Supporting information

Flexible All-Solution-Processed All-Plastic Multijunction Solar Cells for Powering Electronic Devices

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A seperate video has also been uploaded as a part of the supporting information.

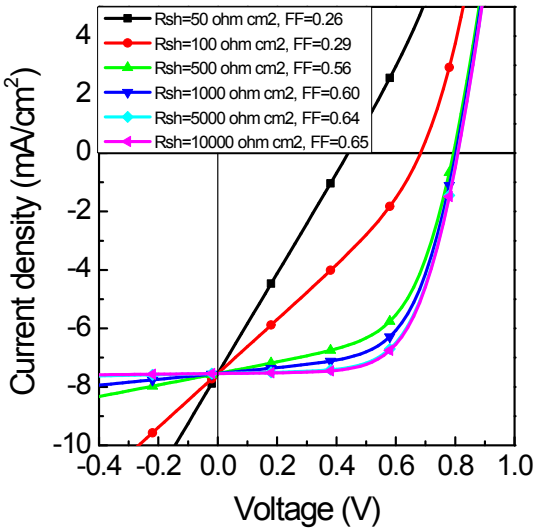

Figure S1. Fitted *J-V* characteristics with different R_{sh} with the one-diode equivalent circuit model based on a fabricated device (glass/ITO/PEI/P3HT:ICBA/PEDOT-T, R_s =8 Ω cm^2).

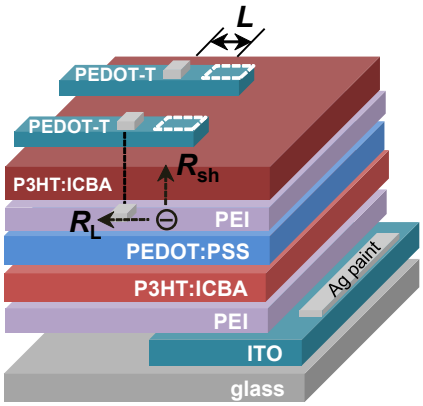

Figure S2. Schematic diagram of the possible lateral resistance of the charge recombination layer in the tandem solar cells.

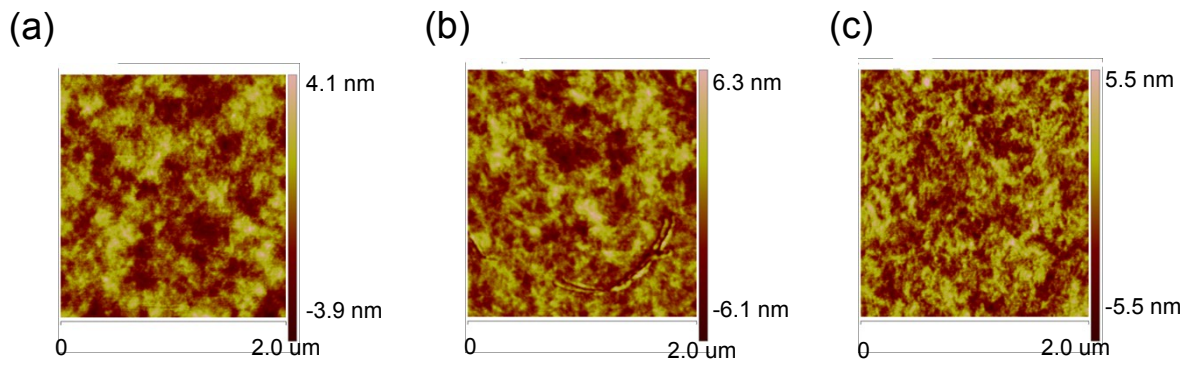

Figure S3. Atomic force images of the PEDOT:PSS films: a) AI 4083; (b) PH1000:AI 4083 = 1:3; (c) PH1000.

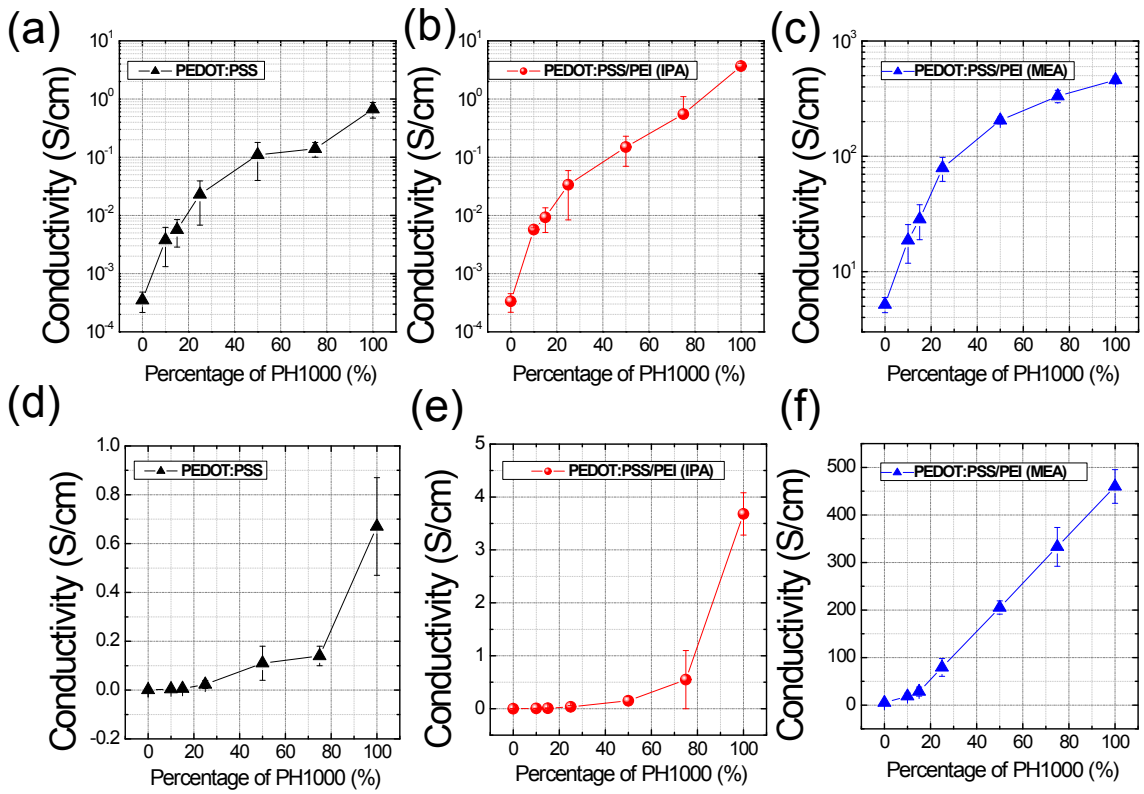

Figure S4. Conductivity of the PEDOT:PSS films (PH1000:AI 4083 mixture) with different percentages of PH1000 before and after PEI treatment: (a, d) Films of PH1000:AI 4083 mixture before PEI treatment in semi-log and linear scale; (b, e) Films PH1000:AI 4083 mixture/PEI in semi-log and linear scale where PEI is processed from 2-propanol solvent; (c, f) Films PH1000:AI 4083 mixture/PEI in semi-log and linear scale where PEI is processed from MEA solvent.

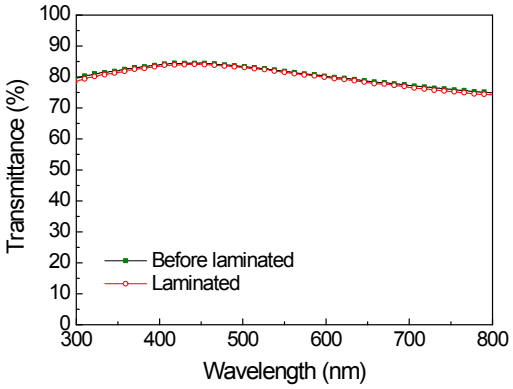

Figure S5. Transmittance of the top laminated electrode of PEDOT-T before and after the lamination.

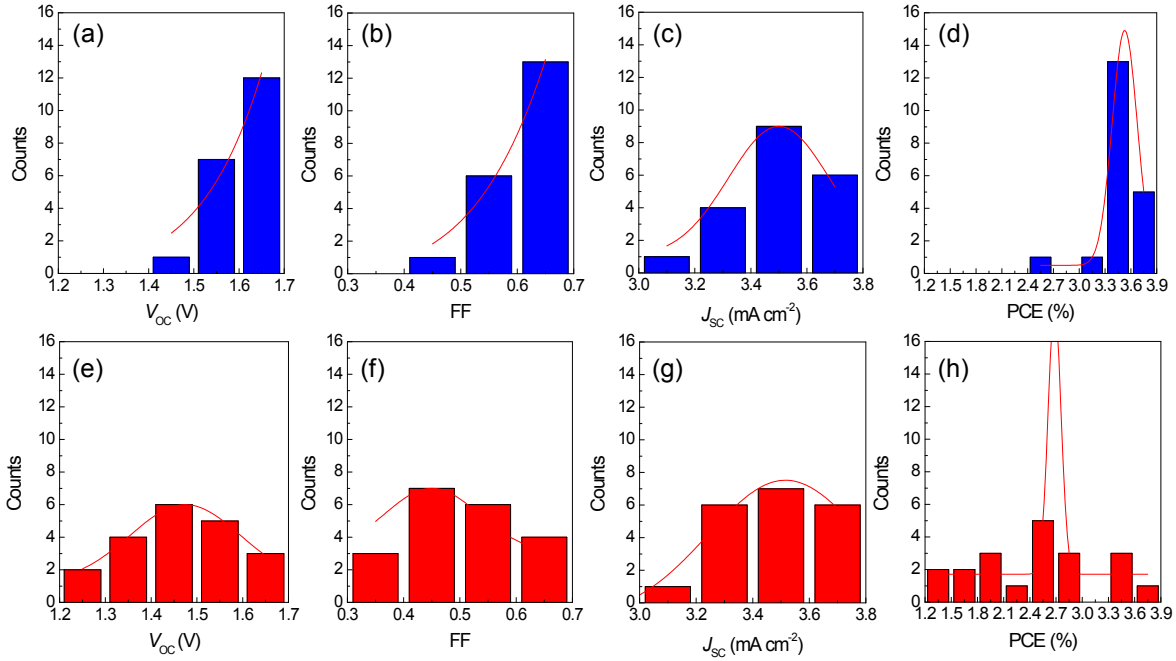

Figure S6. Performance distributions of the two-junction solar cells (device structures: glass/ITO/PEI/P3HT:ICBA/CRL/P3HT:ICBA/PEDOT-T) with different CRL: (a-d) with the CRL of PEDOT:PSS-m13/PEI (IPA); (e-h) with the CRL of the patterned PEDOT:PSS/ PEI (MEA). (20 cells for each type)

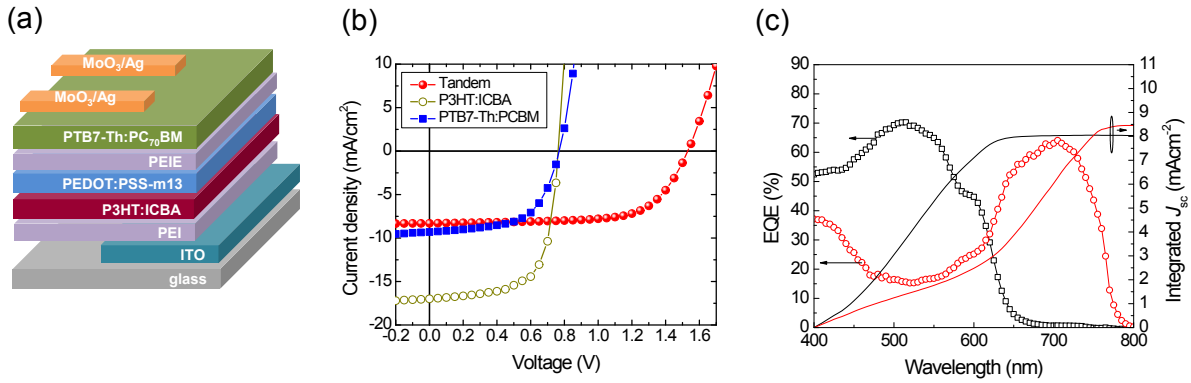

Figure S7. a) Device structure of the high-efficiency tandem solar cells with spectrally compensated active layers with ITO glass and MoO_3/Ag electrodes (non-all plastic); b) *J-V* characteristic of tandem and single-junction devices. c) EQE characteristics (the integrated current from the EQE curve is also displayed) of the reference tandem device with structure in (a).

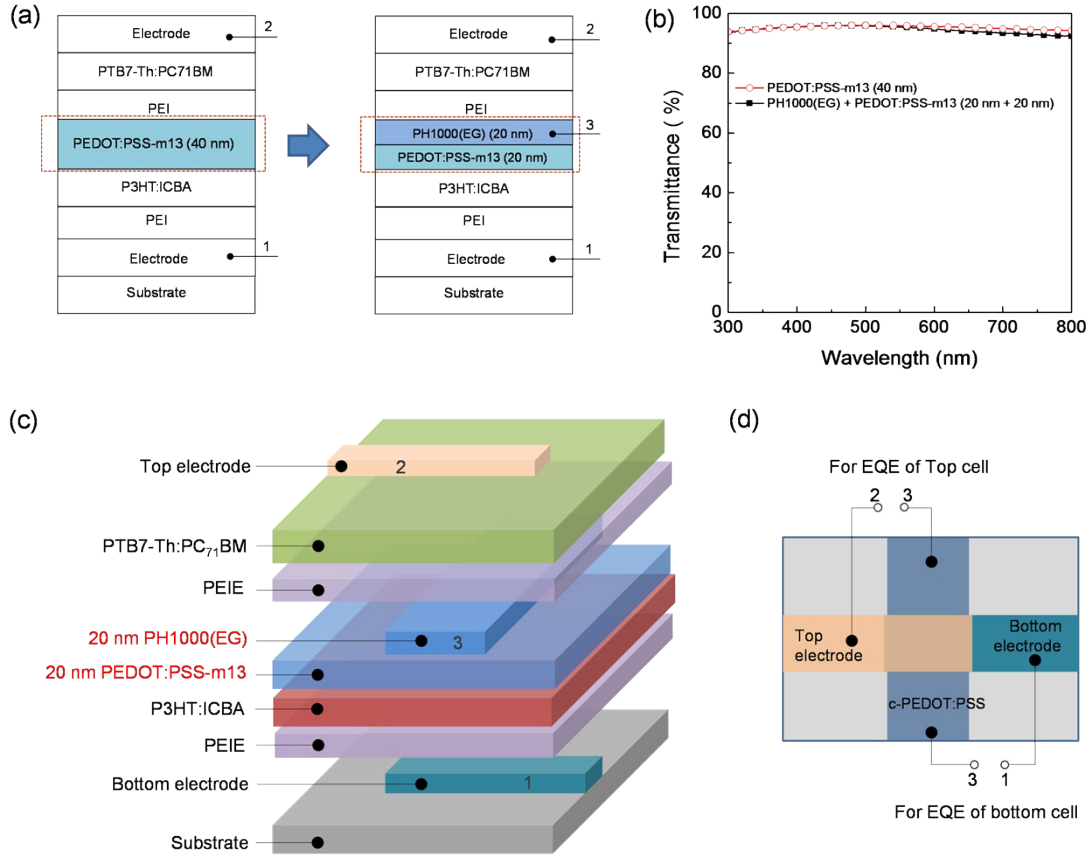

Figure S8. a) To realize the three-terminal structure for EQE measurement, the low-conductivity PEDOT:PSS-m13 layer (40 nm) in the two-terminal devices was replaced by 20 nm PH1000(EG)/20 nm PEDOT:PSS-m13 bilayer; b) Transmittance of the PEDOT:PSS-m13 (40 nm) layer and the PEDOT:PSS-m13 (20 nm)/PH1000(EG) (20 nm)b) bilayer; c) Schematic illustration of the device layout; d) Top view of the three-terminal electrodes layout. Electrodes 1 and 3 are connected when measuring EQE of bottom sub-cell; electrode 2 and 3 are connected for EQE of top sub-cell.

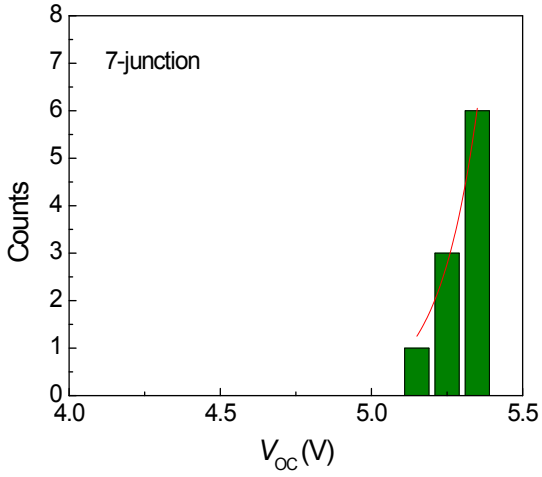

Figure S9. V_{OC} distributions of the all-solution-processed all-plastic 7-junction solar cells (10 devices)

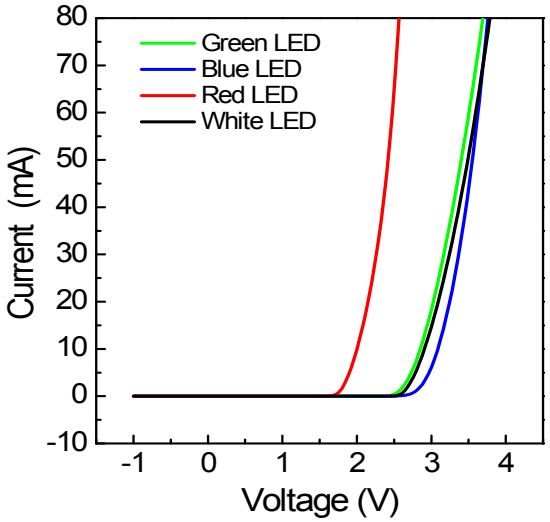

Figure S10. *I-V* curves of the LEDs with different emission colors.

1. Analysis of the conductivity of charge recombination layer (CRL) to minimize the effect of its lateral leakage

Based on the fit of *J-V* characteristics as shown in Figure S1, a shunt resistance of R_{sh} needs to be > 1,000 Ωcm^2 to achieve a fill factor over 0.60 for the organic solar cell. That is 2.5 x 10^4 Ω with a device area of 0.04 cm^2.

Take the top sub-cell to analyze the effect of lateral resistance (R_L) of the charge recombination layer in a tandem solar cell (Figure S2), where the silver paint or test clip penetrates the active layer that leads to its contact to the CRL. Considering the effect of lateral resistance, the new R'_{sh} follows the equation:

$$\frac{1}{R'_{sh}} = \frac{1}{R_{sh}} + \frac{1}{R_L} \quad \text{(S1)}$$

R_L is roughly estimated with the equation:

$$R_L = \rho \frac{L}{S} = \frac{1}{\sigma} \frac{L}{S} \quad \text{(S2)}$$

where σ is the conductivity of the charge recombination layer (CRL), L is the estimated transporting length from the effective device area to the Ag paint (about 3 mm in the real cell), S is the cross-sectional area, which is equal to the thickness (40 nm) of the CRL multiplies the width of the effective device area (about 3 mm).

Then,

$$R_L = \frac{1}{\sigma} \frac{3mm}{40nm \times 3mm} = \frac{1}{\sigma} \frac{2.5 \times 10^5}{cm} \quad \text{(S3)}$$

To minimize the effect of R_L to the R_{sh}, that is, R'_{sh} is as close to R_{sh} as possible, the R_L is required to be > 100 R_{sh},

Then,

$$\frac{1}{\sigma} \frac{2.5 \times 10^5}{cm} > 100 \times 2.5 \times 10^4 \quad \text{(S4)},$$

Therefore, σ < 0.1 S/cm

2. Experimental section

PEDOT:PSS/PEI conductivity tuning and characterization:

Glass substrates were cleaned in sequential ultrasonic baths of detergent in deionized water, deionized water, acetone, and ethanol. Nitrogen was used to dry the glass substrates after the last bath. After that, the glass substrate were treated by O_2 plasma for 2 min. Two PEDOT:PSS formulations (PH1000 and AI 4083) were mixed at different ratio and then spin coated onto the glass substrates at 700 rpm for 40 s and annealed at 150 °C for 5 min in air. Polyethylenimine (Mw =25,000, Sigma-Aldrich) was dissolved into 2-methoxyethanol or 2-propanol with a weight concentration of 0.1%. PEI was spin coated onto the substrates at a speed of 5,000 rpm for 1 min and an acceleration of 1,000 rpm/s and annealed at 100 ºC for 5 min on a hot plate in ambient air. The sheet resistance was measured by using four-point probe (RTS-8). The film thickness was measured by a surface profiler (Veeco Dektak 150).

Device preparation and characterization:

For single-junction all-plastic solar cell: Polyethersulfone (PES) was used as the substrates for all the flexible solar cells. For PH1000 patterning, a piece of polydimethylsiloxane (PDMS) was put down on half of the PES substrates as a shadow mask and then the PES substrates were treated by 6 min O_2 plasma (PDC-2, Harrick). High conductivity PEDOT:PSS PH1000 with 5% ethylene glycol (EG) and 0.1% nonionic surfactant PEG-TmDD (superwet-304, SurfyChem) was spin coated on PES substrates at a speed of 1000 rpm for 60 s and an acceleration of 1000 rpm/s and annealed at 150 °C for 5 min on a hot plate in air. PH1000 only wets half of the PES substrates with plasma treatment. The thickness of PH1000 was 150 nm. Polyethylenimine (Mw =25,000, Sigma-Aldrich) was dissolved into 2-methoxyethanol or 2-propanol with a weight concentration of 0.1%. PEI was spin coated onto the substrates at a speed of 5,000 rpm for 1 min and an acceleration of 1,000 rpm/s and annealed at 100 ºC for 5 min on a hot plate in ambient air. Then the substrates were transferred into a N_2-filled glove box. The active layer of poly(3-hexylthiophene) (P3HT,

Sunshine): indene-C60 bis-adduct (ICBA, Lumtec) (1: 1, weight ratio) was spin-coated on each substrate from 40 mg/ml dichlorobenzene solution at a speed of 800 rpm for 40 s and an acceleration of 1,000 rpm/s. The active layer were annealed at 150 °C for 5 min on a hot plate in the glove box. The thickness of the active layer was 200 nm. Film-transfer laminated PEDOT:PSS PH1000 with PDMS as the transfer medium was used as the top electrodes as described previously. In brief, a piece of polydimethylsiloxane (PDMS) transfer medium was adhered on a clean glass substrate and was then exposed to oxygen plasma for 50 s to tune its surface hydrophilicity. PH1000 with 5 wt.% ethylene glycol and 0.1 wt.% surfactant was spin-coated onto the PDMS at 1,000 rpm for 60 s and dried in air for 9 min without thermal annealing. During drying, the PDMS with PH1000 was cut into 2 mm-wide finger electrodes. Before transferring the electrodes, the P3HT:ICBA receiving surface was treated in oxygen plasma for 5 s. Then the PDMS with PH1000 was transferred onto the P3HT:ICBA surface and then the top PDMS was slowly peeled off and PH1000 was left on the active layer. The overall devices were thermally annealed at 150 °C for 5 min in a N_2-filled glove box to finish the device fabrication. The effective device areas about 5 mm^2 were determined precisely under an optical microscope (DM4000 M, Leica).

For high-efficiency two-junction all-plastic solar cells (P3HT:ICBA/PTB7-Th:PCBM): On the prepared PES/PH1000/P3HT:ICBA samples, a 40 nm-thick charge recombination layer of PEDOT:PSS-m13/PEI(IPA) was prepared. Prior to the coating of aqueous PEDOT:PSS formulation, the hydrophobic surface of P3HT:ICBA was tuned to hydrophilic via a short-time (5 s) flash of air plasma. The PEDOT: PSS-m13 was prepared by mixing PEDOT:PSS PH1000: AI 4083 at a weight ratio of 1:3 and spin coated on top of the P3HT:ICBA at 4000 rpm for 1 min and annealed at 150 °C for 5 min in a glove box. The PEI modification layer was prepared by spin-coating from a 0.1 wt.% 2-propanol solution and annealed at 100 °C for 5 min. Next, the bottom active layer of PTB7-Th: $PC_{71}BM$ was deposited by spin-coating a mixed solvent of chlorobenzene/ 1,8-diiodoctane (97:3 by

volume) solution (a total concentration of 25 mg/ml) at 1,200 rpm for 1 min. Finally, the top electrode was fabricated using the same method (film-transfer lamination) as the single-junction cells mentioned above.

For non-all-plastic tandem solar cells: P3HT:ICBA and PTB7-Th: $PC_{71}BM$ were used as the front and bottom sub-cells active layers materials. The PEIE solution (Mw = 75 000 g/mol) was diluted into 2-propanol to a weight concentration of 0.1 wt%) was first spin-coated onto ITO substrates with the same procedure as we described previously. Then, the front sub-cell active layer was prepared by spin-coating P3HT:ICBA (about 200 nm) at a speed of 800 rpm for 40 s in a N_2-filled glovebox. The P3HT:ICBA film was solvent-annealed in a covered glass petri dish for 2 h and then thermal annealed at 150 °C for 5 min. After the samples cooled down, they were transferred in ambient air and PEDOT:PSS-m13/PEIE(IPA) charge recombination layer was prepared as the same procedure in the two-junction all-plastic solar cells. Next, the bottom active layer of PTB7-Th: $PC_{71}BM$ was deposited by spin-coating a mixed solvent of chlorobenzene/ 1,8-diiodoctane (97:3 by volume) solution (a total concentration of 25 mg/ml) at 1,100 rpm for 1 min. Samples were then loaded into a vacuum thermal deposition system (Mini-Spectros, Kurt J. Lesker), and a 6 nm-thick layer of MoO_3 and a 80 nm-thick layer of Ag were evaporated through a shadow mask.

For multijunction all-plastic solar cells: On the prepared PES/PH1000/P3HT:ICBA samples, a 40 nm-thick charge recombination layer of PEDOT:PSS-m13/PEI(IPA) was prepared. The PEI modification layer was prepared by spin-coating from a 0.1 wt.% 2-propanol solution and annealed at 100 °C for 5 min. PEDOT:PSS-m13/PEI(IPA)/P3HT:ICBA was repeatedly deposited to obtain multijunction cells. All the PEDOT:PSS-m13/PEI(IPA) charge recombination layers fully covered the bottom active layer without patterning.

Thickness of the each P3HT:ICBA layer was tuned from thin (substrate side) to thick (top electrode) by changing the spinning speed and the concentration of the solution. Finally,

the top electrode was fabricated using the same method (film-transfer lamination) as the single-junction cells mentioned above.

The *J-V* characteristics of the devices were measured inside a N_2-filled glove box using a Keithley 2400 sourcemeter in the dark and under 100 mW cm^{-2} Air Mass 1.5G illumination from a solar simulator (Newport, SP94023A-SR1) calibrated using a standard silicon photodiode. The device area determined by the overlap of the top and the bottom PEDOT:PSS electrodes is about 5 mm^2. During the measurement, an aperture with an area of 4 mm^2 was used to minimize the overestimation of the current density. The light intensity at each wavelength was calibrated with a single-crystal Si photovoltaic cell. The film thickness measurement was performed using a surface profiler (Veeco Dektak 150). Transmittance (*T*) of the PEDOT:PSS films was conducted on a Spectrophotometer (UV-3600, Shimadzu Scientific Instruments).

The external quantum efficiency (EQE) of two-junction tandem cells with P3HT:ICBA and PTB7-Th:$PC_{71}BM$ active layers (both the all-plastic and reference cells) was measured using a 150 W xenon lamp (Oriel) equipped with a monochromator (Comerstone 74004). The method employed to measure the EQE by introducing a conductive intermediate polymer as the third electrode to access the EQE of sub-cells independently as reported by Bahro et al.[s1] The optical properties of the third electrode should be similar to the initial charge recombination layer of two-terminal devices. This method is also called " Current Contact Approach" included in the recent paper by Leo et al. [s2] (Supporting information, subsection 3.3 " Current Contact Approach").

Fig. S8 is the three-terminal device structure designed for EQE measurement. The 40 nm low-conductivity PEDOT:PSS-m13 in the charge recombination layer of the two-terminal devices was replaced by a bilayer PEDOT:PSS comprising of a 20 nm highly-conductive PH1000(EG) layer and a 20 nm PEDOT:PSS-m13 layer (Fig. S8a). The transmittance of the PEDOT:PSS-m13 (40 nm) and PEDOT:PSS-m13 (20 nm)/PH1000(EG) (20 nm) is similar

(Fig. S8b). Fig. S8c and d (top view) show the patterning layout of the three electrodes. During the measurement, an aperture with an area of 4 mm^2 was used to minimize the overestimation of the current density.

Water splitting experiments:

With sufficiently high photovoltage, 4-junction solar cells are used to split water. The water splitting system includes two platinum electrodes and a 1 M KOH solution as the electrolyte. The platinum electrodes used in the experiments were 10 cm long and 0.35 mm in diameter. The all-plastic 4-junction solar cell is wired to the immersed Pt electrodes, and simulated solar irradiation provides the energy for water splitting.

Driving LEDs and LCDs:

For driving LEDs demonstration, different emission colors LEDs (red, green and blue) were connected to a bended 6-junction all-plastic solar cell with a flashlight illumination. To illustrate the process clearly, the flashlight was turned on and off repeatedly to light on and off the LEDs.

For the demonstration of driving LCDs, a LCD was directly connected to a 6-junction all-plastic solar cell. Indoor room light (a fluorescent lamp) was used as the light source to illuminate the cell. To illustrate the process clearly, the solar cell is blocked from the room light repeatedly and the LCD was thus turned on and off.

3. Table S1. Reported PCE values of fully-solution-processed single-junction and tandem (including modules) organic solar cells

Year	PCE (%)	Architecture	Substrate	References
2010	1.8	Single	Glass	Zhou et al., *Appl. Phys. Lett.* **2010**, *97*, 153304
2011	3.8	Single	Flexible	Gaynor et al., *Adv. Mater.* **2011**, *23*, 2905.
2014	2.77	Single	Flexible	Li et al., *Adv. Mater.* **2014**, *26*, 7271.
	4.8			Nickel et al., *Sol. Energy Mater. Sol. Cells* **2014**, *130,* 317.
2015	2.44	Tandem module	Flexible	Guo et al., *Adv. Energy Mater.* **2015**, *5,* 1401779.
	2.66			Angmo et al., *Adv. Funct. Mater.* **2015**, *25,* 4539.
	4.85	Tandem (fully printed)		Guo et al., *Energy Environ. Sci*. **2015**, *8,* 1690.
	5.81		Glass	Guo et al., *Energy Environ. Sci.* **2015**, *8*, 1690.
	6.1 ± 0.4	Tandem	Flexible	This Work

4. Table S2. Device parameters of the all-plastic multijunction (from 1- to 7-junction) solar cells

Number of Junctions	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)
1	0.8	6.2	53	2.6
2	1.6	3.4	64	3.5
3	2.3	3.0	58	4.0
4	3.0	2.5	67	5.1
5	3.8	1.1	52	2.1
6	4.7	0.53	53	1.3
7	5.4	0.4	40	0.85

References

S1. D. Bahro, M. Koppitz, A. Mertens, K. Glaser, J. Mescher, A. Colsmann, *Adv. Energy Mater.,* 2015, **5**, 1501019.

S2. R. Timmreck, T. Meyer, J. Gilot, H. Seifert, T. Mueller, A. Furlan, M. M. Wienk, D. Wynands, J. Hohl-Ebinger, W. Warta, R. A. J. Janssen, M. Riede, K. Leo, *Nat. Photonics,* 2015, **9**, 478-479.