

## Supporting Information

### Large-Scale, Ultra-Dense and Vertically Standing Zinc Phthalocyanine

### $\pi\pi$ -Stacks as the Hole-Transporting Layer on the ITO Electrode \*\*

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## 1. General Information.

All the chemical reagents were purchased reagent-grade from Acros or Aldrich Corporation and were used without further purification unless otherwise stated. All solvents were purified using standard procedures.

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker AVANCE 400 using tetramethylsilane (TMS;  $\delta = 0$  ppm) as an internal standard. Mass spectra (MALDI-TOF-MS) were determined on a Bruker BIFLEX III mass spectrometer. FT-IR spectra were recorded on a TENSOR-27 spectrometer using KBr pellets. UV-vis absorption was recorded on a Hitachi U-3010 spectrophotometer. XRD measurements were performed by using a X-ray powder diffraction (XRD, BRUKER D8 Focus) with Cu K $\alpha$  as the radiation source ( $\lambda = 1.5418 \text{ \AA}$ ) and operated at 40 kV and 40 mA.

The SEM was recorded with a field emission scanning electron microscope (FESEM, Hitachi S-4800), operating at an accelerating voltage of 1.5 kV. TEM measurements were performed on a JEOL JEM-2011 electron microscope, operating at an accelerating voltage of 200 kV. The Atomic Force Microscopy (AFM) and conductive -AFM (c-AFM) measurements were performed with Dimension Icon Atomic Force Microscope with ScanAsyst in tapping mode and fixed point conductive atomic force microscopy Mode.

The electrochemical measurements were carried out in a solution of potassium ferricyanide (2 mM  $\text{K}_3\text{Fe}(\text{CN})_6$ , 1 M  $\text{KNO}_3$ ) in water with a computer-controlled Zennium electrochemical workstation. The obtained ITO, a Pt wire, and an Ag/AgCl electrode were used as the working, counter, and reference electrodes, respectively. The electrochemical cyclic voltammetry (CV) for characterizations of the HOMO energy level of ZnPC was performed using a Zahner IM6e electrochemical workstation in a 0.1 mol/L tetrabutylammonium hexafluorophosphate ( $\text{Bu}_4\text{NPF}_6$ ) dimethylformamide (DMF) solution with a scan speed at 0.1 V/s.

X-ray photoelectron spectroscopy (XPS) data were obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300W AlK $\alpha$  radiation. The base pressure was about  $3 \times 10^{-9}$  mbar. The binding energies were referenced to the C1s line at 284.8 eV from adventitious carbon.

## 2. Synthetic procedure of the zinc phthalocyanine (ZnPc).

The tetra-amino ZnPc was prepared by following the literature methods.<sup>[1]</sup> Then, tetra-amino ZnPc (0.6 g, 0.79 mmol) was dissolved in 50mL tetrahydrofuran (THF). Under an ice-water bath, methyl 4-chloro-4-oxobutanoate (0.53 g, 3.48 mmol) and N, N-diisopropylethylamine (0.45g, 3.5 mmol) were added. After 30min, the reaction mixture was stirring at room temperature for 30min. The solvent was removed and the residue was purified by neutral- $\text{Al}_2\text{O}_3$  column chromatography ( $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}=100:1$ ). The product tetra 4-methoxy-4-oxobutanamido ZnPc was obtained (0.44 g, 0.40 mmol, yield 51%). After that, tetra 4-methoxy-4-oxobutanamido ZnPc (0.40 g, 0.37 mmol) was dissolved in a 50mL mixture of THF and MeOH (v/v=1:1). To the reaction mixture, 2% NaOH aqueous solution (1mL) was added. The reaction mixture was stirring at 60 $^\circ\text{C}$  over night. The most solvent (40mL) was removed. The residue was acidized by 1M HCl to pH=4, then 80mL water was added. Dark green precipitate was appeared, filtered off and washed by water to give the final product, tetra 3-carboxypropanamido ZnPc (0.32 g, 0.31 mmol, yield 83%).  $^1\text{H}$  NMR (400MHz, DMSO,  $\delta$ (ppm)): 10.83 (d, 4H,  $J=12\text{Hz}$ , NH), 9.75 (d, 4H,  $J=16 \text{ Hz}$ , ArH), 9.23(s, 4H, ArH), 8.32 (d, 4H,  $J=16 \text{ Hz}$ , ArH), 2.88 (t, 8H,  $J=4 \text{ Hz}$ ,  $\text{CH}_2$ ), 2.75 (t, 8H,  $J=4 \text{ Hz}$ ,  $\text{CH}_2$ );  $^{13}\text{C}$  NMR (100MHz, DMSO- $d_6$ ): 174, 170, 152, 145, 141, 138, 122, 120, 112, 31, 29; IR  $\nu_{\text{max}}$  (KBr): 3547, 3337, 3075, 2951, 2865, 1711, 1678 , 1511, 1414, 1369, 1260, 1107, 662  $\text{cm}^{-1}$ ; MALDI-TOF MS(m/z):  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{48}\text{H}_{36}\text{N}_{12}\text{O}_{12}\text{Zn}$ , 1037.19; found 1037.20. HR-ESI MS (m/z):  $[\text{M}+\text{H}]^+$  calcd

for  $C_{48}H_{36}N_{12}O_{12}Zn$ , 1037.19; found 1037.19. UV-Vis (DMF,  $1 \times 10^{-4}$  mol/L)  $\lambda_{max}$  (nm) and  $\epsilon$  ( $L \cdot mol^{-1} \cdot cm^{-1}$ ): 294 ( $0.285 \times 10^{-5}$ ), 353 ( $0.657 \times 10^{-5}$ ), 622 ( $0.369 \times 10^{-5}$ ), 688 ( $1.118 \times 10^{-5}$ ).

### 3. The cleaned procedure of the indium tin oxide (ITO) glass.

The indium tin oxide (ITO) glass was precleaned, respectively, with deionized water, acetone and isopropanol and treated in a Novascan PSD-ultraviolet-ozone chamber for 30 min.

### 4. The prepare procedure of the amorphous ZnPc film device.

An Au electrode device as show in **Figure S5** was prepared by vacuum deposition of Au on a Cr coated Si substrate. Then a 0.1 mM ZnPc solution (in MeOH) was dropwise on the device. After the solvent was completely evaporated, the device was dried under vacuum for about 30 minutes.

### 5. Estimations of the conductivity of the ZnPc nanorods using the Hertz's model.<sup>[2]</sup>

The conductivity ( $\sigma$ ) of the nanorod is calculated using the following Eq.:

$$\sigma = IL/(VS) \quad (1)$$

Where,  $L$  is the height (e.g. length) of the ZnPc nanorod and  $S$  the effective cross-sectional area of the conductive part. The radius of the effective cross-sectional area ( $S$ , assumed to be circular),  $\rho$ , is estimated from Eq. (2) by following the Hertz's model (Figure 3b in the main text):

$$\rho = \left( \frac{3 \cdot F \cdot R}{4 \cdot E^*} \right)^{1/3} \quad (2)$$

Where,  $F$  is the applied force,  $R$  the tip radius (about 20 nm according to the data provided by the manufacturer),  $F$  the loading force applied by the AFM tip ( $F = \text{setpoint (V)} \times \text{deflection sensitivity (nm/V)} \times \text{spring constant (N/m)} = 2V \times 100 \text{ nm/V} \times 2.8 \text{ N/m} = 560 \text{ nN}$ ) and  $E^*$  the effective elasticity modulus determined by  $1/E^* = 1/E_{tip} + 1/E_{ZnPc}$ . We assume that the elasticity modulus for the ZnPc nanorod is similar to that of the common organic polymer materials, about 2 Gpa, and that of the mixture of MPc and polymers, about 2.5-4 Gpa (unfortunately, to the best of our knowledge, there are no measurements of the mechanical properties for pure MPc derivatives). The  $E_{tip}$  is relative to the metal of Pt/Ir, in the order of  $10^2$  Gpa normally, for example, 169 GPa for Pt. Therefore,  $1/E^* \approx 1/E_{ZnPc}$ . According to the values of  $R$  (20 nm),  $F$  (560 nN) and  $E^*$  (herein, we select the value of 2 GPa), the contact radius of  $\rho$  is estimated as  $\sim 16$  nm. This yields an effective  $S$  value of  $800 \text{ nm}^2$ . The length of the nanorod ( $L$ ) is estimated from section analysis of AFM height sensor data, as shown in Figure S4. Applying this effective  $S$  and  $L$  values to Eq. (1), the conductivity is then calculated and listed in Table S1.

### 6. Estimation of the hole mobilities of the ZnPc nanorods following the Space charge limited currents (SCLC) semi-empirical equation measured with c-AFM.<sup>[3]</sup>

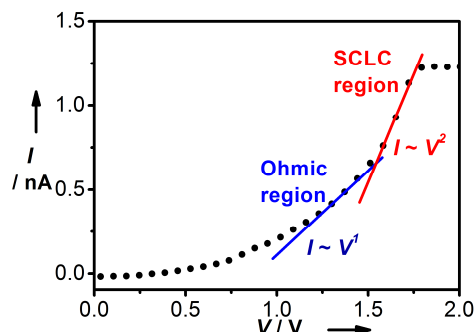
$$J = \alpha \epsilon \epsilon_0 \mu e^{0.89\gamma(VL)^{1/2}} \frac{V^2}{L^3} \delta \left( \frac{L}{d} \right)^{1.6 \pm 0.1} \quad (3)$$

The  $\alpha$  in Eq. (3) is the prefactor ( $\alpha = 8.2$ ),  $\epsilon_0$  the permittivity of free space ( $\epsilon_0 = 8.85419 \times 10^{-12} \text{ F/m}$ ),  $\epsilon$  the permittivity of ZnPc film ( $\epsilon = 10 \text{ F/m}$ )<sup>[4]</sup>,  $\delta$  an empirical dimensionless parameter ( $\delta = 7.8$ ),  $d$  the diameter of the tip-substrate contact area ( $d = 32 \text{ nm}$ ),  $\gamma$  expresses the apparent field dependence (or charge density dependence) of the mobility,  $\mu$  the charge

carrier mobility,  $V$  the applied voltage,  $J$  the average current density at the AFM tip, and  $L$  the lengths of the ZnPc nanorods.

After natural logarithm processing of Eq. (3), a transformation formula can be got as:

$$\ln\left(\frac{JL^{1.4}d^{1.6}}{V^2}\right) = 0.89\gamma\left(\frac{V}{L}\right)^{1/2} + \ln(\alpha \varepsilon \varepsilon_0 \mu \delta) \quad (4)$$



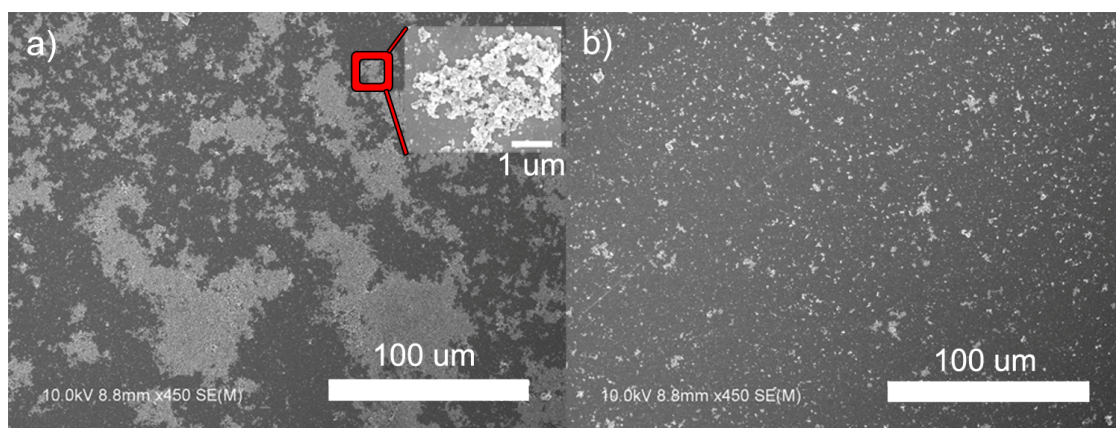
In the case of the c-AFM, the measured  $I$ - $V$  curve (As show in the figure above) shows ohmic behavior at low voltage bias, with the current density varying linearly with  $V$  (blue line area), whereas at the high voltage, sudden charge injection induces SCLC behavior with  $I \sim V^2$  (red line area).

We extract the data of the SCLC region, with  $\left(\frac{V}{L}\right)^{1/2}$  for the X axis to  $\ln\left(\frac{JL^{1.4}d^{1.6}}{V^2}\right)$  for the Y axis, drawing and linear fit gives out a straight line. The intercept of the line is  $\ln(\alpha \varepsilon \varepsilon_0 \mu \delta)$ , and then the probably value of the mobility ( $\mu$ ) can be calculated (Figure S7).

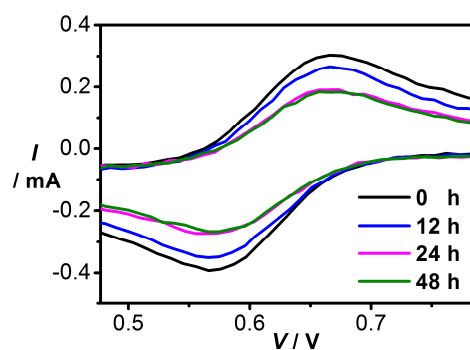
## 7. Fabrications and Characterizations of organic Solar Cells (OSCs).

The ZnPc OSC devices were fabricated with configurations of ITO/densely nanorod-arrayed ZnPc film (av. 36 nm)/poly-(3-hexyl) thiophene (P3HT): [6, 6]-phenyl-C<sub>61</sub>-butyric acid methyl ester (PC61BM)/Ca/Al. A 1,2-dichlorobenzene solution of P3HT/PCBM (40 mg/mL) spin-coated on the surface of the densely nanorod-arrayed ZnPc film to form a photoactive layer (ca. 200nm). Then, the Ca/Al cathode was deposited on the photoactive layer by the vacuum evaporation (ca. 20/60 nm). The effective area of one cell is 6 mm<sup>2</sup>. The current-voltage ( $I$ - $V$ ) measurement of the devices was conducted on a computer-controlled Keithley 2400 Source Measure Unit. A xenon lamp with AM1.5 filter was used as the white light source, and the optical power at the sample was 100 mW/cm<sup>2</sup>. EQE measurements were carried out on an oriel IQE 200 (Newport). The conventional OSC devices were fabricated with configurations of ITO / PEDOT: PSS/P3HT/PCBM/Ca/Al. A thin layer (ca. 30 nm) of poly (3, 4-ethylene- dioxythiophene): poly (styrenesulfonate) (PEDOT: PSS, Baytron P VP AI 4083, Germany) was spin-coated onto the ITO glass with spin-coating speed of 2000 rpm and baked at 150°C for 10 min. Other steps are the same as the above mentioned.

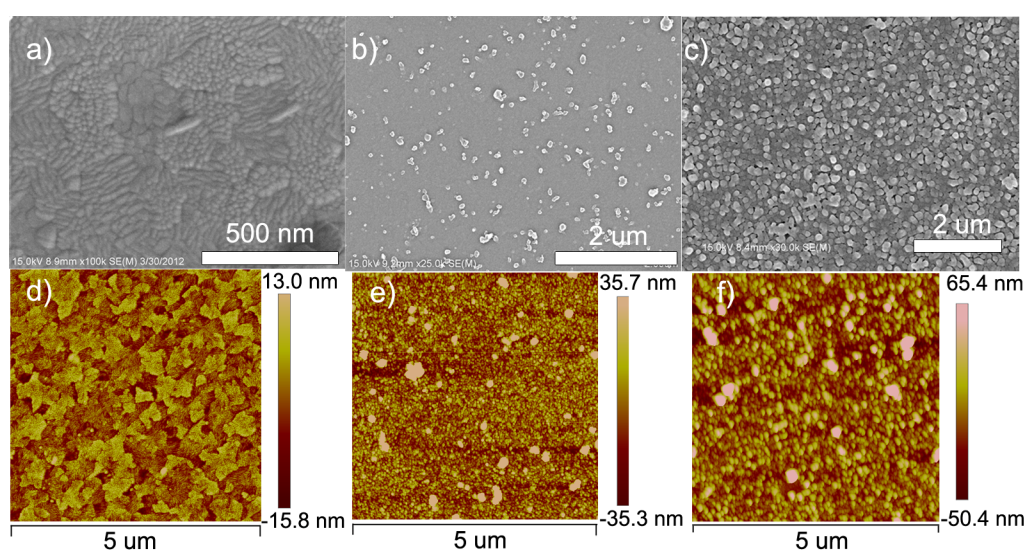
## 8. Supporting figures.



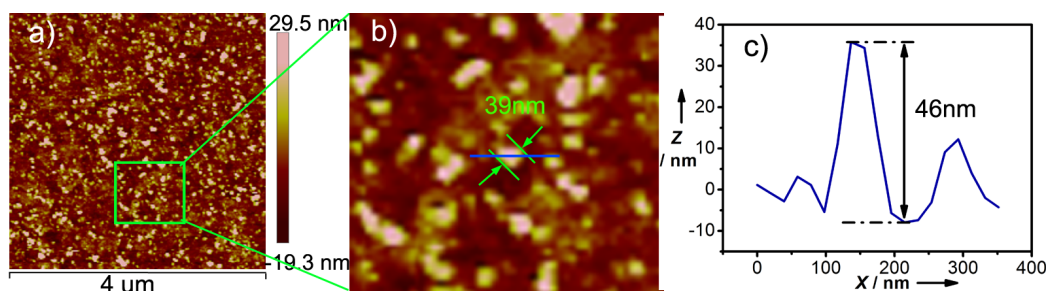
**Figure S1.** SEM images of a) ZnPc nanofibers randomly precipitating on the surface of the nanorod-arrays, b) after sonication treatment for 5 seconds, showing that most of the nanofibers are removed.



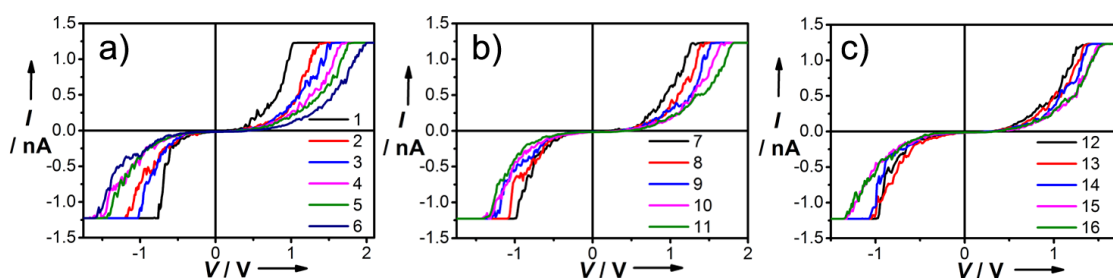
**Figure S2.** Cyclic voltammograms (CV) of the self-assembled single molecular layer of ZnPc on the ITO substrate after reacting for different time from 0 h to 48 h. The CVs were carried out in an aqueous solution of potassium ferricyanide (2 mM  $K_3Fe(CN)_6$ , 1 M  $KNO_3$ ) with a scan rate of 100mV/s.



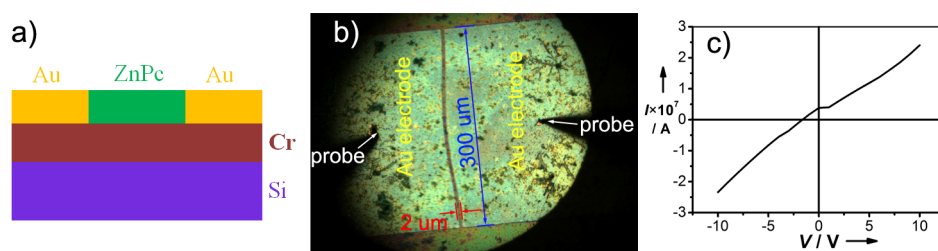
**Figure S3.** SEM and AFM images of the ZnPc nanorod-arrays formed at different immersing time: a) and d) 0 day (e.g. the bare ITO), b) and e) 2 days, c) and f) 4 days.



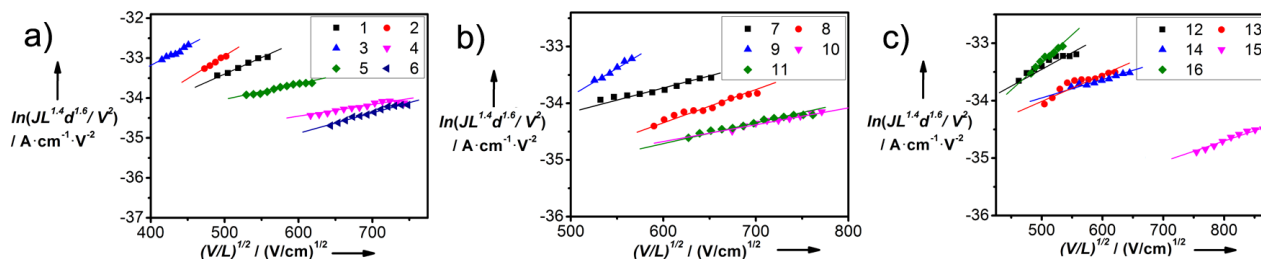
**Figure S4.** a) AFM image of the sparse nanorod-arrayed ZnPc film. b) Enlargement of the green pane area of the image a), getting the ZnPc nanorod's diameter by the tape mode. c) The section analysis (the blue line at b)) of AFM height sensor data, giving the height (e.g. length) of the nanorod.



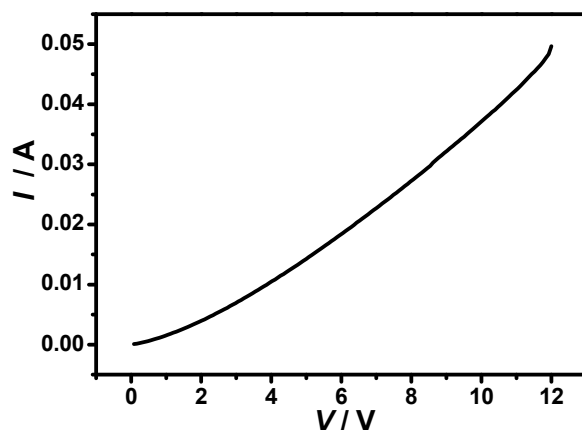
**Figure S5.** The  $I$ - $V$  curve of the c-AFM SCLC measurements for the ZnPc nanorods of 1~6 a), 7~11 b) and 12~16 c), respectively. Test temperature is 25°C.



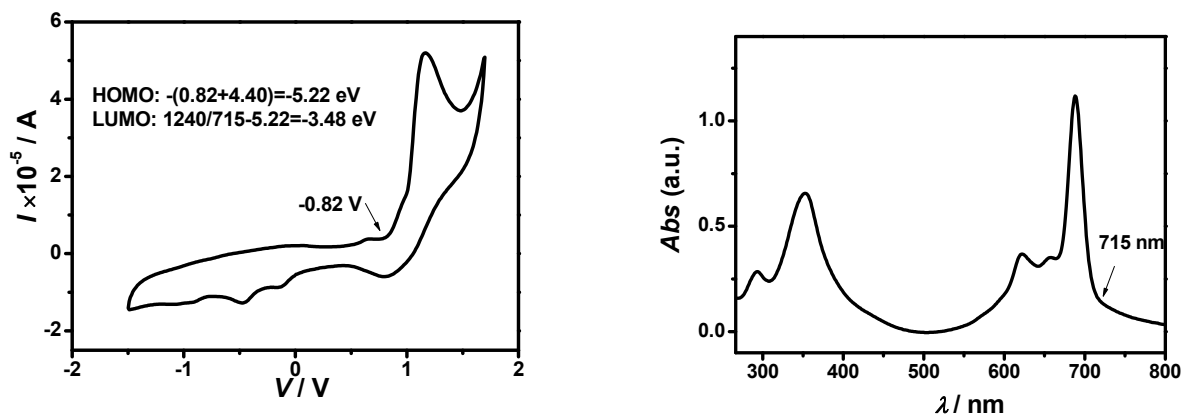
**Figure S6.** Two-terminal measurements on bulk thin film sample of ZnPc under the air condition and room temperature. a) The device structure, b) the groove microscope figure, and c) the  $I$ - $V$  curve of the device, recorded with a Keithley 4200 SCS and a Micromanipulator 6150 probe station under the air condition and at room temperature. The groove's length: 300 μm, width: 2 μm, height: 70 nm. The conductivity is calculated to  $2.0 \times 10^{-5} \text{ S}\cdot\text{cm}^{-1}$ . Test temperature is 25°C.



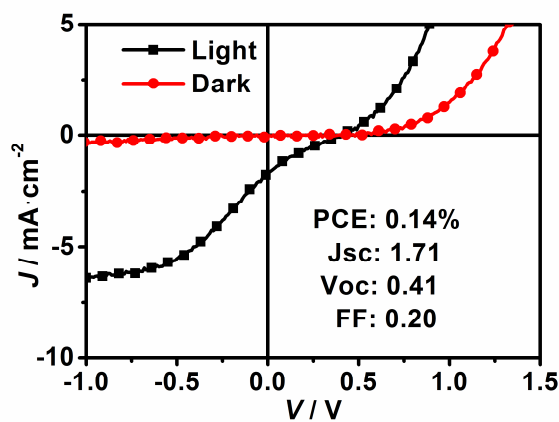
**Figure S7.** The  $J$ - $V$  curve extracted from the SCLC region of the  $I$ - $V$  curves (Figure S5) measured from the ZnPc nanorods of 1~6 a), 7~11 b) and 12~16 c), respectively. Test temperature is 25°C.



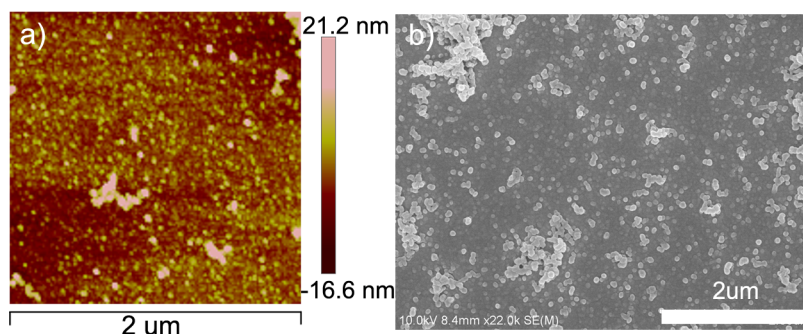
**Figure S8.** The typical  $I$ - $V$  curve of the amorphous ZnPc film (av. 1000 nm) measured using SCLC method with the device configuration of ITO/PEDOT:PSS/the amorphous ZnPc film / Au (60 nm). Such a curve does not show any SCLC regions within the experimental voltage range, thus we can not get the hole mobility of the amorphous ZnPc film.



**Figure S9.** The CV of ZnPc in the 0.1 M  $\text{Bu}_4\text{NPF}_6$  DMF solution at 0.1 V/s, with Ag/AgCl as the reference electrode (Left). Noted that the LUMO energy level was estimated from the absorption spectrum, in which the off-set in the long-wavelength side is about 715 nm (Right).



**Figure S10.** The  $J$ - $V$  curve of a typical OSC with the configuration of ITO/the amorphous ZnPc film (av. 40 nm)/ P3HT:PC61BM (200 nm)/Ca (20 nm)/Al (60 nm).



**Figure S11.** a) A typical AFM image of the 8 nm thick nanorod-arrayed ZnPc film on the ITO substrate, showing the un-matured deposition of the thinner film and rough surface. b) A typical SEM image of the 60 nm thick, densely nanorod-arrayed ZnPc film, showing the un-removed, disordered ZnPc nanofibers randomly precipitating on the surface.

## 9. Supporting table.

**Table S1.** The data of the 16 ZnPc nanorods determined by c-AFM measure

| No. | Height<br>[nm] | Diameter<br>[nm] | $\sigma$<br>[S·cm <sup>-1</sup> ] | $\mu$<br>[cm <sup>2</sup> ·V <sup>-1</sup> ·s <sup>-1</sup> ] |
|-----|----------------|------------------|-----------------------------------|---|
| 1   | 32.7           | 41.2             | 0.00059                           | 0.0045  |
| 2   | 54.3           | 62.1             | 0.0012                            | 0.0064  |
| 3   | 75.0           | 78.1             | 0.0019                            | 0.0075  |
| 4   | 32.7           | 51.6             | 0.00096                           | 0.0019  |
| 5   | 46.0           | 39.5             | 0.0014                            | 0.0029  |
| 6   | 35.4           | 52.7             | 0.0012                            | 0.0013  |
| 7   | 29.8           | 41.5             | 0.00066                           | 0.0029  |
| 8   | 29.8           | 54.5             | 0.00073                           | 0.0020  |
| 9   | 44.6           | 59.9             | 0.0012                            | 0.0044  |
| 10  | 26.8           | 40.5             | 0.00076                           | 0.0016  |
| 11  | 30.1           | 39.4             | 0.00091                           | 0.0014  |
| 12  | 38.9           | 44.6             | 0.00079                           | 0.0052  |
| 13  | 35.9           | 52.3             | 0.00091                           | 0.0032  |
| 14  | 32.7           | 41.5             | 0.00077                           | 0.0031  |
| 15  | 21.2           | 42.8             | 0.00059                           | 0.0012  |
| 16  | 51.7           | 69.0             | 0.0013                            | 0.0050  |

\*Test temperature is 25°C

## Reference

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