Rational Design of Triazatruxene-based Hole Conductors for Perovskite Solar Cells

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Experimental section

Materials

For synthesis of triazatruxene-based compounds, all reagents were obtained from commercial sources and used without further purification, unless otherwise noted. Chemical reactions were performed under dry N_2, unless stated. All dry reactions were performed with glassware that was flamed under high-vacuum and backfilled with N_2. All extracts were dried over powdered $MgSO_4$ and solvents removed by rotary evaporation under reduced pressure. Flash chromatography was performed using Silicycle UltraPure SilicaFlash P60, 40-63 μm (230-400 mesh). For solar cell fabrication, the chemicals were commercially available either from Sigma Aldrich or Acros and they were employed without any treatment or purification. Spiro-OMeTAD was acquired from Merck KGaA. CH_3NH_3I was synthesized by mixing an equimolar amount of methylamine (40% in water) and HI (57% in water) and reaction took place over an ice bath to control the temperature.

Synthesis of triazatruxene-based HTMs

a) 5,10,15-trihexyl-10,15-dihydro-5H-diindolo[3,2-a:3',2'-c]carbazole (1).

Triazatruxene core was prepared by known procedure as published in literature[1]. To a solution of triazatruxene (400 mg, 1.2 mmol, 1 eq.) in DMF (10 mL), NaH (0.1 g, 4.1 mmol, 3.5 eq.) was added at room temperature and stirred for half hour, then 1-bromohexane (0.76 g, 4.63 mmol, 4 eq.) was added via syringe and the mixture was then refluxed for 2h. The cooled mixture was poured into water and extracted with DCM. The organic phase was dried over $MgSO_4$. The product was isolated off on a silica gel column with 20 % DCM in hexane to give a product as a pale yellow solid (450 mg, 92%). ^1H NMR (400 MHz, $CDCl_3$-d) δ 8.32 (d, J = 8.0 Hz, 3H), 7.70 – 7.63 (m, 3H), 7.55 – 7.44 (m, 3H), 7.37 (m, 3H), 4.99 – 4.90 (m, 6H), 2.02 (m, 6H), 1.41 – 1.28 (m, 18H), 0.84 (t, J = 7.0 Hz, 9H).

b) 3,8,13-tribromo-5,10,15-trihexyl-10,15-dihydro-5H-diindolo[3,2-a:3',2'-c]carbazole (2).

To a solution of previous product (5,10,15-trihexyl-10,15-dihydro-5*H*-diindolo[3,2-a:3',2'-c]carbazole; 350 mg, 0.58 mmol, 1 eq.) in 30 mL $CHCl_3$, NBS (310 mg, 1.75 mmol, 3 eq.) in 5 mL DMF was added dropwise via syringe at 0 °C. After addition reaction mixture was stirred for 1h at room temperature. The mixture was extracted with DCM and organic phase was dried over $MgSO_4$. The product was isolated off on a silica gel column with 10 % DCM in hexane to give a product as a pale-yellow solid (400 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$-d) δ 8.05 (d, J = 8.0 Hz, 3H), 7.71 (s, 3H), 7.55 (d, J = 8.0 Hz, 3H), 4.99 – 4.90 (m, 6H), 2.02 (m, 6H), 1.41 – 1.28 (m, 18H), 0.84 (t, J = 7.0 Hz, 9H).

Characterization

^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance-400 (400 MHz), Bruker AvanceIII-400 (400 MHz), Bruker DPX-400 (400 MHz) or Bruker DRX-600 (600 MHz) spectrometer and are reported in ppm using solvent as an internal standard: Chloroform-d at 7.24 ppm and 77.23 ppm for ^{1}H and ^{13}C, respectively; Benzene-d_6 at 7.16 ppm and 128.39 ppm for ^{1}H and ^{13}C, respectively; Dimethyl Sulfoxide-d_6 at 2.50 ppm and 39.51 ppm for ^{1}H and ^{13}C, respectively.

UV-visible spectra were measured using Cary 60 spectrophotometer in 1cm cuvette using dilute solution of HMDI and HPDI in chlorobenzene solvent. CV measurements were done with an Autolab Eco Chemie cyclic voltammeter. DSC and TGA measurements were carried out in nitrogen atmosphere using Mettler Toledo equipment (model Star System).

For *J-V* curves, a 450W Oriel xenon lamp with a Schott K113 Tempax Sunlight filter (Praezisions Glas&OptikGmbH) was employed to obtain AM1.5G spectra. A Si reference diode with an IR cut-off filter (KG-3, Schott) was employed to calibrate Sun Intensity. For IPCE measurements, a 300-W xenon lamp (ILC Technology) was used with a Gemini-180 double monochromator (Jobin Yvon Ltd) to tune the wavelength with a Lock-in amplifier (Stanford Research Systems, model SR830 DSP). Light bias was adjusted by white LED light at ~5% of Sun incidence intensity. Both for *J-V* and IPCE measurements the active area was fixed to 0.6cm^2 using a black mask and *J-V* curves were recorded in reverse direction (from V_{oc}) after 10 s delay under illumination at a scan speed of 100 mV/s; we have found this as an optimal condition to avoid hysteresis.

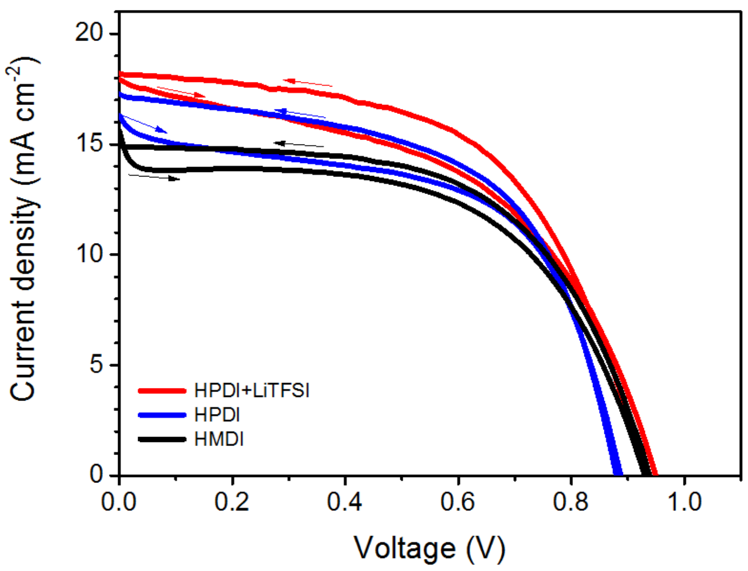

Fig.S1: *J-V* graphs of fabricated device showing hysteresis behaviour for different HTMs (HMDI and HPDI) and HPDI with LiTFSI dopant.

Table S1. Photovoltaics parameters derived from *J-V* measurements for $CH_3NH_3PbI_3$ perovskite based solar cells using the synthesized triazatruxene molecules.[a]

HTM		J_{SC} (mA·cm^{-2})	V_{OC} (V)	Fill Factor	*PCE* (%)
HMDI+LiTFSI+ *t*-BP		13.70	0.868	0.715	8.50
	Avg.±SD	12.65±1.08	0.861±0.03	0.632±0.077	7±1.57
HPDI+LiTFSI+ *t*-BP		9.97	0.901	0.650	5.84
	Avg.±SD	9.82±0.15	0.903±0.02	0.648±0.02	5.75±0.09

[a] Average data and standard deviation calculated for 3 cells in the same batch. Mask size: 0.16cm^2.

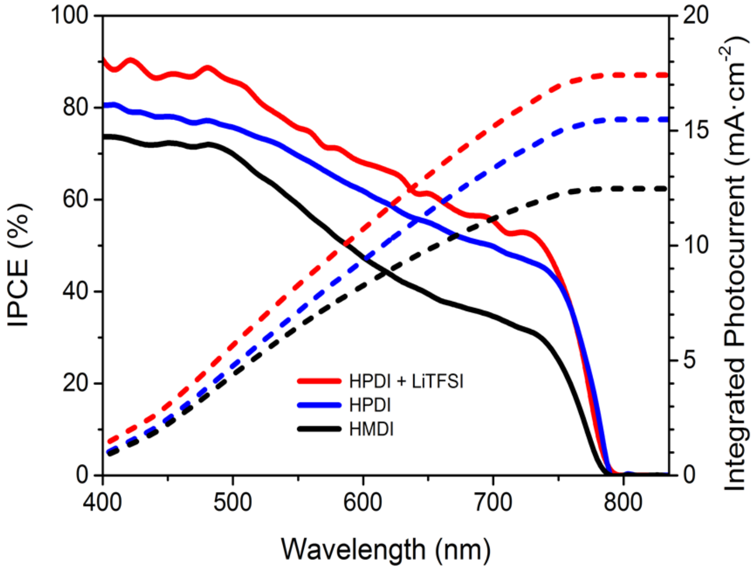

Figure S2. Integration of the IPCE spectra yields a current density of 12.48, 15.48 and 17.42 mA/cm^2 for HMDI, HPDI and HPDI+LiTFSI respectively, which is in agreement with J_{sc}.

References

1 M. Franceschin, L. Ginnari-Satriani, A. Alvino, G. Ortaggi, and A. Bianco, *Eur. J. Org. Chem.*, 2010, 134–141.

2 Y. Arakawa, S. Nakajima, R. Ishige, M. Uchimura, S. Kang, G. Konishi, and J. Watanabe, *J. Mater. Chem.*, 2012, **22**, 8394.