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Conjugated Copolymers as Doping- and Annealing-free Hole Transport Materials for Highly Stable and Efficient *p-i-n* Perovskite solar Cells

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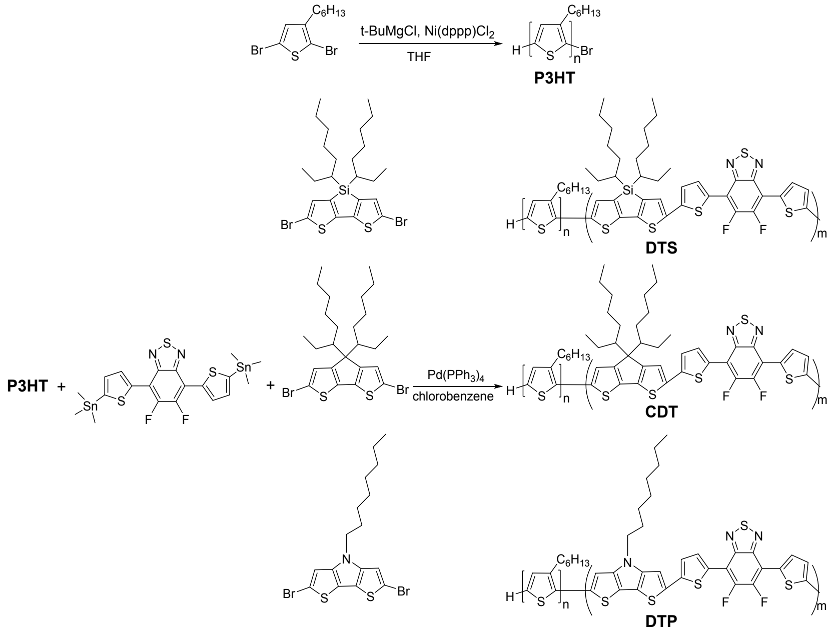
1. Materials and methods

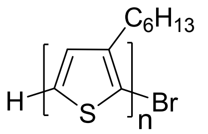
All reagents were commercially available and used as received without further purification. Pre-polymer P3HT was prepared according to the literature.[1, 2] NMR spectroscopy were recorded on a Bruker Advance 400 MHz spectrometer. ^{1}H NMR chemical shifts are reported relative to residual solvent signals.

2. Synthetic procedures and characterization data



Scheme S1 Synthetic routes of pre-polymer P3HT and the copolymers DTS, CDT, DTP.

2.1. Synthesis of pre-polymer P3HT



A 50 mL round-bottom flask equipped with a two-way stopcock was heated under reduced pressure and then cooled to room temperature under an argon atmosphere. 2,5-Dibromo-3-hexylthiophene (0.80 mL, 3.77 mmol) in dry THF (20.0 ml) were added into the flask via a syringe. To the solution was added t-butylmagnesium chloride (23.0% in THF, 1.20 mL, 2.36 mmol) via a syringe and the mixture was stirred at 40 °C for 1.5 h. After cooling to room temperature, a suspension of Ni(dppp)Cl (13.0 mg, 0.024 mmol) in THF (10.0 mL) was added to the mixture via a syringe. After the reaction mixture was stirred at room temperature for 1.0 h, 5.0 M hydrochloric acid was added and the mixture was extracted with $CHCl_3$. The organic layer was washed with water, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The obtained produce was washed well with MeOH and further washed/fractionated by Soxhlet extraction with methanol, hexane, acetone to give a black red solid (196 mg, yield: 32.3%). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ 6.97 (m, br), 2.80 (m, br), 1.70 (m, br), 1.54 (m, br), 1.43 (m, br), 1.34 (m, br), 0.91 (m, br).

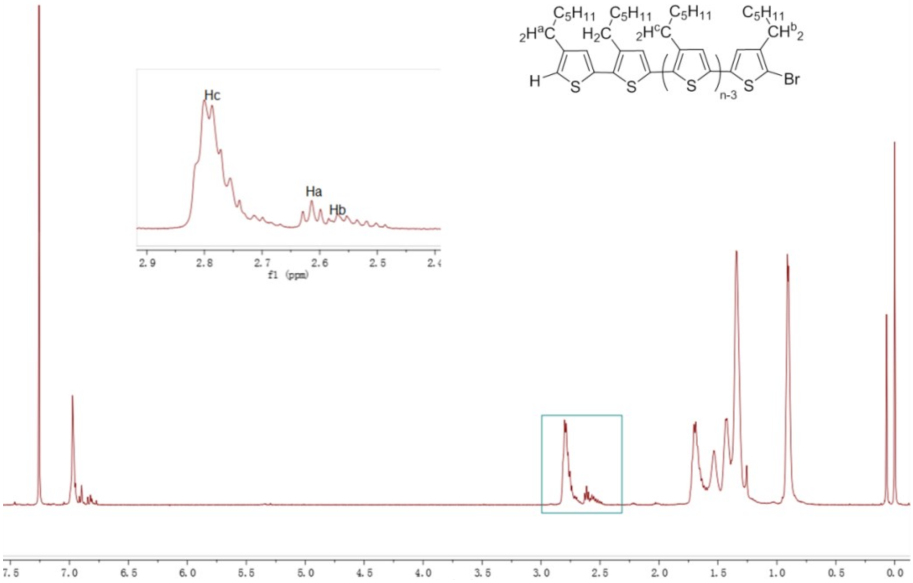
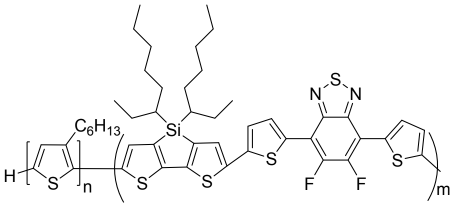


Figure S1. ^1H NMR spectrum (400 MHz, $CDCl_3$, 298K) of pre-polymer P3HT.

2.2. Synthesis of polymer DTS



P3HT (110 mg, 0.01 mmol), 5,6-difluoro-4,7-bis(5-(trimethylstannyl)thiophen-2-yl)benzo[c][1,2,5]thiadiazole (131 mg, 0.21 mmol) and $Pd(PPh_3)_4$ (4.6 mg, 0.004 mmol) was added into a baked 10-mL Schlenk tube with a side arm, and then degassed three times with nitrogen. 2,6-dibromo-4,4-bis(2-ethylhexyl)-4*H*-silolo[3,2-b:4,5-b']dithiophene in 5.0 mL chlorobenzene was added via a syringe, and then the mixture was stirred at 150 °C for 24 h. After cooling to room temperature, 200 mL of methanol was added to the solution and stirred for 12 h to precipitate the polymer. The precipitate was collected and further washed/fractionated by Soxhlet extraction with methanol, hexane, acetone to give a dark green solid (105 mg, yield: 50.8%). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.47 (m, br), 6.98 (m, br), 2.81 (m, br), 1.71 (m, br), 1.54 (m, br), 1.45 (m, br), 1.36 (m, br), 1.25 (m, br), 0.91 (m, br). Because the integral ratio of H_a to H_c is equal to 1 / (n-2), and the integral ratio of H_c to H_d is equal to (n-2) / m, the ratio of two block lengths (n: m) is calculated to be 13.6.

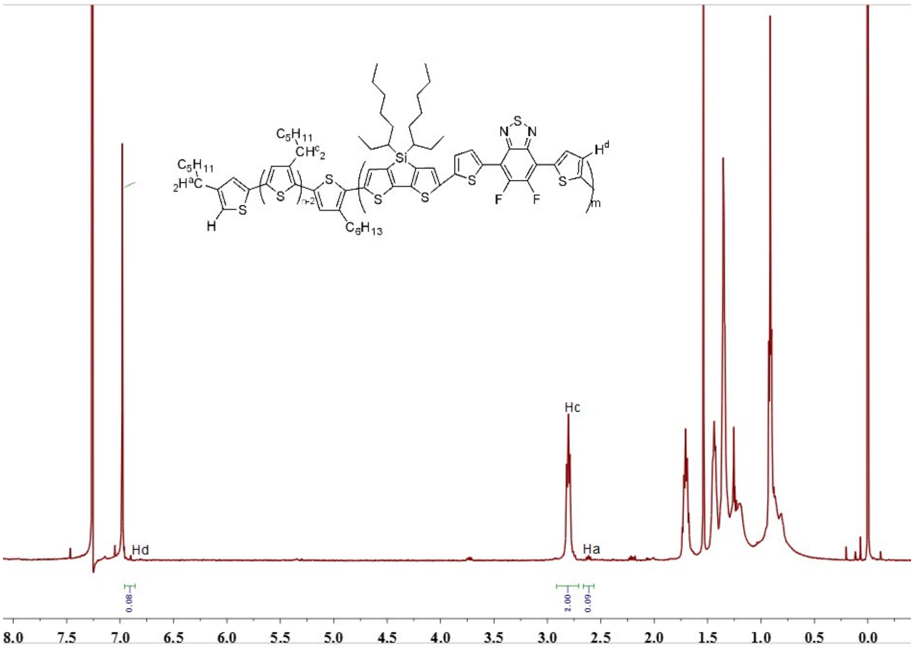
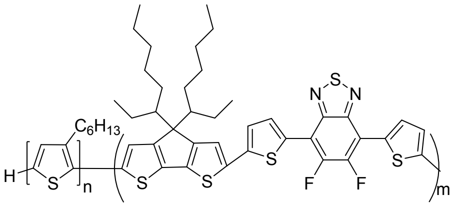


Figure S2. ^1H NMR spectrum (400 MHz, $CDCl_3$, 298K) of polymer DTS.

2.3. Synthesis of polymer CDT



CDT was synthesized from monomers P3HT, 5,6-difluoro-4,7-bis(5-(trimethylstannyl)thiophen-2-yl)benzo[c][1,2,5]thiadiazole and 2,6- dibromo-4,4-bis(2-ethylhexyl)-4*H*-cyclopenta[2,1-b:3,4-b']dithiophene according to the procedure for preparing DTS as a dark green solid in 40.2% yield. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.47 (m, br), 6.98 (m, br), 3.73 (m, br), 2.80 (m, br), 2.18 (m, br), 1.71 (m, br), 1.54 (m, br), 1.45 (m, br), 1.34 (m, br), 1.24 (m, br), 0.91 (m, br). According to the integral ratios of H_a to H_c, and H_c to H_d, the ratio of two block lengths (n: m) is calculated to be 9.3.

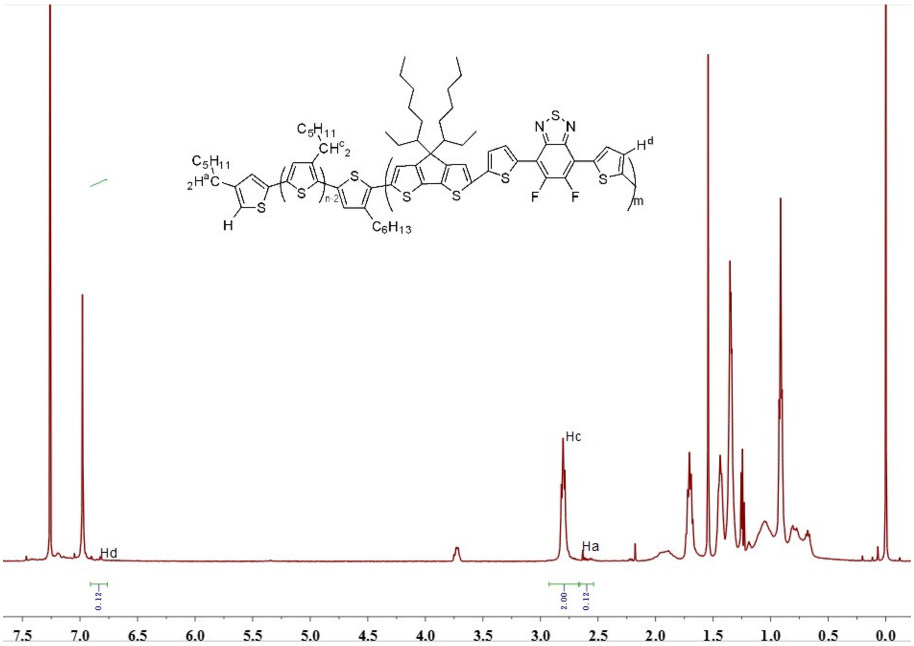
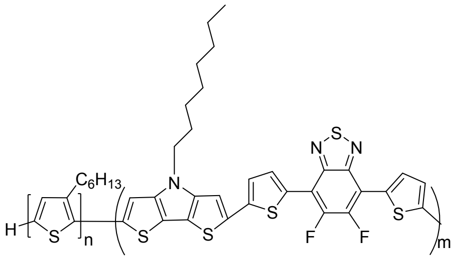


Figure S3. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298K) of polymer CDT.

2.4. Synthesis of polymer DTP



DTP was synthesized from monomers P3HT, 5,6-difluoro-4,7-bis(5- (trimethylstannyl)thiophen-2-yl)benzo[c][1,2,5]thiadiazole and 2,6-dibromo-4-*n*-octyldithieno[3,2-b:2',3'-d]pyrrole according to the procedure for preparing DTS as a dark green solid in 84.1% yield. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 7.47 (m, br), 6.98 (m, br), 2.80 (m, br), 1.71 (m, br), 1.54 (m, br), 1.44 (m, br), 1.35 (m, br), 1.25 (m, br), 0.91 (m, br), 0.07 (m, br). According to the integral ratios of H_a to H_c, and H_c to H_d, the ratio of two block lengths (n: m) is calculated to be 18.2.

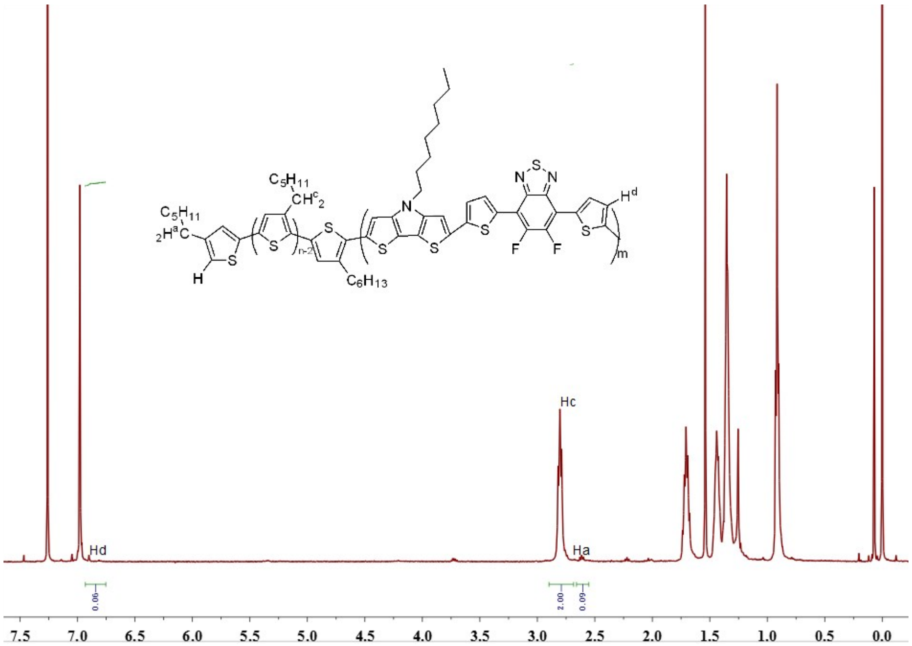


Figure S4. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298K) of polymer DTP.

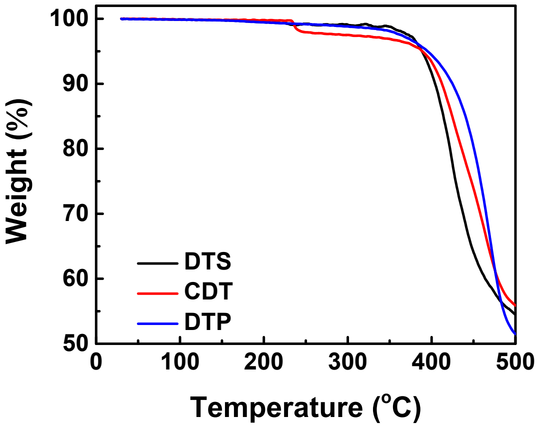


Figure S5. Thermogravimetric analysis (TGA) of DTS, CDT and DTP.

3. Electrochemical characteristics

Table S1. Electrochemical characteristics of DTS, CDT and DTP.

HTM	E_{HOMO} [eV]^b	E_{LUMO} [eV]^a	E_g [eV]^a	E_{LUMO} [eV]^b	E_g [eV]^b
DTS	-5.23	-3.68	1.55	-3.56	1.67
CDT	-5.14	-3.59	1.55	-3.60	1.54
DTP	-5.01	-3.63	1.38	-3.56	1.45

^{a} Data based on absorption spectrum; ^{b} Data based on CV method;

4. Photovoltaic characteristics

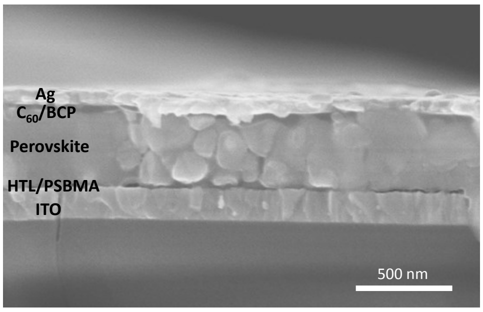


Figure S6. The cross-section scanning electron microscopy (SEM) image of ITO/HTL/PSBMA/perovskite/C_{60}/BCP/Ag.

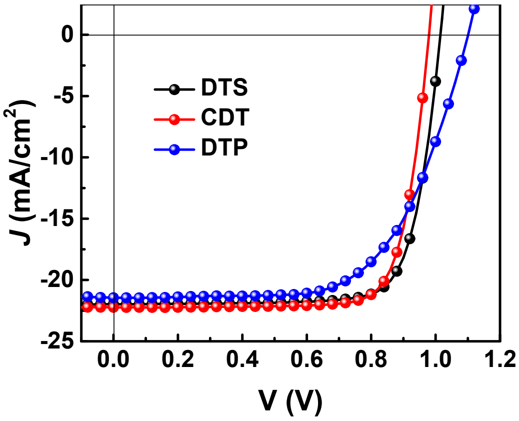


Figure S7. *J-V* curves for devices fabricated with DTS, CDT and DTP.

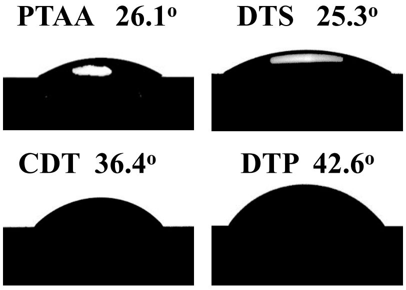


Figure S8. Pictures of DMF contact angle (θ_{DMF}) on the films of PTAA, DTS, CDT and DTP.

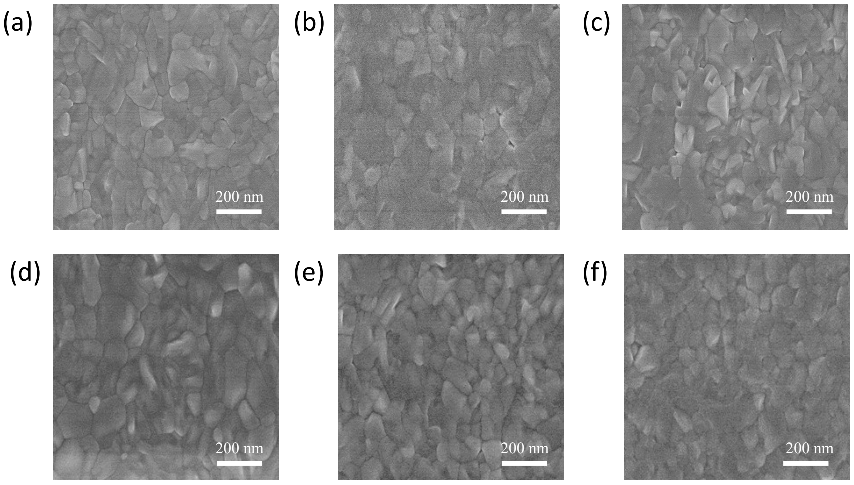


Figure S9. Top-view SEM images of perovskite films on DTS (a), CDT (b) and DTP (c) films. And SEM images of perovskite films on DTS/PSBMA (a), CDT/PSBMA (b) and DTP/PSBMA (c) films.

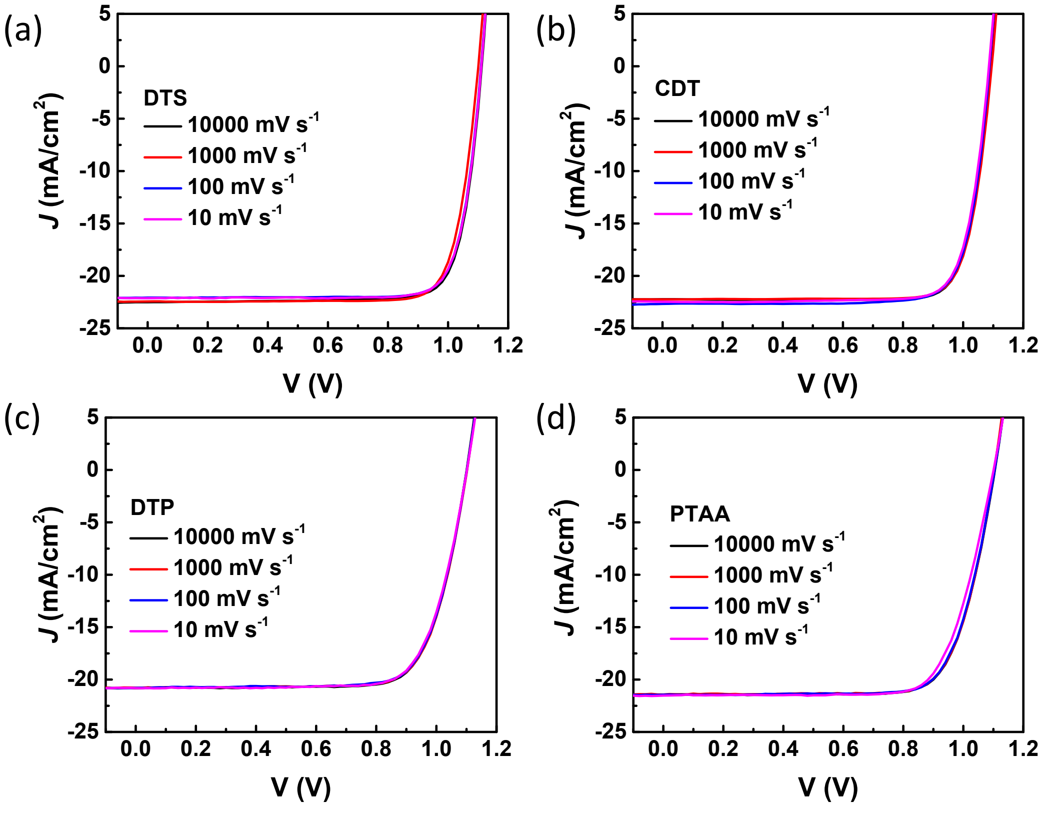


Figure S10. *J*–*V* curves of the devices based on HTL/PSBMA/CH3NH3PbI3/C60/BCP/Ag at different scan speed.

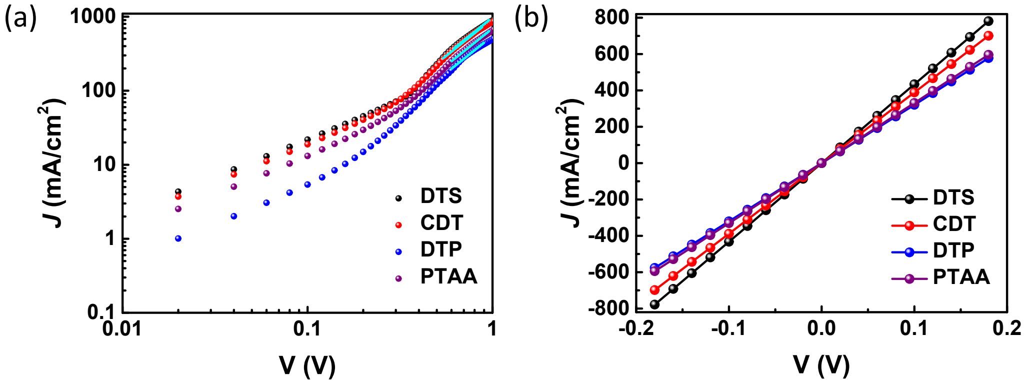


Figure S11. (a) Measured *J–V* curves for ITO/PEDOT: PSS/HTL/Ag devices with different HTLs. (b) The *J-V* diagrams of conductivity of different HTL films. The device structure is ITO/HTL/Ag.

Table S2. Photovoltaic parameters of devices based on DTS, CDT, DTP.

HTL	*Voc* (V)	*Jsc* (mA/cm^2)	FF (%)	PCE (%)	
				Max.	Aver.
DTS	1.01	21.97	77.46	17.27	16.60 ± 0.35
CDT	0.98	22.23	78.17	17.02	16.41 ± 0.98
DTP	1.10	21.44	63.05	14.87	14.38 ± 0.43

Table S3. Photovoltaic characteristics of the Pero-SCs at different scan speed.

HTL	scan speed (mV s^{-1})	*Voc* (V)	*Jsc* (mA/cm^2)	FF (%)	PCE (%)
DTS	10000	1.11	22.51	81.07	20.29
	1000	1.11	22.44	81.37	20.09
	100	1.10	22.07	81.98	20.08
	10	1.11	22.13	81.59	20.05
CDT	10000	1.09	22.23	81.75	19.86
	1000	1.09	22.24	81.36	19.81
	100	1.09	22.67	80.00	19.73
	10	1.09	22.45	80.59	19.64
DTP	10000	1.10	22.24	75.89	17.40
	1000	1.10	22.23	75.83	17.36
	100	1.10	22.54	75.59	17.30
	10	1.10	22.40	75.14	17.24
PTAA	10000	1.10	21.46	75.91	18.00
	1000	1.10	21.43	75.96	17.96
	100	1.10	22.54	75.74	17.94
	10	1.10	21.52	74.56	17.67

Table S4. The charge carrier mobilities of hole-only devices with different HTLs.

Interlayer	Hole mobilities (cm^2 V^{-1} s^{-1})
DTS/PSBMA	1.84×10^{-3}
CDT/PSBMA	1.41×10^{-3}
DTP/PSBMA	1.04×10^{-3}

Table S5. The hole mobilities and conductivities of different HTLs.

HTL	Hole mobilities (cm^2 V^{-1} s^{-1})	Conductivity (S cm^{-1})
DTS	8.83×10^{-5}	1.3×10^{-5}
CDT	8.43×10^{-5}	1.2×10^{-5}
DTP	4.96×10^{-5}	9.6×10^{-6}
PTAA	6.25×10^{-5}	9.9×10^{-6}

Table S6. Photovoltaic characteristics of the Pero-SCs at both forward and reverse scan modes.

Interlayer	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)	I_h
DTS/PSBMA Forward	1.06	22.40	84.2	20.07	0.006
DTS/PSBMA Reverse	1.07	22.54	83.7	20.15	
CDT/PSBMA Forward	1.09	22.23	81.8	19.86	0.005
CDT/PSBMA Reverse	1.09	22.24	81.4	19.81	
DTP/PSBMA Forward	1.04	21.59	78.6	17.59	0.016
DTP/PSBMA Reverse	1.04	21.51	78.5	17.27	

Table S7. The parameters of the equivalent circuit for Pero-SCs.

Interlayer	R_s (Ω)	R_{tr} (Ω)	C_{tr} (nF)
DTS/PSBMA	7.9	36.6	2.8
CDT/PSBMA	6.9	42.7	2.7
DTP/PSBMA	7.8	52.0	2.4

5. References

1 R. Miyakoshi, A. Yokoyama and T. Yokozawa, *J Am Chem Soc*, 2005, **127**, 17542-17547.
2 R. Miyakoshi, A. Yokoyama and T. Yokozawa, *Macromol Rapid Commun*, 2004, **25**, 1663-1666.