Supporting Information

Ideal rear contact formed via employing a conjugated polymer for Si/PEDOT:PSS hybrid solar cells

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PFN synthesis: 80 mg tetrabutylammonium bromide and 8 ml of a 50 wt% aqueous solution of sodium hydroxide were added into the mixture solution including 4 g 2,7-dibromofluorene and 60 ml dimethyl sulfoxide (DMSO) under nitrogen atmosphere. 20 ml DMSO solution of 3-dimethylaminopropylchloride hydrochloride (5g, 32 mmol) was added dropwise into the mixture solution. After stirring at room temperature for 6 h, 50 ml DI water was used to dilute and dissolve all salts. The product was extracted with ether (300 ml) and the combined organic layer was washed with 10% NaOH solution (200 ml), DI water (300 ml) and brine (100 ml). The solution was dried over $MgSO_4$, filtered, and stripped of solvent by vaccum evaporation to yield a crude solid. The crude solid was recrystallized from $MeOH/H_2O$ to afford 2,7-Dibromo-9,9-bis(3'-(N, N-dimethylamino)propyl)-fluorene as white crystals. Then this 2,7-Dibromo-9,9-bis(3'-(N, N-dimethylamino)propyl)-fluorene (0.248 g, 0.5 mmol) 2,7-bis(4,4,5,5-tetrametyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (0.321 g, 0.5 mml), tetrakis(triphenylphosphine)palladium [$(PPh_3)_4Pd(0)$] (10 mg) and several drops of Aliquat 336 were dissolved in a mixture solution of 3 ml toluene and 2 ml Na_2CO_3 aqueous solution(2 M). The mixture was refluxed at 80 °C with vigorous stirring for 3 days under an argon atmosphere. After cooling to room temperature, it was poured into 200 ml methanol. The precipitated material was recovered by filtration through a funnel. The resulting solid material was washed for 24 h using acetone to remove oligomers and catalyst residues to receive the poly[(9,9-bis(3'-(N, N-diethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)] (PFN). ^1H NMR (500 MHz, $CDCl_3$): δ(ppm) 7.82-7.80 (m, 4.0H), 7.68-7.63(m, 8.0H), 2.20-1.95(m,24.0H), 1.18-1.11(m, 24.0H), 0.81-0.77(m, 10H). Elem. Anal. Calculated for PFN: C, 86.43%; H, 9.69%; N, 3.88%. Found: C, 85.38%; H,9.70%; N, 376%. M_n=22400, M_n/ M_w=1.6.

the surface of PFN layer has some discrete islands, as shown in Fig. S1.

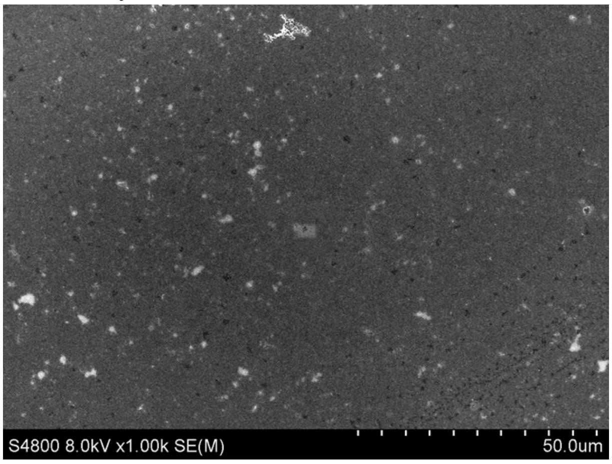

Fig. S1 The discrete PFN particles distributed on the silicon surface.

The typical transmission line model (TLM) method was applied to measure the contact resistance of the cathode interface between Al metal and n-type silicon (with PFN and without PFN). The resistance was determined by the current-voltage (*I*-*V*) curves between two contacts, measured by a Semiconductor parameter analyzer (Keithley 4200-SCS, USA). The typical arrangement for the TLM test pattern is shown in Fig. S2. An array of Al contacts (darker gray in the figure), with various spacing, is formed over the polished side of silicon. The total resistance is given by

$$R_T = \frac{R_S}{W} L + 2R_C \quad (1)$$

where R_T is the measured total resistance, R_S is the sheet resistance of n type silicon, R_C is the contact resistance associated with the Al/Si interface, L is the distance between the two contacts, and W is the length of the Al contact. The contact resistance depends on the size of the Al contact, so it is not a good point of standard quantity comparison. Instead, the contact resistivity can display the interface quantity well, as expressed in equation 2.

$$\rho_C = R_C L_T W \quad (2)$$

where ρ_C is the contact resistivity, L_T is the transfer length, the average distance that an electron travels in the silicon wafer beneath the contact before it flows up into the contact. Here, we chose three different distances for TLM, which the setting values of L_1, L_2 and L_3 were 300, 400 and 850 μm, respectively. The length W of Al grid was 500 μm. The voltage vs. current curves of Al contacts is displayed in Figure S3a. And R_T values from Figure S3a were 38.20, 45.09 and 55.91 Ω. The relation between R_T and distance was presented in Fig. S3b.

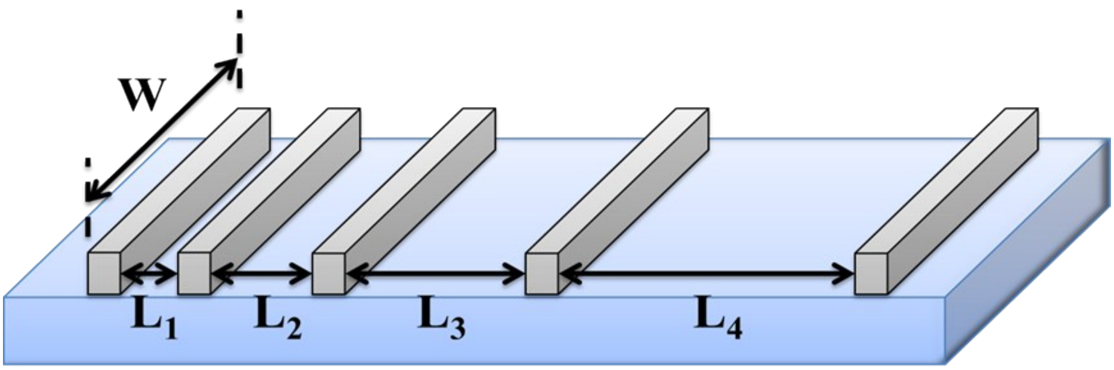

Fig. S2 The measurement schematic of the TLM test pattern.

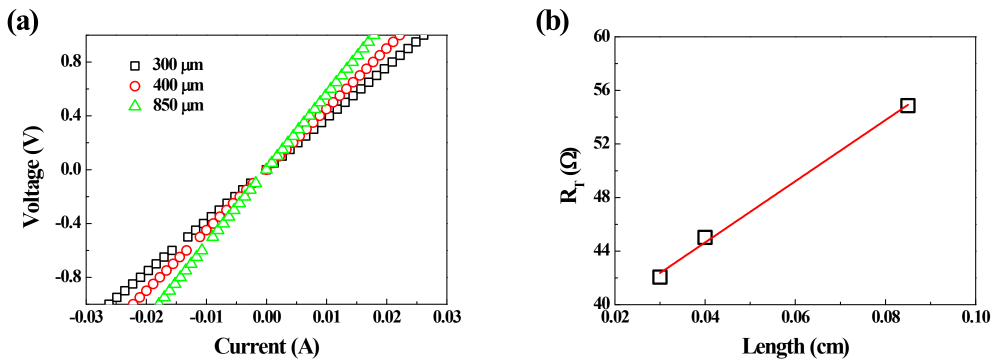

Fig. S3 The *I-V* curves (a) and R_T values versus distances (b) of Al contacts with different distances.

The current *vs.* voltage curves of hybrid solar cells were measured under a simulated sunlight (100 mW/cm^2) illumination in Fig. S4. The devices based on the different PFN thickness displayed almost the same photovoltaic parameters, summarized in Table S1. However, the device exhibited slightly higher efficiency, with a PFN interfacial layer prepared at a spin speed of 1000 rpm.

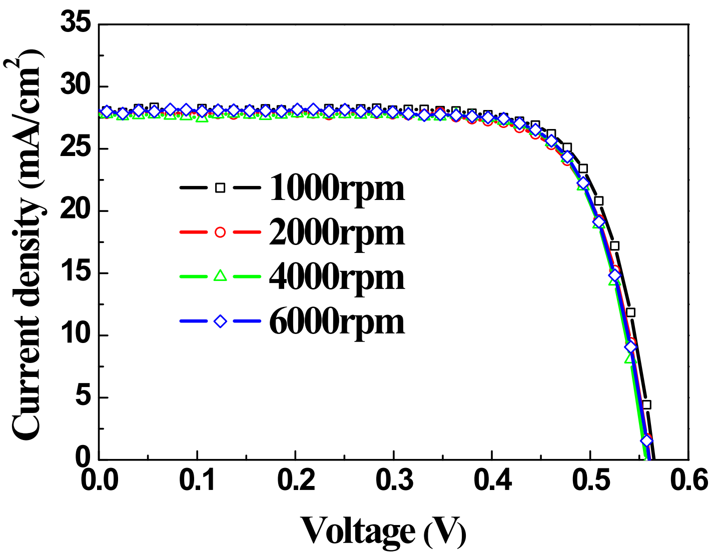

Fig. S4 Photovoltaic characteristics of hybrid solar cells based on the different thickness of PFN modification layer from the different spin speeds.

Table S1 Photovoltaic parameters of hybrid solar cells based on the different thickness of PFN interfacial layer.

Spin speed (rpm)	V_{oc} (V)	J_{sc} (mA/cm^2)	*FF* (%)	*η* (%)	R_S (Ω•cm^2)
1000	0.562±0.005	28.08±0.15	76.56±0.45	12.09±0.24	6.6±0.53
2000	0.558±0.005	27.87±0.17	75.1±0.65	11.68±0.36	6.28±0.47
4000	0.554±0.005	27.7±0.21	76.81±0.32	11.79±0.30	7.72±0.50
6000	0.558±0.005	28.01±0.11	75.62±0.40	11.83±0.20	6.95±0.44

Table S2 The minority carrier lifetime (τ) of PFN-modified Si surfaces with the different PFN thicknesses at spin speed of 1000 rpm.

Spin times	τ（before modification，μs）	τ（after modification，μs）	thickness (nm)
1	13.3	15.9	10±0.5
2	13.5	16.9	12.5±0.2
3	13.4	16.8	17.3±0.2
4	13.3	16.9	20.2±0.3
5	13.4	17.9	33.4±0.5