Supporting Information

Star-shaped cyclopentadithiophene-based dopant-free hole-transporting material for highperformance perovskite solar cells

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Materials and Reagents

All commercial solvents and chemicals were purchased from Aldrich, with the purity more than 98%. The Thin-layer chromatography (TLC) was conducted with Merck KGaA precoated TLC Silica gel 60F254 on aluminum sheets. Flash column chromatography was performed on glass columns packed with silica gel using Silicycle UltraPure SilicaFlash P60, 40–63 mm (230–400 mesh). Unless otherwise specified, all reactions and manipulations were carried out under a nitrogen atmosphere. Solvents of reagent grade were used for syntheses and those of spectroscopy grade for spectra measurements. Solvents were dried by standard procedures.

Characterization

¹H and ¹³C NMR spectra were recorded on a Bruker 400 and 500 MHz spectrometer. Matrix-assisted laser desorption ionization-time of flight (MALDI-TOF) mass spectra were recorded on a Jeol JMS 700 double-focusing spectrometer. UV spectra were measured on a Jasco V-530 double beam spectrophotometer. Fluorescence spectra were recorded on a Hitachi F-4500 fluorescence spectrophotometer. CV experiments were performed with a CHI-621A electrochemical analyzer. All measurements were carried out at room temperature with a conventional three-electrode configuration that consisted of a platinum working electrode, an auxiliary electrode, and a non-aqueous Ag/AgNO₃ reference electrode. The SEM images were obtained by using a field-emission scanning electron microscope (JEOL-7401). A Nano-Scope NS3A system (Digital Instrument) was used to obtain the AFM images of the surface morphologies and thicknesses of various thin films.

Solar cell fabrication.

A TiO₂ compact layer (~30 nm in thickness) was deposited by spin-coating a titanium isopropyl solution onto a F:SnO₂ (FTO) substrate. A 150 nm-thick mesoporous TiO₂ film (particle size: ~ 20 nm,

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crystalline phase: anatase) was spin-coated onto the compact-TiO₂/FTO substrate using homemade pastes and heated at 500 °C for 30 min. After sintering the TiO₂ layer, the electrode was cooled to room temperature and immersed in 0.04 M aqueous TiCl₄ at 70 °C for 30 min. The film was then rinsed by deionized water and then annealed at 500 °C for 30 min again. After cooling to room temperature the substrate was transferred to a nitrogen-filled glove box. A solution consisting of PbI₂ (1.25 M) and methylammonium iodide (1.25 M) in y-butyrolactone (GBL) and DMSO (7/3, v/v) was deposited onto the substrate by a two-step spin-coating process at 1000 and 5000 rpm for 10 and 20 s, respectively. During the second spin-coating step, the substrate was treated with 50 µL toluene by drop-casting. The substrate was dried on a hot plate at 100 °C for 10 min. The T-CPDT and C-CPDT molecules studied in this work were dissolved in chlorobenzene (40 mg/mL) and spin-coated on the substrate at 2000 rpm for 30 s. The solution of spiro-OMeTAD was prepared in chlorobenzene (40 mg/mL) and mixed with 17.5 µL stock solution of lithium bistrifluoromethanesulfonimide (Li-TSFI, 520 mg in 1 mL acetonitrile) and 28.5 µL 4-*tert*-butylpyridine. The solution was spin-coated on substrate at 2000 rpm for 30 s. Finally, the Ag counter electrode was deposited by thermal evaporation (~100 nm). The active area of this electrode was fixed at 0.16 cm². J-V curves were recorded with a Keithley 2400 source meter under simulated AM 1.5G sunlight, calibrated to 100 mW/cm². The reported device characteristics were estimated from the measured J-V curves.

Solar cell performance measurement

Solar cell efficiencies were evaluated under simulated one sun irradiation from a Xe arc lamp with an AM 1.5 global filter. Irradiance was characterized using a calibrated spectrometer and illumination intensity was set using an NREL certified silicon diode with an integrated KG1 optical filter: spectral mismatch factors were calculated for each device in this report to be less than 5%.

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IPCE spectra were measured in air using a commercial IPCE set-up (Enlitech, QE-R).

Mobility measurements

In order to assess the potential of **T-CPDT**, **C-CPDT**, and spiro-OMeTAD as hole transport materials, hole-only devices were fabricated with the device structure ITO/PEDOT:PSS/HTM/AI. Hole mobilities were calculated by the space-charge-limited current (SCLC) method using the Mott–Gurney law, by fitting experimental data to equation (1) in the voltage range where the obtained slope in the double log plot is equal to 2.

$$J = \frac{9}{8} \varepsilon_{\rm r} \varepsilon_0 \mu_{\rm h} \frac{V^2}{d^3} \tag{1}$$

In equation (1), *J* is the current density, ε_0 is the permittivity of free space (8.85 x10⁻¹² F m⁻¹), ε_r is the relative permittivity of the material (approaching 3 for organic semiconductors), μ_h is the hole mobility, *V* is the applied voltage and *d* is the thickness of the active layer.

The hole-only devices were fabricated by spin-coating PEDOT:PSS (Clevios P, VP Al4083) onto pre-cleaned, patterned indium tin oxide (ITO) substrates (15 Ω /square) (Kintec). A film of the HTM was spin-coated on top from chloroform solution with a concentration of 40 mg mL⁻¹. The film thickness was varied by using different spin-coating speeds. As a counter electrode, Al was deposited on top by vacuum evaporation. The current density–voltage curves of the devices were recorded with a Keithley 2400 Source meter.

Computation method

Computations were performed using the Gaussian 03 program package. The geometry was optimized by using B3LYP (Becke three parameters hybrid functional with Lee-Yang-Parr correlation functionals) with the Pople 6-31G(d,p) atomic basis set.^{S1}

Scheme S1. Synthetic procedures for C-CPDT



Synthesis of 3. A heterogeneous mixture of 2 M K₂CO₃ (12 mL), THF (16 mL), 1 (2.07 g, 4.8 mmol), 2 (0.8 g, 2.3 mmol), and Pd(PPh₃)₄ (0.106 g, 4 mol %) under argon was heated at 80 °C for 18 h. The mixture was extracted with CH₂Cl₂. The organic layer was separated and dried over anhydrous MgSO₄. Evaporation of the solvent gave a crude product, which was purified by silica gel column chromatography using CH₂Cl₂/hexane (1/1) as eluent to afford the desired product as a black solid in 82% yield. mp 132-134 °C;¹H NMR (400 MHz, CDCl₃): δ 7.31 (d, *J* = 8.8 Hz, 4H), 7.08-7.04 (m, 10H), 6.89 (d, *J* = 8.8 Hz, 4H), 6.85 (d, *J* = 8.8 Hz, 8H), 3.80 (s, 12H) ppm; ¹³C NMR 100 MHz, CDCl₃): δ 184.1, 156.4, 148.9, 147.7, 142.3, 140.6, 127.1, 126.1, 125.7, 120.3, 115.8, 115.0, 55.72 ppm.; HRMS (MALDI-TOF) *m/z* [M⁺] calcd for C₄₉H₃₈N₂O₅S₂: 798.2222; found: 798.2225.

Synthesis of 4. Compound **3** (0.4 g, 0.50 mmol), P(*o-i*Pr)₃ (0.19 g, 2.34 mmol), and CBr₄ (0.2 g, 0.60 mmol) were dissolved in dry CH₂Cl₂ (34 mL). The reaction mixture was stirred for 18 h at room temperature, thereafter, distilled water was added to quench the reaction. The organic layer was separated, washed with water, dried over anhydrous MgSO₄, filtered and evaporated under reduced pressure. The reaction crude was purified by flash chromatography (silica gel, hexane/dichloromethane 1:1), yielding a black solid in 85%. mp 148-150 °C; ¹H NMR (500 MHz, DMSO-d6): δ 7.78 (s, 2H), 7.46 (d, *J* = 8.5 Hz, 4H), 7.05 (d, *J* = 9.0 Hz, 8H), 6.93 (d, *J* = 9.0 Hz, 8H), 6.79 (d, *J* = 8.5 Hz, 4H), 3.75 (s, 12H) ppm; ¹³C NMR (125 MHz, DMSO-d6): δ 155.9, 148.1, 144.1,

142.9, 139.7, 136.5, 136.0, 126.8, 125.9, 125.4, 119.3, 117.8, 115.0, 96.0, 55.24 ppm; HRMS (MALDI-TOF) *m/z* [M⁺] calcd for C₅₀H₃₈O₄N₂S₂Br₂: 952.0640; found: 952.0643.

Synthesis of C-CPDT. A heterogeneous mixture of 2M K₂CO₃ (10 mL), THF (14 mL), **4** (0.2 g, 0.21 mmol), (4-(3,6-Dimethoxy-9H-carbazol-9-yl)phenyl)boronic acid (**5**) (0.15 g, 0.44 mmol), and Pd(PPh₃)₄ (0.01 g, 4 mol %) were heated at 80 °C under argon for 18 h. The mixture was extracted with CH₂Cl₂, and the organic extracts were dried over anhydrous MgSO₄. Evaporation of the solvent gave a product, which was purified by silica gel column chromatograph with CH₂Cl₂/hexane (2/1) as eluent to afford the desired product as a red solid in 93% yield. mp > 300 °C; ¹H NMR (500 MHz, CDCl₃): δ 7.84 (d, *J*=2.0 Hz, 4H), 7.81-7.76 (m, 8H), 7.40 (d, *J*=9.0 Hz, 4H), 7.20 (d, *J*=8.5 Hz, 4H), 7.02 (d, *J*=9.0 Hz, 8H), 6.96-6.90 (m, 12H), 6.69 (d, *J*=8.5 Hz, 4H), 6.28 (s, 2H), 3.86 (s, 12H), 3.73 (s, 12H) ppm; ¹³C NMR (125 MHz, CDCl₃): δ 156.3, 154.5, 148.2, 142.4, 140.4, 139.7, 138.9, 136.2, 133.4, 132.6, 127.0, 126.5, 126.0, 124.2, 120.6, 115.5, 115.0, 110.9, 103.3, 56.28, 55.67 ppm; HRMS (MALDI-TOF) *m*/*z* [M⁺] calcd for C₉₀H₇₀N₄O₈S₂ (M⁺) 1398.4635 found 1398.4655.





Fig. S1 Calculated gas-phase absorption spectra of (a) T-CPDT and (b) C-CPDT.



Fig. S2 The optimized structure of (a) **T-CPDT**, (b) **C-CPDT** and (c) spiro-OMeTAD calculated with DFT on B3LYP-6-31G(d,p).

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Fig. S3 Photoemission yield spectra of T-CPDT and C-CPDT in air.

Fig. S4 Space-charge-limited-current plots in the *J*-*V* characteristics of the devices with **T-CPDT**, **C-CPDT** and spiro-OMeTAD as HTM, respectively.

Fig. S5 (a) Steady-state photoluminescence (PL) spectra of the perovskite film, perovskite/**T-CPDT** film, perovskite/**C-CPDT**, and perovskite/spiro-OMeTAD film. (b) Time-resolved photoluminescence (TRPL) spectra of the perovskite film, perovskite/**T-CPDT** film, perovskite/**C-CPDT**, and perovskite/spiro-OMeTAD film

Fig. S6 The top-view SEM images of (a) T-CPDT and (b) C-CPDT on top of the perovskite film

Fig. S7 AFM micrograms and 3D images of **T-CPDT** (a) and **C-CPDT** (b) films deposited on perovskite/mp-TiO₂/c-TiO₂/FTO.

Fig. S8 Cross-sectional SEM image of the PSC device with C-CPDT as HTM.

Fig. S9 Plots of *J-V* curves for the perovskite solar cells using **T-CPDT**, **C-CPDT**, and spiro-OMeTAD as HTM under forward scan (at illumination of 100 mW/cm², AM1.5G).

Fig. S10 Normalized PCEs of the devices with dopant-free T-CPDT, C-CPDT and doped spiro-

OMeTAD layers.

Fig. S11 ¹H NMR spectrum of compound **3**.

Fig. S12 ¹³C NMR spectrum of compound 3.

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Fig. S13 ¹H NMR spectrum of compound **4**.

Fig. S14 ¹³C NMR spectrum of compound 4.

Fig. S15 ¹H NMR spectrum of compound **C-CPDT**.

Fig. S16 ¹³C NMR spectrum of compound C-CPDT.

HTM	nª	<i>E</i> (ev, nm)	f	Composition
T-CPDT	1	1.96 (634)	0.23	100% HOMO→LUMO
	2	2.51 (495)	0.41	88% HOMO-1→LUMO
	5	2.87 (432)	1.19	62% HOMO→LUMO+1
	6	2.97 (418)	0.58	72% HOMO-4→LUMO
	7	3.32 (373)	0.13	37% HOMO-1→LUMO+1
C-CPDT	1	1.77 (701)	0.20	98% HOMO→LUMO
	3	2.50 (497)	0.18	94% HOMO-2→LUMO
	5	2.42 (457)	0.19	88% HOMO-4→LUMO+2
	6	2.86 (433)	1.49	87% HOMO-1→LUMO+1

Table S1 Calculated TDDFT excitation energies (E), oscillator strengths (f), MO compositions and characters based on DFT at the B3LYP/6-31G (d,p) level.

Table S2 Summary of the fitting results and corresponding dynamic parameters derived from TRPL

decay traces.

HTM	A ₁	τ ₁ (ns)	A ₂	τ ₂ (ns)	τ _{avg.} (ns)
none	0.61	47.31	0.39	7.48	31.78
T-CPDT	0.72	27.44	0.28	5.82	21.39
C-CPDT	0.51	25.8	0.49	6.96	16.57

Table S3 Photovoltaic parameters of the best-performing PSCs with dopant-free T-CPDT and C-

CPDT and doped	l spiro-OMeTAD	as HTMs
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HTM	Scan direaction	V _{oc} [V]	$J_{\rm sc}$ [mA cm ⁻²]	FF (%)	PCE _{max} [%]
T-CPDT	reverse	0.88	21.37	60.9	11.45
	forward	0.87	20.29	57.0	10.06
C-CPDT	reverse	1.14	23.27	74.2	19.68
	forward	1.14	23.29	72.8	19.33
spiro-OMeTAD	reverse	1.09	23.42	75.5	19.27
	forward	1.09	23.25	75.4	19.11

Table S4 Cost Calculation of Compound A	Table S4	l Cost	Calculation	of Com	pound 2	2
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Reagent	Amount	Amount	Price	Total Price
	(g)	(mL)	(\$/g or	(\$)
			\$/mL)	
4H-cyclopenta[2,1-b:3,4-b']dithiophen-4-	1.00		233	233
one				
Water		50	0.0	0.00
Dichloromethane		50	0.0149	0.745
Hexane		400	0.0011	0.44
N-bromosuccinimide	1.94		0. 1012	0.196
MgSO ₄	3		0.06	0.18
Silica gel	100		0.0042	0.42
Total Cost	234.981 \$			
Total amount of compound 2	1.77 g			
Cost of compound 2		1	32.758 \$/g	

Table S5 Cost calculation of 3

Reagent	Amount	Amount	Price	Total
	(g)	(mL)	(\$/g or	Price
			\$/mL)	(\$)
compound 2	0.8		132.758	106.206
4-methoxy-N-(4-methoxyphenyl)-	2.07		8.99ª	18.609
N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-				
yl)				
phenyl)aniline (1)				
Pd(PPh ₃) ₄	0.109		323.6	35.27

K ₂ CO ₃	3.32		0.03	0.0996
Water		100	0.00	0.00
THF		16	0.034	0.544
MgSO ₄	3		0.06	0.18
Hexane		400	0.0011	0.44
Dichloromethane		400	0.0149	5.96
Silica gel	200		0.0042	0.84
Total Cost	168.149 \$			
Total amount of 3	1.50 g			
Cost of 3		112.099 \$/ _{	8	

Table S6 Cost calculation of 4

Reagent	Amount Amount Price		Price	Total Price (\$)	
	(g)	(mL)	(\$/g or \$/mL)		
compound 3	0.4		112.099	44.840	
CBr ₄	0.2		0.79	0.158	
P(<i>o-i</i> Pr) ₃	0.19		0.679	0.129	
Water		100	0.00	0.00	
MgSO ₄	3		0.06	0.18	
Hexane		250	0.0011	0.275	
Dichloromethane		250	0.0149	3.725	
Silica gel	100		0.0042	0.42	
Total Cost	49.727 \$				
Total amount of 4	0.41 g				
Cost of 4			121.285 \$/g		

Table S7 Cost Calculati	on of Compound 4-1
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Reagent	Amount	Amount	Price	Total Price (\$)	
	(g)	(mL)	(\$/g or \$/mL)		
Carbazole	1		0.234	0.234	
DMF		20	0.02	0.40	
Water		50	0.0	0.00	
Dichloromethane		50	0.0149	0.745	
N-bromosuccinimide	2.235		0.1012	0.226	
MgSO ₄	5		0.06	0.30	
Hexane		150	0.0011	0.165	
Dichloromethane		50	0.0149	0.745	
Silica gel	100		0.0042	0.42	
Total Cost	3.235 \$				
Total amount of compound	1.749 g				
3,6-dibromo-9H-carbazole (4-					
1)					
Cost of 3,6-dibromo-9H-			1.850 \$/g		
carbazole (4-1)					

Reagent	Amount	Amount	Price	Total Price (\$)	
	(g)	(mL)	(\$/g or \$/mL)		
3,6-dibromo-9H-carbazole (4-	4		1.850	7.40	
1)					
DMF		130	0.02	2.6	
Water		50	0.0	0.00	
Dichloromethane		400	0.0149	5.96	
NaOMe		67	0.036	2.412	
Cul	9.85		0.536	5.2796	
MgSO ₄	5		0.06	0.30	
Hexane		1000	0.0011	1.10	
Silica gel	400		0.0042	1.68	
Total Cost	26.732 \$				
Total amount of compound	2.04 g				
3,6-dimethoxycarbazole (4-2)					
Cost of 3,6-	13.104 \$/g				
dimethoxycarbazole (4-2)					

Table S9 Cost Calculation of Compound 4-3

Reagent	Amount	Amount	Price	Total Price	
	(g)	(mL)	(\$/g or	(\$)	
			\$/mL)		
3,6-dimethoxycarbazole (4-2)	0.91		13.104	11.925	
1,4-dibromobenzene	3.76		0.28	1.0528	
Water		50	0.0	0.00	
Dichloromethane		50	0.0149	0.745	
K ₂ CO ₃	1.6		0.03	0.048	
Cul	0.4		0.536	0.2144	
DMAc		25	0.20	5.0	
MgSO ₄	2		0.06	0.12	
Hexane		200	0.0011	0.22	
Silica gel	100		0.0042	0.42	
Total Cost		19.745 \$			
Total amount of compound 9-(4-	1.148 g				

Bromo-phenyl)-3,6-dimethoxy-9H-	
carbazole (4-3)	
Cost of 9-(4-Bromo-phenyl)-3,6-	17.199 \$/g
dimethoxy-9H-carbazole (4-3)	

Reagent	Amount	Amount	Price	Total Price	
	(g)	(mL)	(\$/g or	(\$)	
			\$/mL)		
9-(4-Bromo-phenyl)-3,6-	0.76		17.199	13.071	
dimethoxy-9H-carbazole (4-3)					
B(OCH ₃) ₃		0.63	0.125	0.0788	
Water		50	0.0	0.00	
Dichloromethane		100	0.0149	1.49	
HCI	0.876		0.0602	0.0527	
n-BuLi		1.5	0.0119	0.01785	
MgSO ₄	2		0.06	0.12	
Hexane		100	0.0011	0.11	
Silica gel	80		0.0042	0.336	
Total Cost	15.276 \$				
Total amount of (4-(3,6-Dimethoxy-9H-	0.53 g				
carbazol-9-yl)					
phenyl)boronic acid (5)					
Cost of (4-(3,6-Dimethoxy-9H-carbazol-9-yl)	28.823 \$/g				
phenyl)boronic acid (5)					

Table S10 Cost Calculation of Compound 5

Reagent	Amoun	Amoun	Price	Total Price (\$)
	t	t	(\$/g or	
	(g)	(mL)	\$/mL)	
compound 4	0.2		121.285	24.257
4-methoxy-N-(4-methoxyphenyl)-	0.19		8.99ª	1.7081
N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-				
yl)				
phenyl)aniline (1)				
Pd(PPh ₃) ₄	0.01		323.6	3.236
K ₂ CO ₃	2.76		0.03	0.0828
Water		50	0.00	0.00
THF		14	0.034	0.476
MgSO ₄	3		0.06	0.18
Hexane		400	0.0011	0.44
Dichloromethane		600	0.0149	8.94
Silica gel	100		0.0042	0.42
Total Cost	39.290 \$			
Total amount of T-CPDT	0.264 g			
Cost of C-CPDT	148.826 \$/g			

Table S11 Cost Calculation of Compound T-CPDT

Table S12 Cost Calculation of Compound C-CPDT

Reagent	Amount	Amount	Price	Total Price
	(g)	(mL)	(\$/g or	(\$)
			\$/mL)	
compound 4	0.2		121.285	24.257
(4-(3,6-Dimethoxy-9H-carbazol-9-	0.15		28.823	4.323

yl)phenyl)boronic acid (5)				
Pd(PPh ₃) ₄	0.01		323.6	3.236
K ₂ CO ₃	2.76		0.03	0.0828
Water		50	0.00	0.00
THF		14	0.034	0.476
MgSO ₄	3		0.06	0.18
Hexane		400	0.0011	0.44
Dichloromethane		600	0.0149	8.94
Silica gel	100		0.0042	0.42
Total Cost	42.355 \$			
Total amount of C-CPDT	0.27 g			
Cost of C-CPDT	156.870 \$/g			

a Y.-S. Lin, S. Y. Abate, K.-W. Lai, C.-W. Chu, Y.-D. Lin, Y.-T. Tao, S.-S. Sun, *ACS Appl. Mater. Interfaces* 2018, **10**, 41439–41449.

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