Supplementary Information

Side-chain engineering of PEDOT derivatives as dopant-free hole-transporting materials for efficient and stable n-i-p structured perovskite solar cells

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Synthetic procedures:

Poly(5,7-dibromo-2-hexyl-2,3-dihydrothieno[3,4-b][1,4]dioxine) (P6): The monomer 5,7-dibromo-2-hexyl-2,3-dihydrothieno[3,4-b][1,4]dioxine (DBEDOT-C6) (1.9 g, 0.5 mmol) were dissolved in $CHCl_3$ (2 mL), and then 1.5 equivalents Br_2 (0.49 mL) was added at room temperature. The reaction mixture was heated to 50 ^oC and stirred for 48 h. After the reaction was completed, $CHCl_3$ was removed and MeOH (60 mL) was add to this residue. A black precipitation appeared which was collected by filtration and then washed with MeOH to afford a black polymer P6 (1.0 g).

De-doped Procedure: To a stirred mixture of the doped polymers in deoxygenated $CHCl_3$ (40 mL), hydrazine hydrate (10 drops) was added at room temperature. The resulting mixture was stirred overnight at room temperature. $CHCl_3$ was removed under reduced pressure and the resulting residue was collected. The resulting black solid was purified by repeated Soxhlet extraction with deoxygenated MeOH. After purification, the resulting neutral polymers was kept under N_2 (0.71 g, 56%). ^1H NMR spectrum of P6 (400 MHz, $CDCl_3$) is shown in Fig. S2, which is consistent with result in the literature.[1] Anal. Calcd. for $C_{12}H_{16}O_2S$: C 64.12, H 7.20; found: C 63.04, H 7.06.

P10 (0.82 g, 53%) and P14 (1.02 g, 55%) HTMs were prepared by the same synthetic routes as P6. Anal. Calcd. for $C_{16}H_{24}O_2S$: C 68.04, H 9.28, found: C 66.02, H 8.76. Anal. Calcd. for $C_{20}H_{32}O_2S$: C 70.96, H 10.12; found: C 69.70, H 9.46.

^1H NMR of three monomers:

5,7-dibromo-2-hexyl-2,3-dihydrothieno[3,4-b][1,4]dioxine (DBEDOT-C6), ^1H NMR (400 MHz, $CDCl_3$): δ 4.22 (dd, *J* = 11.6, 2.1 Hz, 1H), 4.15 – 4.12 (m, 1H), 3.91 (dd, *J* = 6.1, 5.5 Hz, 1H), 1.77 – 1.68 (m, 1H), 1.63 – 1.21 (m, 12H), 0.90 (t, *J* = 6.8 Hz, 3H).

5,7-dibromo-2-decyl-2,3-dihydrothieno[3,4-b][1,4]dioxine (DBEDOT-C10), ^1H NMR (400 MHz, $CDCl_3$): δ 4.16 (dd, *J* = 11.6, 2.1 Hz, 1H), 4.07 (dd, *J* = 5.4, 2.2 Hz, 1H), 3.84 (dd, *J* = 11.6, 7.8 Hz, 1H), 1.56 – 1.44 (m, 2H), 1.39 – 1.16 (m, 16H), 0.81 (t, *J* = 6.9 Hz, 3H).

5,7-dibromo-2-tetradecyl-2,3-dihydrothieno[3,4-b][1,4]dioxine (DBEDOT-C14), ^1H NMR (400 MHz, $CDCl_3$): δ 4.16 (dd, *J* = 11.6, 2.1 Hz, 1H), 4.07 (dd, *J* = 5.6, 2.3 Hz, 1H), 3.84 (dd, *J* = 11.6, 7.8 Hz, 1H), 1.56 – 1.45 (m, 2H), 1.30 – 1.16 (m, 24H), 0.81 (t, *J* = 6.8 Hz, 3H).

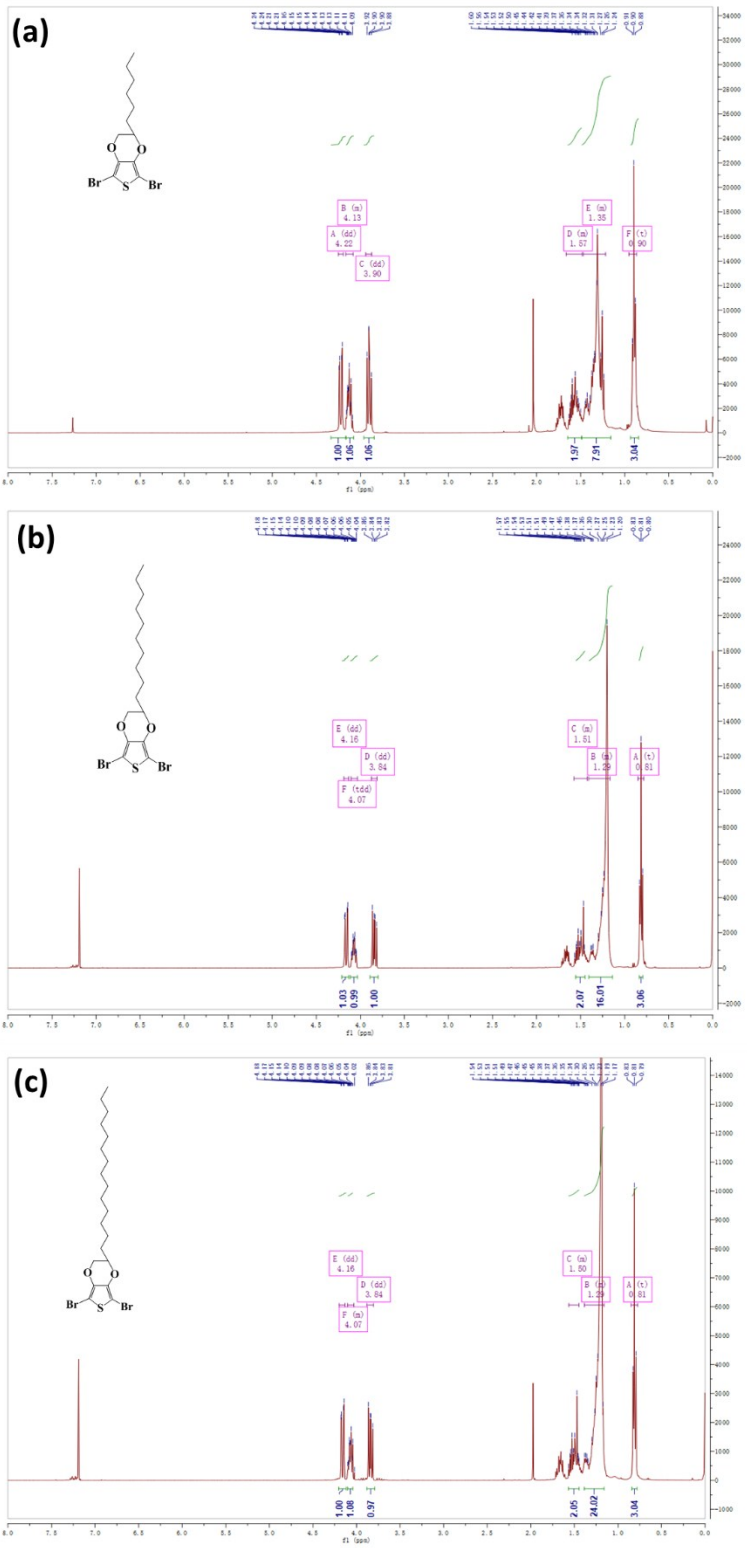

Fig. S1 ^{1}H NMR spectra of (a) DBEDOT-C6, (b) DBEDOT-C10, and (c) DBEDOT-C14 in $CDCl_3$.

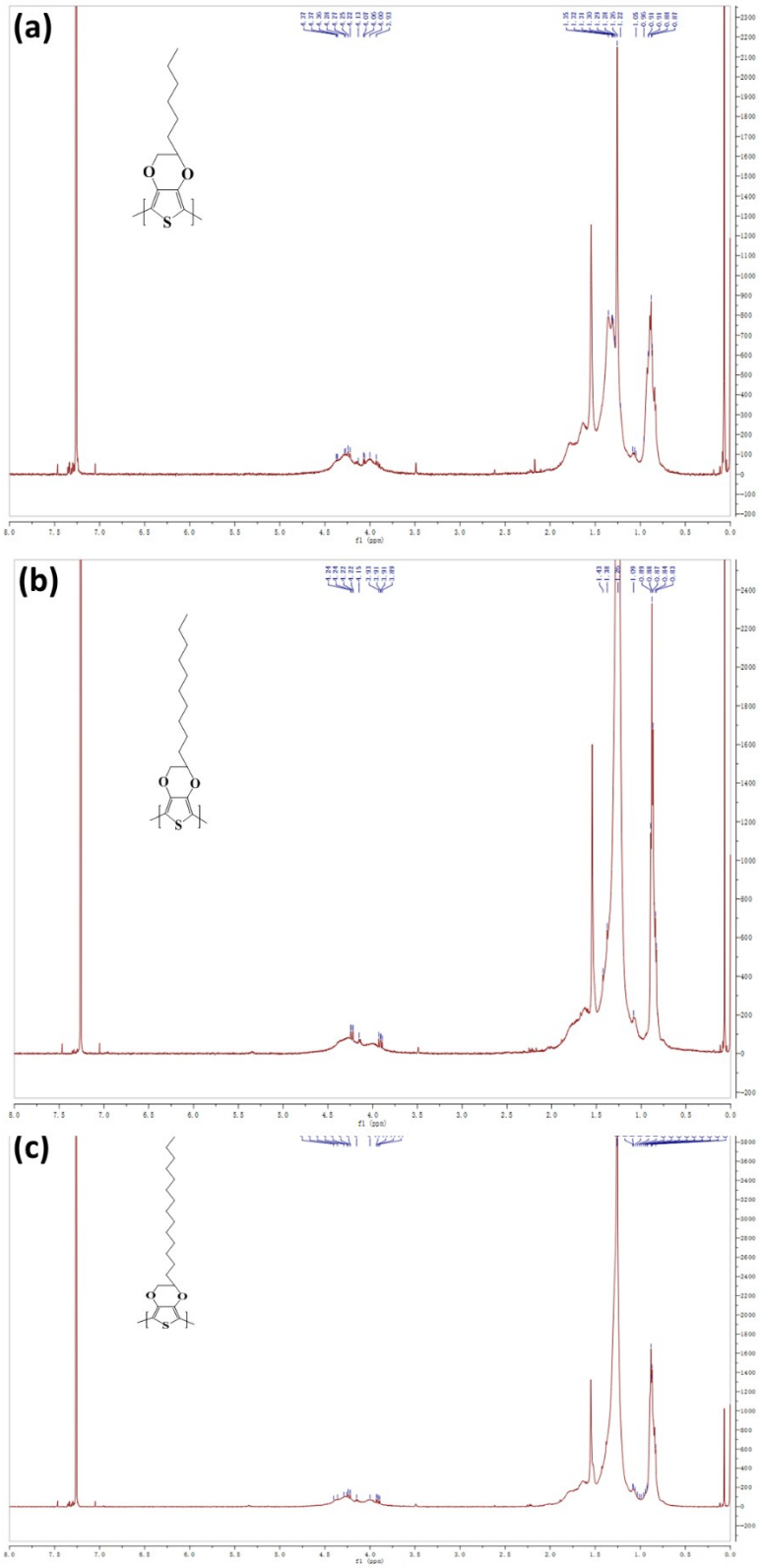

Fig. S2 ^{1}H NMR spectra of (a) P6, (b) P10, and (c) P14 in $CDCl_3$.

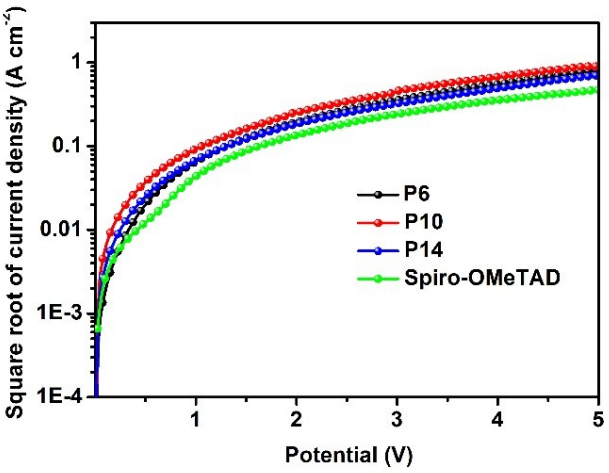

Fig. S3 Square root of current density–voltage curves for P6, P10, P14, and Spiro-OMeTAD.

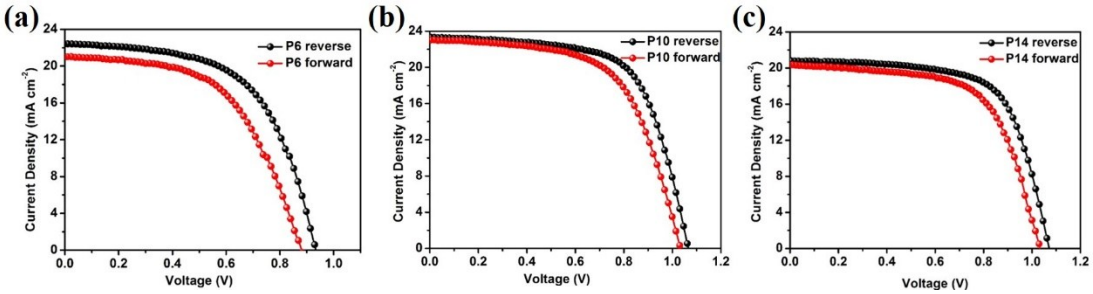

Fig. S4 The *J*–*V* curves of PSCs based on different HTMs from different scan directions under 100 mW cm^{-2} illumination (AM 1.5G): (a) P6, (b) P10, and (c) P14.

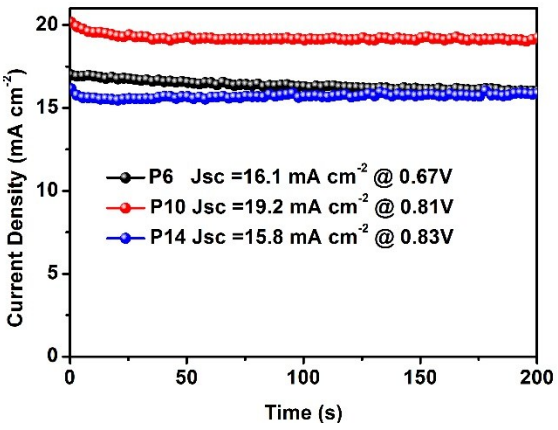

Fig. S5 The steady-state photocurrent curves measured at the maximum power point for PSCs with different HTMs.

Table S1 Photovoltaic performance based on P6, P10, and P14 at forward scan and reverse scans under the 100 mW cm^{-2} illumination (AM 1.5G).

HTMs		V_{oc} (V)	J_{sc} (mA cm^{-2})	FF	PCE (%)
P6	reverse	0.93	22.4	0.58	12.1
	forward	0.88	21.0	0.55	10.2
P10	reverse	1.06	23.3	0.65	16.2
	forward	1.03	22.9	0.61	14.4
P14	reverse	1.07	20.8	0.67	14.8
	forward	1.03	20.3	0.63	13.2

Table S2 Summary of the PL lifetime parameters from fitting curves of the TRPL decay measurements.

Samples	A_1	τ_1 (ns)	A_2	τ_2(ns)	A_1(%)	A_2(%)	τ_{ave}(ns)
Without HTM	0.59	22.58	0.31	169.88	65. 6	34.4	140.1
P6	0.72	7.36	0.2	43.12	78.2	21.8	29.5
P10	0.79	6.02	0.21	27.9	79.0	21.0	18.1
P14	0.78	5.24	0.18	36.33	81.2	18.8	24.3

Table S3 Photovoltaic performance based on dopant-free P10 measured under 100 mW·cm^{-2} illumination (AM 1.5G) at different stages during humidity stability test.

Time (h)	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF	PCE (%)
0	1.08	22.1	0.65	15.6
24	1.08	21.5	0.64	15.0
48	1.07	21.3	0.64	14.8
72	1.05	21.1	0.63	13.9
96	1.05	20.3	0.60	12.7
120	1.04	20.7	0.55	11.9

Table S4 Photovoltaic performance based on doped Spiro-OMeTAD measured under 100 mW·cm^{-2} illumination (AM 1.5G) at different stages during humidity stability test.

Time (h)	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF	PCE (%)
0	1.12	22.9	0.75	19.3
24	1.14	21.8	0.69	17.2
48	1.11	21.7	0.60	14.5
72	1.04	20.2	0.60	12.4
96	1.03	18.6	0.54	10.4
120	1.02	13.8	0.49	6.99

Reference

1. A. Patra, V. Agrawal, R. Bhargav, Shahjad, D. Bhardwaj, S. Chand, Y. Sheynin and M. Bendikov, Macromolecules, 2015, **48**, 8760–8764.