

## **Supporting Information**

### **Fabrication of multilayer organic solar cells through stamping technique**

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## 1. Preparation of PDMS stamp

PDMS stamps were synthesized from an oligomer (Silgard 184A) and a curing agent, which was mixed in a ratio of 10:1 by volume. After mixing, it was poured onto silicon wafer to achieve a smooth surface stamp and then placed in vacuum for one hour to remove the air bubbles. When all the bubbles were removed the mould with the PDMS was placed in the oven for curing for 3~4 hours at 70 °C. Afterwards the cured PDMS was removed from the mould and cut them into the appropriate dimensions.

## 2. The transfer process

At the beginning, the surface of PDMS stamps should be treated with some organic solvents, such as acetone, toluene, chlorobenzene etc., depending on the solvent used for the polymer solution. The organic solvents used here not only clean the PDMS surface, but also change the surface energy on PDMS surface temporarily. This allows the polymer to be spun onto the PDMS surface. After organic solvent treatment, the semi-conducting polymer film is directly spun onto the PDMS surface. As a consequence, the conveying step performed by an external force for conformal contact and thermal annealing at near the glass transition temperature of the transferred polymer and the bottom layer materials for one to two minutes on hot plate. The whole process was performed in a nitrogen-filled glove box.

## 3. The fabrication of the solar cell device

### 3.1 The BHJ device

The RR-P3HT was purchased from Rieke Metals. The regioregularity, weight ( $M_w$ ), number ( $M_n$ ) average molecular weights, polydispersity index ( $PDI$ ) of RR-P3HT are regioregularity=93 %,  $M_w=3.7\times 10^4$ ,  $M_n=2.5\times 10^4$  and  $PDI=1.48$ , respectively. The PCBM was purchased from Nano-C. Prior to the deposition, the blend of RR-P3HT:PCBM was prepared by dissolving it in chloroform with 1:1 weight ratio, followed by stirring the solution for 12 h at 50 °C. The active layer was obtained by spin-coated the blend at 2500 rpm for 60 s. Subsequently, the films were annealed on the top of hotplate at 130 °C. A 30 and 100 nm thick of calcium and aluminum, respectively, was thermally evaporated under vacuum at a pressure below  $6\times 10^{-6}$  Torr through a shadow mask. The active area of the device was controlled at 0.12 cm<sup>2</sup>.

### 3.2 The bi-layer device

For the bi-layer solar cell based on P3HT and PCBM, a cesium carbonate ( $\text{Cs}_2\text{CO}_3$ ) electron injection layer was cast on the ITO substrate which was prepared according to the previous work. Then, a PCBM layer was spin cast from chloroform, subsequently the P3HT was transferred from PDMS stamp. The thicknesses of PCBM and P3HT were controlled at 40 and 100 nm cast from chloroform, respectively. Upon completion of the transfer process, the target sample (ITO/ $\text{Cs}_2\text{CO}_3$ /PCBM/P3HT) was transferred to a vacuum chamber to deposit the anode electrodes for the SCs, which consist of  $\text{V}_2\text{O}_5$  (10 nm) and Al (70 nm).

### 4. Characterization of polymer films and devices

For measuring absorption and photoluminescence (PL) emission properties of polymer films, samples were fabricated on a glass substrate. The UV-vis absorption spectra were measured using a Jasco-V-670 UV-visible spectrophotometer. PL spectra were obtained using a Hitachi F-4500 photoluminescence. Surface morphologies were observed by an atomic force microscopy (AFM, Digital Instruments). The thickness of all polymer films was measured using a surface profiler (Alpha-step IQ, KLA Tencor). Current-voltage ( $J$ - $V$ ) characteristics were measured in the glove box under nitrogen atmosphere with simulated AM 1.5G irradiation at  $100 \text{ mW/cm}^2$  using a xenon lamp based solar simulator (Thermal Oriel 1000W). The light intensity was calibrated by a mono-silicon photodiode with KG-5 color filter (Hamamatsu, Inc.).