

## Electronic Supplementary Information

### High Performance Inverted Organic Solar Cell with Low Band Gap Small Molecule (p-DTS(FBTTh<sub>2</sub>)<sub>2</sub>) Using Fullerene Derivatives-Doped Zinc Oxide Nano-Film Modified with Fullerene-based Self-Assembled Monolayer as Cathode

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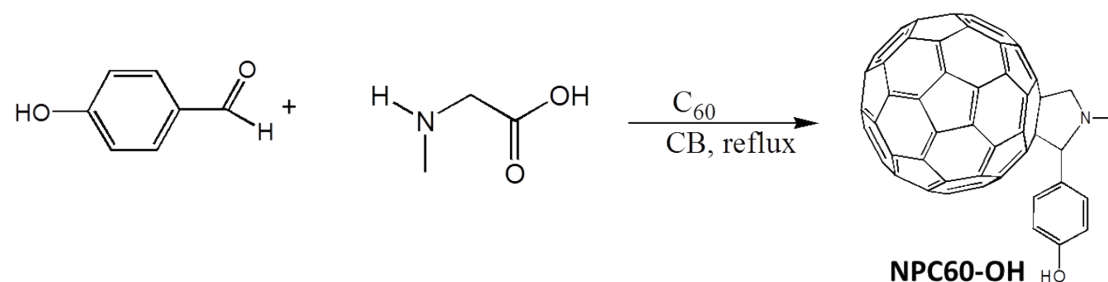
This supporting information includes:

Figure S1 to S4

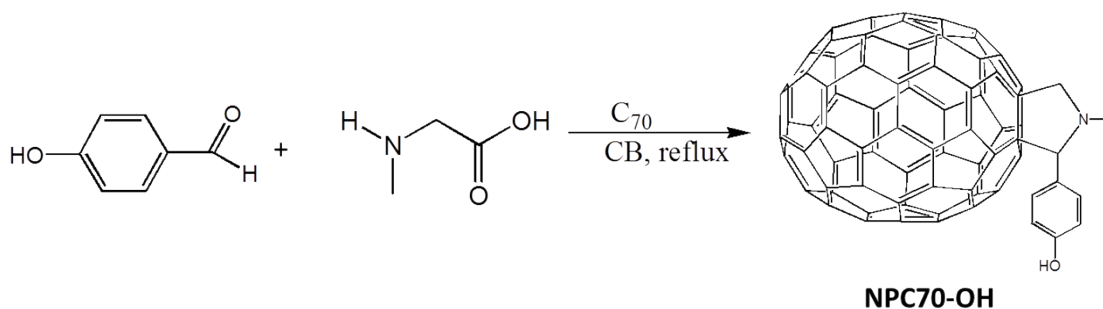
Table S1 to S3

#### Materials

The syntheses of **C60-Substituted Phenol (NPC60-OH (the C60 derivatives))** and **C70-Substituted Phenol (NPC70-OH (the C70 derivatives))** are illustrated in Scheme S1 and Scheme S2 below, respectively.



**Scheme S1.** Synthetic route for C60 derivative of NPC60-OH.



**Scheme S2.** Synthetic route for C70 derivative of NPC70-OH.

### Synthesis of C60-Substituted Phenol (NPC60-OH)

NPC60-OH was synthesized by the procedure similar to the reported procedure<sup>S1</sup>, but the purification steps are different. 4-hydroxybenzaldehyde (0.5 g, 3.5 mmol) and N-methylglycine were dissolved in 120 mL of chlorobenzene in a dried three-necked reaction flask with a magnetic stirring bar and a thermometer under N<sub>2</sub> purging condition at 110 °C. C60 (0.5 g, 0.7 mmol) was added to the stirred solution at room temperature. The reaction was carried out under refluxing temperature at 120 °C with continuously stirring for 1 day. The mixture was cooled down to room temperature and transferred to rotary evaporator for concentrating it to 5-10 mL at about 0.1 torr. After the residue was washed with methanol for several times, and then redissolved in the mixed solvent (THF:Toluene, 1:1, v/v), the resulting solution was concentrated in a rotary evaporator and then reabsorbed on silica gel. The desired compound was purified by silica gel column chromatography with toluene as eluent and then precipitated by acetone. Finally, it was collected by filtration and dried in vacuum oven at 80 °C for more than 20 hr. Total 150 mg NPC60-OH desired compound (yield: 24.6%) was obtained. Structure analysis of NPC60-OH: <sup>1</sup>HNMR (500 MHz, CS<sub>2</sub>:CDCl<sub>3</sub>). δ<sub>H</sub> (ppm): 7.24-7.30 (2H, d), 6.83-6.81 (2H, d), 4.85 (2H, s), 4.78 (1H, broad), 4.72 (1H, s), 2.15 (3H, s). FAB MS calculated C<sub>69</sub>H<sub>11</sub>O<sub>1</sub>N<sub>1</sub>: m/z = 869. Found: m/z 869.

### Synthesis of C70-Substituted Phenol (NPC70-OH)

NPC70-OH was synthesized by the procedure similar to the reported procedure<sup>S1</sup>, but the purification steps are different. 4-hydroxybenzaldehyde (0.5 g, 3.5 mmol) and N-methylglycine were dissolved in 100 mL of chlorobenzene in a dried three-necked reaction flask with a magnetic stirring bar and a thermometer under N<sub>2</sub> purging condition at 110 °C. C70 (0.5 g, 0.6 mmol) was added to the stirred solution at room temperature. The reaction was carried out under refluxing temperature at 120 °C with continuously stirring for 1 day. The mixture was cooled down to room temperature and transferred to rotary evaporator for concentrating it to 5-10 mL at

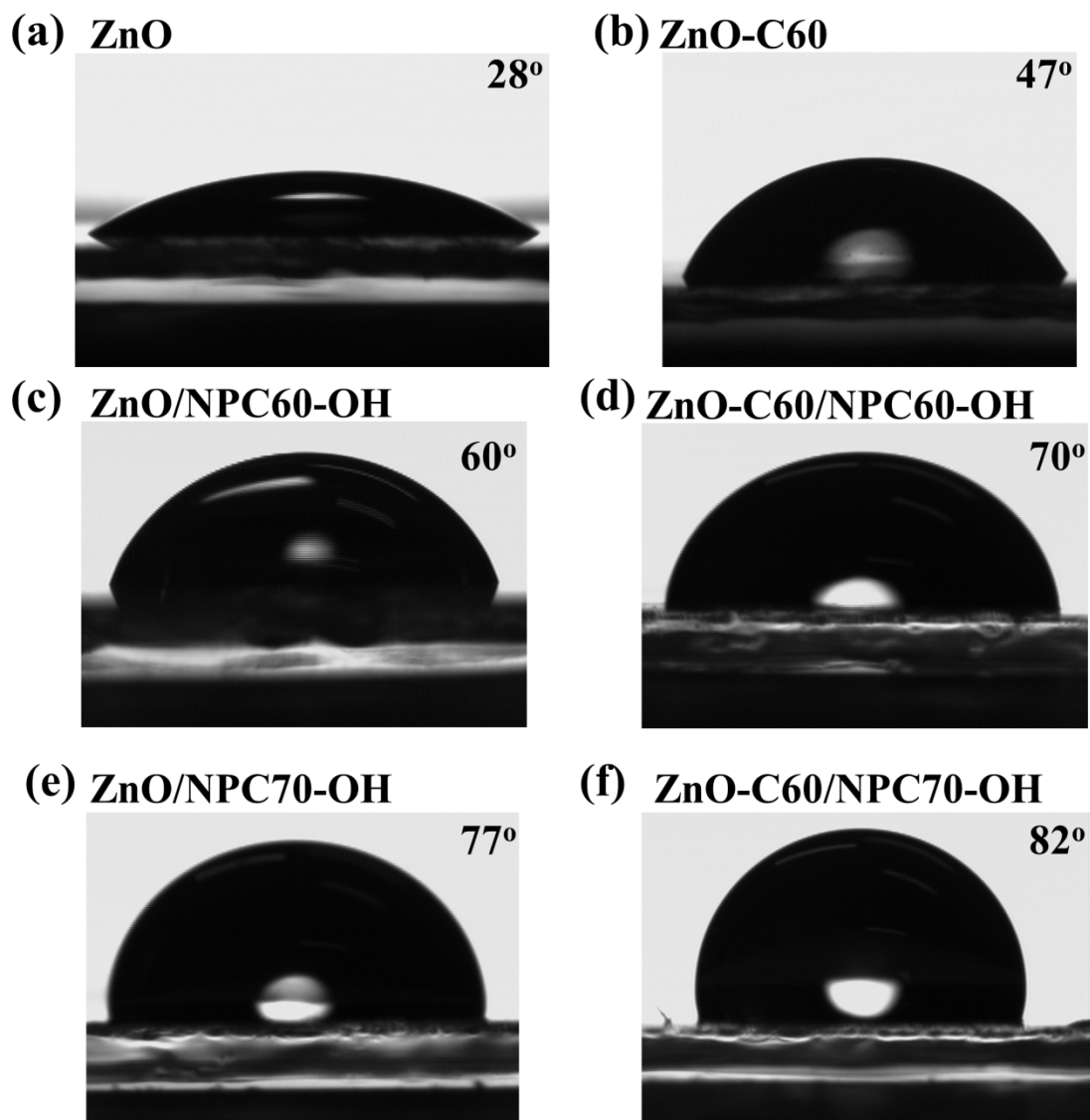
about 0.1 torr. After the residue was washed with methanol for several times, and then redissolved in the mixed solvent (THF: Toluene, 1:1, v/v), the resulting solution was concentrated in a rotary evaporator and then reabsorbed on silica gel. The desired compound was purified by silica gel column chromatography with toluene as eluent and then precipitated by acetone. Finally, it was collected by filtration and dried in vacuum oven at 80 °C for more than 20 hr. Total 110 mg NPC70-OH desired compound (yield: 18.5%) was obtained. Structure analysis of NPC70-OH: <sup>1</sup>HNMR (500 MHz, CS<sub>2</sub>: CDCl<sub>3</sub>). δ<sub>H</sub> (ppm): 7.55 (2H, d), 7.45-7.44 (2H, d), 4.65 (1H, broad), 4.08-4.06 (3H, m), 2.15 (3H, s). FAB MS calculated C<sub>79</sub>H<sub>11</sub>O<sub>1</sub>N<sub>1</sub>: m/z = 989. Found: m/z 989.

### **General measurements and device fabrication and characterization:**

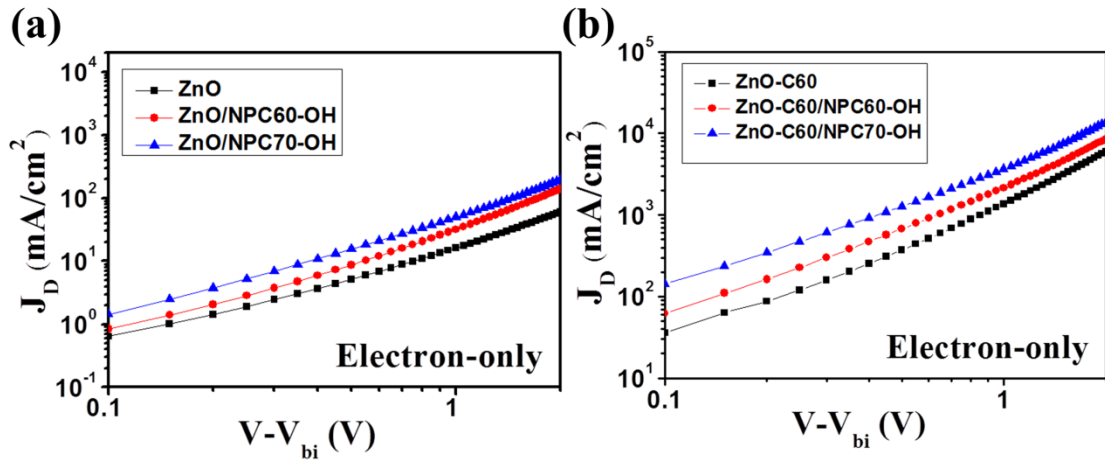
<sup>1</sup>HNMR and <sup>13</sup>CNMR spectra of NPC60-OH and NPC70-OH were recorded on a VARIAN UNITYINOVA 500 NMR in the NSC Regional Instrument Centre at National Tsing Hua University, Taiwan. FAB Mass spectra were also collected using MICROMASS TRIO-2000 in the NSC Regional Instrument Centre at National Chiao Tung University, Taiwan. The thickness of the active layer film, hole transport layer, ZnO and ZnO-C60 film were measured by a Tencor P-10 Surface Profiler. Contact angle with water as a probe was measured using contact angle meter (GBX DIGIDROP). For X-ray photoelectron spectroscopy (XPS) measurements, ZnO and ZnO-C60 film were obtained from spin-coating their precursors on top of ITO glasses followed with sintering in air at 180 °C for 60 min. XPS spectra were obtained with a photoelectron spectroscopy system (VG, MULTILAB 2000) under a base pressure of 1×10<sup>-9</sup> mbar by using monochromatized Mg (Kα) X-rays (hν = 1254.6 eV). Electron mobility was determined using the electron only device ITO/Al/ZnO or ZnO-C60/SAM or without/Al along with the use of single carrier space charge limited current (SCLC) equation for the calculation. The current density in SCLC follows the Mott–Gurney Law by the equation<sup>S2</sup>:  $J = 9\epsilon\epsilon_0\mu(V-V_{bi})^2/8L^3$  where ε<sub>0</sub> is the permittivity of free space, ε is the dielectric constant of the materials, μ is the carrier mobility, V is the applied voltage across device, V<sub>bi</sub> is the build-in voltage, and L is the thickness of the film. Cyclic voltammetric data were obtained using CV instrument analyzer with a conventional three-electrode cell including a platinum foil as the working electrode, another platinum coil as the counter electrode, and Ag/Ag<sup>+</sup> electrode as the reference electrode. For measurement of NPC60-OH and NPC70-OH, the mixed solvent chlorobenzene/THF/acetonitrile (1:1:1, v/v/v) with 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) was used as electrolyte.

**J-V characterization and EQE measurement:**

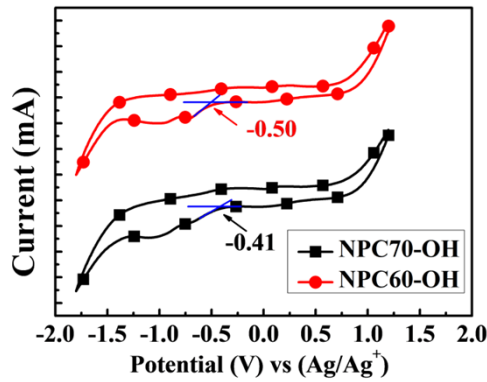
The current-voltage ( $J$ - $V$ ) characteristics of the unencapsulated PSCs were measured in air using a Keithley 2400 source-measure unit and an AM 1.5 G solar simulator (Oriel 94021A, 150 W from Newport). The illumination intensity of 100 mW/cm<sup>2</sup> irradiation was calibrated using a standard monocrystal Si reference cell (Oriel 91150V from Newport) to ensure the accurate light source intensity. The external quantum efficiency (EQE) was conducted using the measurement system (model QE-R) built by Enli Technology Co. Ltd. Same data acquisition system was used for the external quantum efficiency measurement. Under full computer control, light from a 150 W xenon lamp (Oriel, U.S.A.) was focused through a monochromator onto the PSC under testing. The wavelength of the light from the monochromator was increased progressively in the visible region to generate the EQE ( $\lambda$ ) as defined by  $\text{EQE}(\lambda) = 12400(J_{\text{sc}}/\lambda\phi)$ , where  $\lambda$  is the wavelength,  $J_{\text{sc}}$  is short-circuit current density (mA/cm<sup>2</sup>), and  $\phi$  is the incident radiative flux (mW/cm<sup>2</sup>).



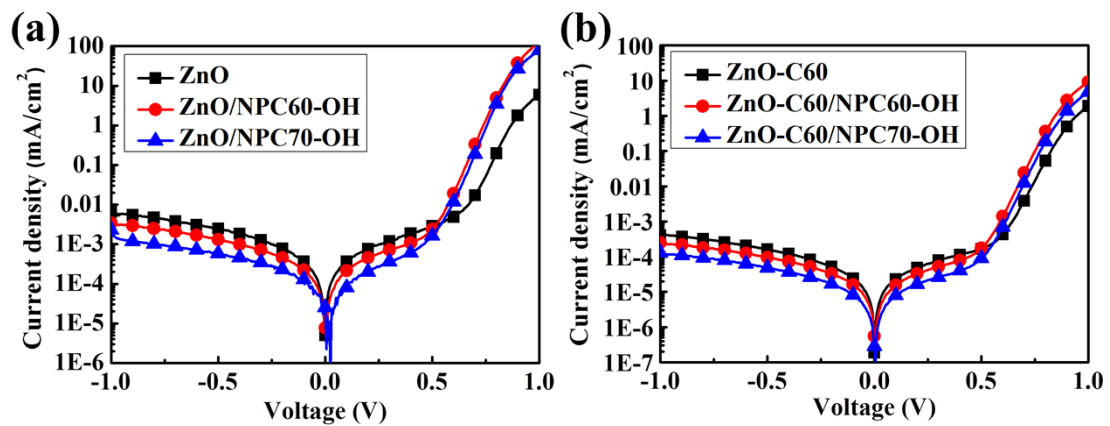
**Figure S1.** The contact angle images by dropping DI water on the substrates pre-cleaned by CB/THF (1:1, v/v): (a) ITO/ZnO (40 nm), (b) ITO/ZnO-C60 (40 nm), (c) ITO/ZnO (40 nm)/NPC60-OH, (d) ITO/ZnO-C60 (40 nm)/NPC60-OH, (e) ITO/ZnO (40 nm)/NPC70-OH, and (f) ITO/ZnO-C60 (40 nm)/NPC70-OH. The inset number on the right-up corner is contact angle.



**Figure S2.** Current density versus bias voltage of the electron-only devices: (a) ITO/Al/ZnO/SAM or without/Al and (b) ITO/Al/ZnO-C60/SAM or without/Al (double-log). ( $V_{bi}$  is taken as zero since aluminum is used for both electrodes).



**Figure S3.** Cyclic voltammety measurements of NPC70-OH and NPC60-OH in mixed solutions of 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) dissolved in chlorobenzene/THF/acetonitrile (1:1:1 by volume ratio).



**Figure S4.** The J-V curves (a) and (b) of the devices ITO/cathode (40 nm)/SAM or without/p-DTS(FBTTh<sub>2</sub>)<sub>2</sub>:PC<sub>71</sub>BM/MoO<sub>3</sub> (10 nm)/Ag (100 nm) under dark condition.

**Table S1.** i-SMSC performance parameters for the devices ITO/ZnO or ZnO-C<sub>60</sub>/SAM without/p-DTS(FBTTh<sub>2</sub>)<sub>2</sub>:PC<sub>71</sub>BM/MoO<sub>3</sub> (10 nm)/Ag (100 nm).

Cathode	SAM	Under illumination		Under dark	
		Rsh <sup>a</sup> (Ωcm <sup>2</sup> )	Rs <sup>b</sup> (Ωcm <sup>2</sup> )	Rsh <sup>c</sup> (Ωcm <sup>2</sup> )	Rs <sup>d</sup> (Ωcm <sup>2</sup> )
ZnO	non	826±31	6.62±0.21	277±31	0.11±0.003
ZnO	NPC60-OH	1186±43	4.98±0.17	477±43	0.07±0.007
ZnO	NPC70-OH	1361±61	3.72±0.19	1428±61	0.04±0.002
ZnO-C60	non	1886±57	3.11±0.23	5000±157	0.41±0.011
ZnO-C60	NPC60-OH	2050±56	2.52±0.25	6670±176	0.13±0.007
ZnO-C60	NPC70-OH	2177±59	1.78±0.17	12500±239	0.06±0.004

a. Rsh, calculated from the inverse slope of J-V curve under illumination at  $V = 0$ .<sup>S4</sup>

b. Rs, calculated from the inverse slope of J-V curve under illumination at  $I = 0$ .<sup>S4</sup>

c. Rsh, calculated from the inverse slope of J-V curve under dark at  $V = 0$ .<sup>S5</sup>

d. Rs, calculated from the inverse slope of J-V curve under dark at  $V = 1$  V.<sup>S5</sup>

e. The average Rs and Rsh is based on more than three devices.

**Table S2.** Electron mobility of the interlayers ZnO and ZnO-C60 determined using the electron-only device ITO/Al/ZnO or ZnO-C60/SAM or without/Al along with the use of space charge limited current equation<sup>a</sup> in the calculation.

Interlayer	SAM	Electron mobility ( $\mu$ ) (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )
ZnO	non	1.23±0.39×10 <sup>-4</sup>
ZnO	NPC60-OH	1.50±0.35×10 <sup>-4</sup>
ZnO	NPC70-OH	2.33±0.33×10 <sup>-4</sup>
ZnO-C60	non	6.43±0.35×10 <sup>-3</sup>
ZnO-C60	NPC60-OH	1.01±0.25×10 <sup>-2</sup>
ZnO-C60	NPC70-OH	1.49±0.31×10 <sup>-2</sup>

a. The average  $\mu$  is based on more than three devices.

**Table S3.** Electrochemical data of NPC70-OH and NPC60-OH (EA) by CV.

Compound	E <sub>red</sub> <sup>on</sup> (V)	EA (eV)
NPC70-OH	-0.41(±0.010)	-4.30(±0.010)
NPC60-OH	-0.50(±0.015)	-4.21(±0.015)

a. The potential values are referred to Ag/Ag<sup>+</sup> reference electrode. The reduction potential can be defined as  $E_{red}^{on}(V) = 0.5(E_{pc} + E_{pa})$ , where  $E_{pc}$  is the cathodic peak

potential and  $E_{pa}$  is the anodic peak potential. Electron affinities (EA) can be calculated by the equation:  $EA = -e(E_{red}^{on} + 4.71 \text{ V})^{S6}$ , where  $E_{red}^{on}$  is the onset reduction potential in volts vs Ag/Ag<sup>+</sup>.

b. The average  $E_{red}^{on}$  and EA are based on more than three devices.

## References

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