Supporting information

Cost-Effective Hole Transporting Material for Stable and

Efficient Perovskite Solar Cells with Fill Factors up to 82%

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1. Experimental section

1.1 General Details.

Commercially available reagents were purchased from Sigma-Aldrich, J&K or Energy and used without further purification. Toluene, and tetrahydrofuran (THF) were freshly distilled before use. 4-Methoxy-N-(4-methoxyphenyl)-N-(4-(7-(tributylstannyl)-2,3dihydrothieno[3,4-b][1,4]dioxin-5-yl)phenyl)aniline (4) was synthesized according to literature.¹ Other solvents were used directly. ¹H NMR and ¹³C NMR spectra were recorded on Bruker AVANCE III 500 MHz spectrometer with tetramethylsilane (TMS) as internal standard. Mass spectra were obtained by Bruker ultrafleXtreme MALDITOF/TOF. The absorption spectrawere UVmeasured by Visspectrophotometer (Evolution 220, Thermo Fisher). Photoluminescence (PL) spectrum was conducted on Horiba Jobin Yvon Model FM-4NIR spectrophotometer. The electrochemical cyclic voltammetry (CV) was conducted on an CHI760D electrochemical workstation (Chenhua Shanghai) with Pt plate as working electrode, Pt slice as counter electrode, and Ag/AgCl electrode as reference electrode in tetrabutylammonium hexafluorophosphate (Bu₄NPF₆, 0.1 M) acetonitrile solutions at a scan rate of 50 mV s⁻¹. Ferrocene/ferrocenium (Fc/Fc⁺) was used as the internal standard (the energy level of Fc/Fc⁺ is -4.8 eV under vacuum),² and the formal potential of Fc/Fc⁺ was measured as 0.55 V vs. Ag/AgCl electrode. The HOMO energy level was determined from the onset oxidation (E_{onset}^{ox}) as HOMO = -4.25- E_{onset}^{ox} (eV); while the LUMO energy level was calculated with HOMO and optical bandgap (E_g^{opt}) by the formula as: LUMO = HOMO + E_g^{opt} (eV). Thermogravimetric analysis (TGA) was conducted under nitrogen atmosphere at a heating rate of 20 °C min⁻¹ from 50 °C to 800 °C. The instrument type was TGA/SDTA851E (Mettler Toledo). DSC was conducted on PerkinElmer Thermal Analysis at a scan rate of 10 °C min⁻¹ from 50 °Cto 250 °C.

All calculations were carried out using density functional theory (DFT) calculations at the B3LYP/6-31G(d,p) level using Gaussian 09 program suite. The theoretical models were optimized initially using HF/3-21G level. The hole reorganization energy (λ_{hole}) was calculated by $\lambda_{hole}=E^+(N)-E^+(C)+E(C)-E(N)$,³where E⁺(N), E⁺(C), E(C) and E(N) are calculated to be -7726.4430, -7726.4446, -7726.6217 and -7726.6233 Hartree, respectively.

Hole Mobility Measurements: Hole-only devices with the configuration of ITO/PEDOT:PSS/TRUX-E-T (spiro-OMeTAD)/MoO₃/Ag were used to evaluate charge mobilities by space charge-limited currents (SCLC) model. The thickness of HSL was around 100 nm. The charge mobilities were determined by fitting the dark current according to the following equation:

$$J(V) = \frac{9V^2}{8L^3} \varepsilon_0 \varepsilon_r \mu_0 e^{(0.89\gamma \sqrt{V/L})}$$

Where *J* is the dark current density (mA cm⁻²), μ_0 is the zero-field mobility (cm² V⁻¹ s⁻¹), ε_0 is the permittivity of free space, ε_r is the relative permittivity of the material, *V* is the effective voltage ($V = V_{\text{Applied}} - V_{\text{Built-in}} - V_{\text{series resistane}}$), and *L* is the thickness of the active layer.

1.2 Synthesis



Truxene (1)

1-Indanone (11.0 g, 82.23 mmol) was added to amixed solution of acetic acid (60 mL) and concentratedhydrochloric acid (30 mL). Then the solution was heated to 100 °C for 24 h. After cooling to room temperature, the mixture waspoured into 800 ml of ice water, and stirred for 1 h. The yellow precipitate was filtered, and washed with water, ethanol, cold acetone and cold dichloromethane.Compound **1** was obtained as light yellow solid (6.1 g, 63.9%). ¹H NMR (500 MHz, CDCl₃, δ): 7.96 (d, *J* = 7.7 Hz, 3H), 7.70 (d, *J* = 7.4 Hz, 3H), 7.50 (d, *J* = 7.5 Hz, 3H), 7.41 (d, *J* = 7.3 Hz, 3H), 4.28 (d, *J* = 4.6 Hz, 6H).

5,5,10,10,15,15-Hexabutyltruxene (2)

Compound 1 (6.0 g, 17.52 mmol) was dissolved in 150 mL dry THF under N₂atmosphere. After cooling to -78 °C, *n*-BuLi (73 mL, 175.22 mmol, 2.4 M in *n*-

hexane) was addeddropwise and the mixture was stirred at -78 °C for 2 h.A solution of $C_6H_{13}Br$ (28.92 g,175.22 mmol) in 50 mL THF was injected slowly. The mixture was slowly warmed to room temperature and stirred overnight. Then the solution was quenched with saturated ammonium chloride solution (100 mL), extracted with ethyl acetate for three times, dried over MgSO₄. After the organic phase was concentrated under reduced pressure, the crude product was purified by column chromatography on silica gel using petroleum ether as the eluent. Compound **2** was obtained as off-white solid (11.0 g, 74.1%). ¹H NMR (500 MHz, CDCl₃, δ): 8.36 (d, *J* = 7.6 Hz, 3H), 7.46 (d, *J* = 7.1 Hz, 3H), 7.37 (p, *J* = 7.2 Hz, 6H), 3.04 – 2.89 (m, 6H), 2.16 – 2.00 (m, 6H), 0.98 – 0.77 (m, 36H), 0.59 (t, *J* = 7.1 Hz, 18H), 0.48 (m, 12H).

2,7,12-Tribromo-5,5,10,10,15,15-hexahexyltruxene (3)

To a solution of compound **2** (10.0 g, 11.80 mmol) in 50 ml ofchloroform, anhydrous FeCl₃(38.3 mg, 0.24 mmol) was added as catalyst. A solution ofbromine (7.2 g, 44.84 mmol) in 15ml of chloroform was added dropwise under ice bath. The mixture was gradually warmed to room temperature andstirred for 24 h. After quenching with saturated NaHSO₃ aqueous solution, the mixture was extracted with chloroform for three times, and the organic phase was dried over MgSO₄. After the solvent was removed, the yellow residue was recrystallized from ethanol to give an off-white powder **3** (11.8 g, 92.2%).¹H NMR (500 MHz, CDCl₃, δ): 8.17 (d, *J* = 8.5 Hz, 3H), 7.56 (d, *J* = 1.9 Hz, 3H), 7.51 (dd, *J* = 8.4, 2.0 Hz, 3H), 2.83 (m, 6H), 2.01 (m, 6H), 1.02 – 0.72 (m, 36H), 0.61 (t, J = 7.2 Hz, 18H), 0.45 (m, 12H).



Figure S1. ¹H NMR spectrum for compound 1.



Figure S2.¹H NMR spectrum for compound 2.

8.17 7.755 7.256 7.257 7.256 7.257 7.256 7.257 7.256 7.257 7.250 7.257 7.250 7.257 7.2500 7.250 7.200 7.2500 7.2500 7.2500 7.2500 7.2500 7.2500 7.2500 7.2500 7.2500 7.2500 7.2500 7.2500 7.2500 7.2500 7.2500 7.2500 7.2500 7.2500 7.2500 7.20000 7.20000 7.2000 7.2000 7.20000 7.20000 7.20000 7.20000 7



Figure S3. ¹H NMR spectrum for compound 3.



Figure S4. ¹H NMR spectrum for TRUX-E-T.



Figure S5.¹³C NMR spectrum for TRUX-E-T.

3. Mass spectra



Figure S6. MADLI-TOF Mass spectrometry for TRUX-E-T.

4. Thermal properties



Figure S7. Thermogravimetric analysis curves of TRUX-E-T.



Figure S8. Differential scanning calorimetryheating and cooling curves of TRUX-E-T.



Figure S9. Space-charge-limited (SCLC) *J*–*V* characteristics of TRUX-E-T- and spiro-OMeTAD-based hole-only devices.



Figure S10. Tapping-mode AFM images of (a) perovskite and (b) perovskite/TRUX-E-T.



Figure S11. *J-V* curves of PVSCs with TRUX-E-T and spiro-OMeTAD HSLs under reverse and forward scans under 100 mW/cm² illumination.

5. Materials cost for synthesis of TRUX-E-T



	Weight	Weight	Weight	Price of	Chemical	Target
Chemical	Reagent	Solvent	Workup	Chemical	Cost	product
	g/g	g/g	g/g	\$/kg	\$	\$/g
1-Indanone	11			515.94	5.68	Product
HCl		35.37		2.95	0.10	1
HOAc		63		3.29	0.21	1.01
Ethanol			15.78	3.23	0.05	
Acetone			7.85	7.76	0.06	
CH ₂ Cl ₂			6.63	1.75	0.01	
Truxene (1)	6			1010	6.06	Product
<i>n</i> -BuLi (2.4 M in <i>n</i> -hexane)	11.22			69.44	0.78	2
$C_6H_{13}Br$	28.92			48.99	1.42	1.04
THF		177.6		7.73	1.37	
NH ₄ Cl			40	3.01	0.12	
Ethyl acetate			180.4	2.57	0.46	
$MgSO_4$			5	8.77	0.04	
Silica gel			50	7.54	0.38	
Petroleum ether			260	3.04	0.79	
5,5,10,10,15,15-						Product
Hexabutyltruxene (2)	10			1040	10.4	3
Br ₂	7.2			17.10	0.12	1.08
FeCl ₃	0.04			24.64	0.01	
CHCl ₃		244.2		7.83	1.91	
NaHSO ₃			25	2.55	0.06	
MgSO ₄			5	8.77	0.04	
Ethanol			78.9	3.23	0.25	



	Weight	Weight	Weight	Price of	Chemical	Target
Chemical	Reagent	Solvent	Workup	Chemical	Cost	product
	g/g	g/g	g/g	\$/kg	\$	\$/g
2,7,12-						TRUX-
Tribromo-						E-T
5,5,10,10,15,15-						25.93
hexahexyltruxen	0.45			1080	0.49	
e (3)						
4-(2,3-						
Dihydrothieno[3,						
4-b][1,4]dioxin-						
5-yl)-N,N-bis(4-	1.1			10580	11.64	
methoxyphenyl)-	0.07			4927.53	0.34	
aniline (4)		34.8		6.6	0.23	
$Pd(PPh_3)_4$			650	3.04	1.98	
Toluene			180.4	2.57	0.46	
Petroleum ether			80	7.54	0.60	
Ethyl acetate			30	2.78	0.08	
Silica gel						
Methanol						

However, since this figure does not take into account several important parameters (e.g. energy consumption, waste treatment and labor), it was multiplied by a factor of 1.5^4 to get a more realistic estimation of lab synthesis costs of ~\$38.9/g. This is about 1/13 of the costs of purified spiro-OMeTAD (~\$500/g, high purity, Merck).

References

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