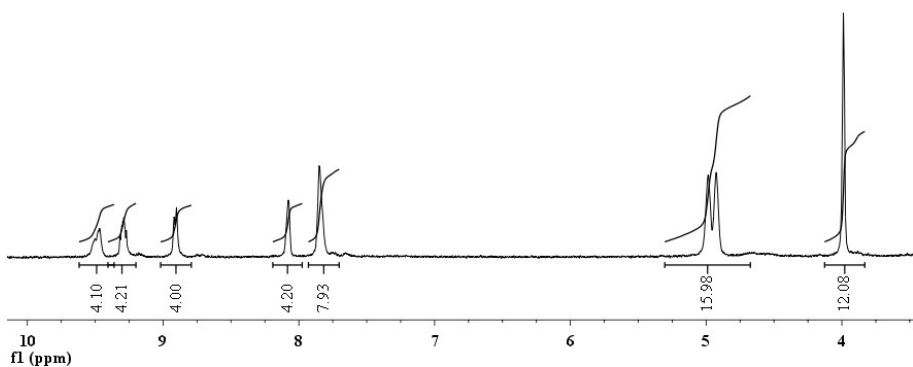
and dispersing the solid using bath ultrasonication for 30 min of a power of 140 W, until the supernatant liquid was colourless,  $\text{pH} \approx 7$  and no  $\text{SO}_4^{2-}$  ion was detected in it by adding  $\text{Ba}^{2+}$  ion. The dry GO was obtained by centrifugation followed by drying at  $40\text{ }^\circ\text{C}$  for 24 h under vacuum. The dry GO and graphite powders were directly used in the X-ray diffraction (XRD) analysis respectively (Figure S2). The XRD analysis exhibits that the interlay space of GO ( $2\theta = 10.7^\circ$ , 0.828 nm) is larger than that of the pure graphite ( $2\theta = 26.6^\circ$ , 0.335 nm), as a result of the introduction of oxygenated functional groups on carbon sheets.



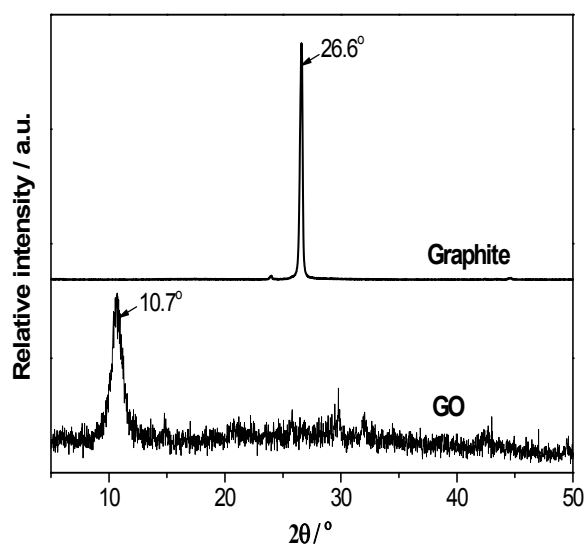
**Scheme S1.** Synthetic route of complex ImZnPc.



**Scheme S2.** Schematic illustration of Fabrication Procedure of Quartz or ITO/(GO/ ImZnPc)<sub>n</sub> Films



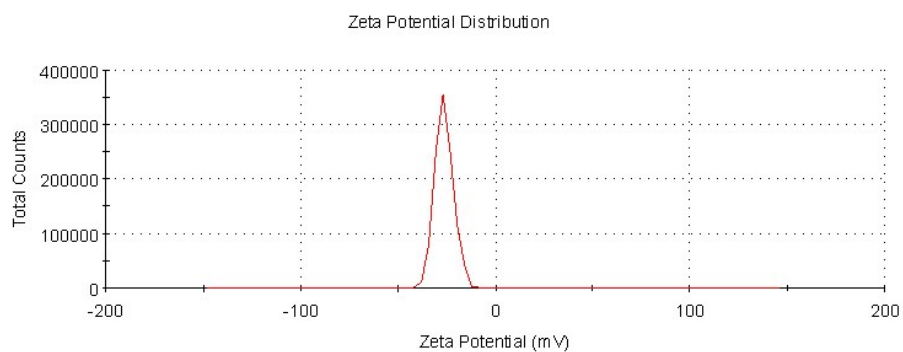
**Fig. S1**  $^1\text{H}$  NMR spectrum of ImZnPc in  $\text{DMSO-}d^6$ .



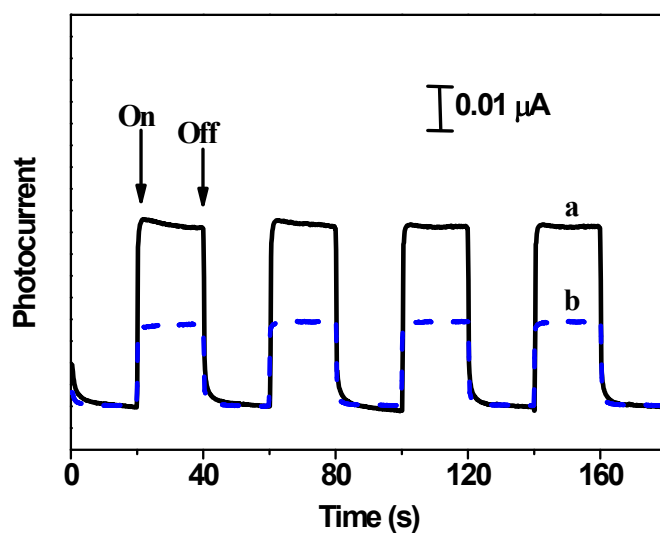
**Fig. S2** The XRD patterns of GO and Graphite.



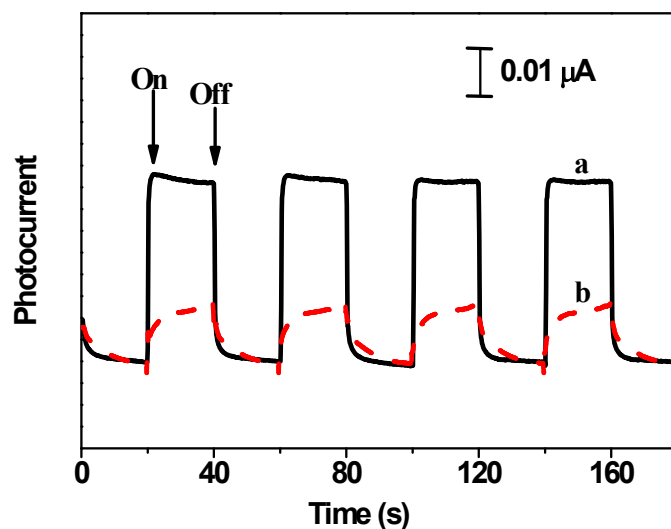
**Fig. S3** The TEM image of GO dispersion in water.



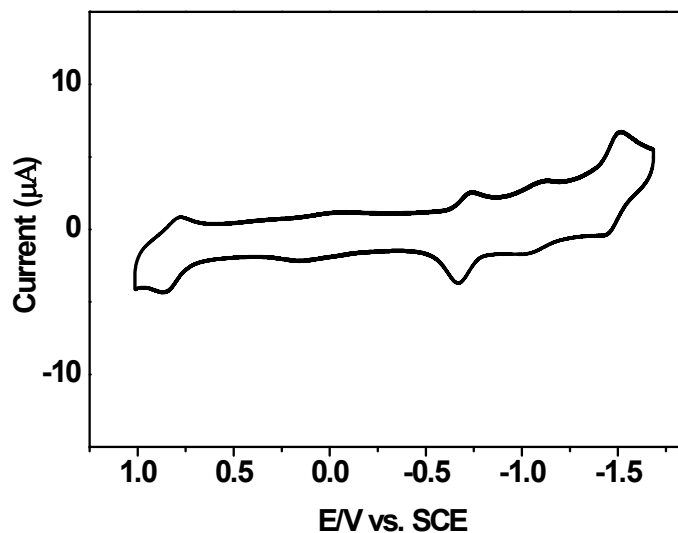
**Fig. S4** Zeta potential distributions of GO.



**Fig. S5** Photocurrent responses for ITO/(GO/ImZnPc)<sub>1</sub> film electrodes at an applied potential of 0 V vs SCE. Conditions: 100 mW/cm<sup>2</sup> simulated sunlight; electrode area = 0.25 cm<sup>2</sup>; supporting electrolyte: 0.1 M Na<sub>2</sub>SO<sub>4</sub> (a) air-equilibrated; (b) in the presence of the electron donor H<sub>2</sub>Q (1 × 10<sup>-4</sup> M).



**Fig. S6** Photocurrent responses for ITO/(GO/ImZnPc)<sub>1</sub> film electrodes at an applied potential of 0 V vs SCE. Conditions: 100 mW/cm<sup>2</sup> simulated sunlight; electrode area = 0.25 cm<sup>2</sup>; supporting electrolyte: 0.1 M Na<sub>2</sub>SO<sub>4</sub> (a) air-equilibrated; (b) deoxygenated with N<sub>2</sub>.



**Fig. S7** Cyclic voltammograms of ImZnPc ( $5 \times 10^{-4}$  mol · dm<sup>-3</sup>) in 0.1 mol · dm<sup>-3</sup> Bu<sub>4</sub>NPF<sub>6</sub>/DMSO electrolyte system.