Supporting Information

Dicyanovinylene and Thiazolo[5,4-*d*]thiazole-Core Containing D-A-D Type Hole Transporting Materials for Spiro-OMeTAD Free Perovskite Solar Cell Applications with Superior Atmospheric Stability

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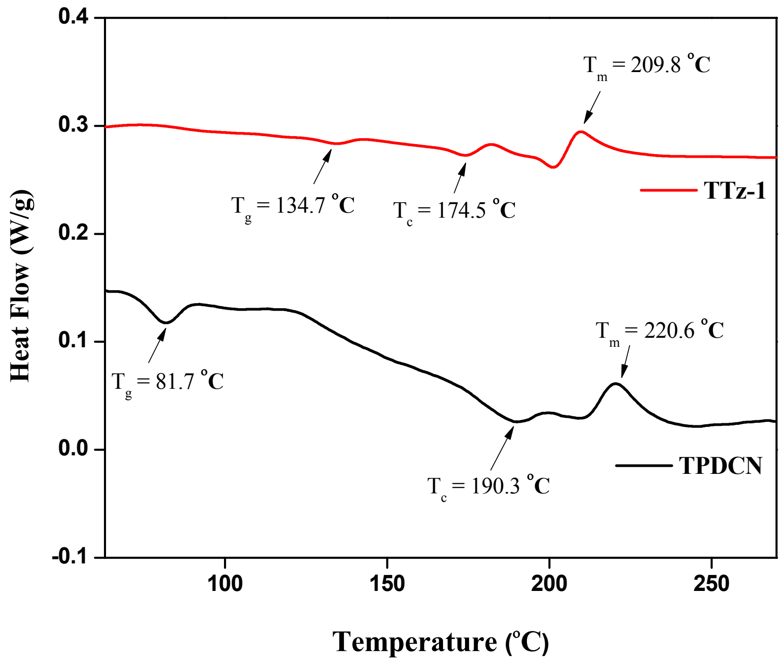


Figure S1. DSC curves of TPDCN and TTz-1 (heating rate at 10 °C min^{-1})

Synthesis of hole transporting materials

Bis-(4-methoxyphenyl)phenylamine (1) and 4-(bis(4-methoxyphenyl)amino)benzaldehyde (2) were synthesized using a slight modification to the literature procedures.[1] Compound 1 (51%, orange colour solid). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.17-7.13 (t, 2H), 7.04 (d, *J* = 9.0 Hz, 4H), 6.93 (d, *J* = 7.7 Hz, 2H), 6.87-6.82 (t, 1H), 6.79 (d, *J* = 9.0 Hz, 4H), 3.78 (s, 6H). Compound 2 (64%, white colour solid). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 9.74 (s, 1H), 7.60 (d, *J* = 8.2 Hz, 2H), 7.10 (d, *J* = 8.8 Hz, 4H), 6.86 (d, *J* = 8.6 Hz, 4H), 6.82 (d, *J* = 8.2 Hz, 2H), 3.80 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 190.46, 157.46, 154.22, 138.97, 131.58, 128.21, 127.91, 116.90, 115.21, 55.64.

Optical band gap calculation

The optical band gap was calculated using following equation 1.

$$E_g^{opt} = 1240/\lambda_{onset} \quad \ldots\ldots\ldots\ldots\ldots \quad (1)$$

Where, λ_{onset} is onset of the wavelength identified by the tangent method from UV-visible spectra. The λ_{onset} value of TTz-1, TPDCN and Spiro-OMeTAD are 490, 529 nm and 416 nm, respectively.

Optical band gap (E_g^{opt}) TTz-1 = 2.53 eV; TPDCN = 2.34 eV and Spiro-OMeTAD = 2.98 eV.

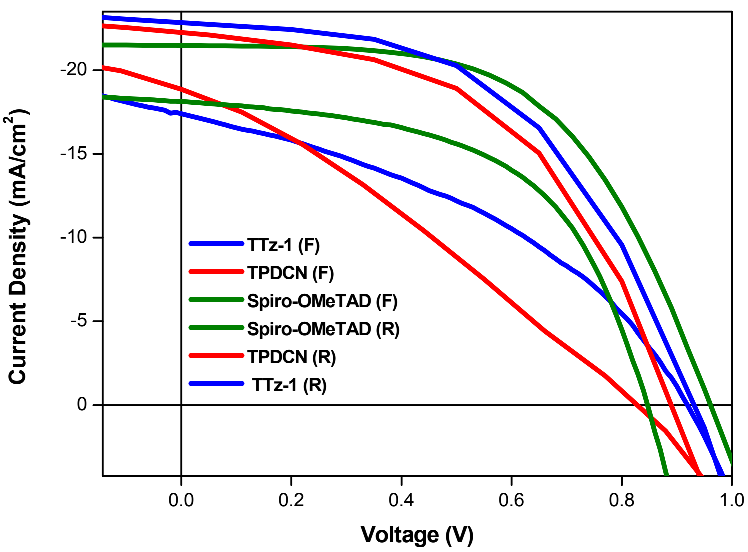


Figure S2. J-V curves of PSC device of TTz-1, TPDCN and spiro-OMeTAD used as the hole transporting materials (HTMs)

Table S1. Summary of average photovoltaic properties of PSCs based TTz-1, TPDCN and spiro-OMeTAD device forward (F) and reverse (R) sweep direction for 10 devices.

HTM		Voc (V)	Jsc (mA cm^{-2})	FF (%)	PCE (%)
TPDCN	F	0.80 ± 0.02 (0.82)	16.20 ± 2.65 (18.85)	27 ± 2 (29)	3.49 ± 1.09 (4.58)
	R	0.86 ± 0.02 (0.88)	21.31 ± 0.90 (22.21)	50 ± 1 (51)	9.17 ± 0.94 (10.11)
TTz-1	F	0.87 ± 0.04 (0.91)	16.30 ± 1.09 (17.39)	38 ± 2 (40)	5.38 ± 0.95 (6.33)
	R	0.91 ± 0.02 (0.93)	21.91 ± 0.80 (22.71)	52 ± 1 (53)	10.38 ± 0.99 (11.37)
Spiro-OMeTAD	F	0.87 ± 0.03 (0.90)	16.92 ± 0.44 (17.36)	37 ± 2 (39)	5.44 ± 0.31 (6.13)
	R	0.95 ± 0.01 (0.96)	21.13 ± 0.36 (21.49)	55 ± 1 (56)	11.04 ± 0.58 (11.62)

The average photovoltaic values were obtained from 10 devices (The values within the bracket are for the champion device).

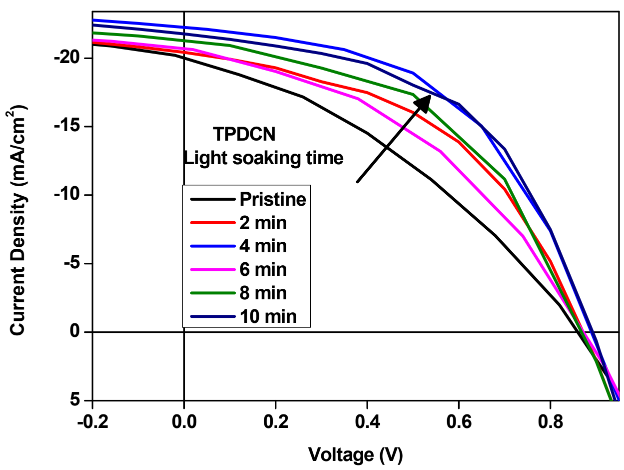


Figure S3. Light-soaking effect of TPDCN-based devices

Table S2. Photovoltaic properties of TPDCN device with light soaking effect.

Light soaking time (min)	Voc (V)	Jsc (mA cm^{-2})	Fill Factor (%)	PCE (%)
0	0.85	20.01	34	6.01
2	0.87	20.68	40	7.38
4	0.87	20.43	46	8.33
6	0.87	21.24	47	8.67
8	0.88	21.77	51	9.96
10	0.88	22.21	51	10.11

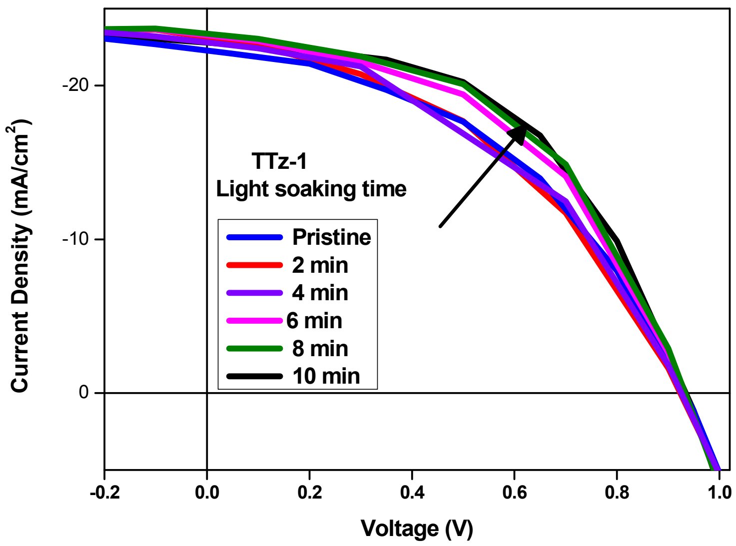


Figure S4. Light-soaking effect of TTz-1-based devices

Table S3. Photovoltaic properties of TTz-1 device with light soaking effect.

Light soaking time (min)	Voc (V)	Jsc (mA cm^{-2})	Fill Factor (%)	PCE (%)
0	0.91	22.30	41	8.50
2	0.92	22.80	41	8.72
4	0.92	22.28	46	9.53
6	0.93	22.60	48	10.41
8	0.93	22.82	50	10.95
10	0.93	22.71	53	11.37

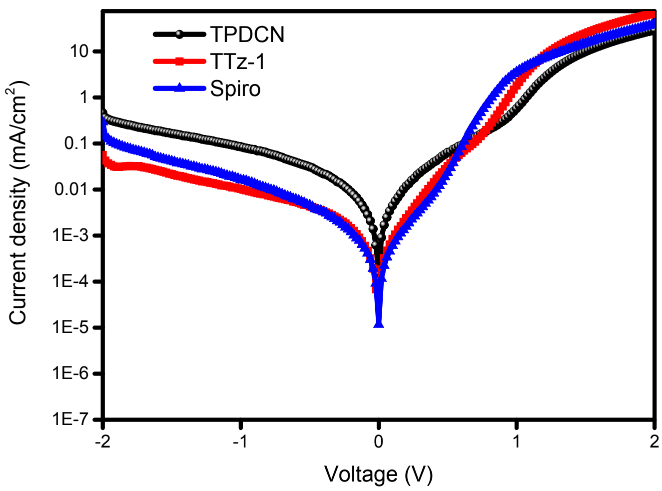
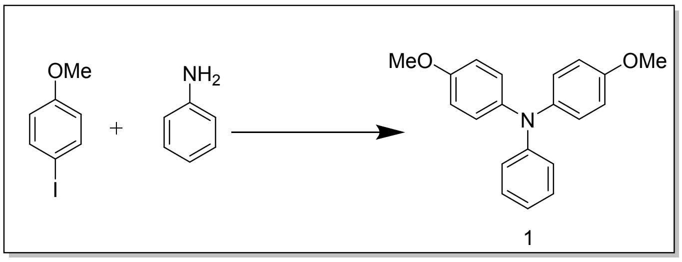


Figure S5. Dark I-V curve of the device having different HTMs

Light soaking effects in the TTz-1 and TPDCN-based devices compared to Spiro-OMeTAD-based devices were studied *via* dark data analysis. Leakage current density (J_0) values are for TPDCN (1.51×10^{-4} mA/cm^2), TTz-1 (6×10^{-5} mA/cm^2) and Spiro-OMeTAD (1.16×10^{-5} mA/cm^2) from dark I-V data. The Spiro-OMeTAD-device shows low leakage current, which depicts that interface is better and recombination is reduced at Perovskite/HTL interface. Open circuit voltage was improved for this device and light soaking effect was not observed for spiro-OMeTAD based device.

Evaluation basis for cost of HTMs

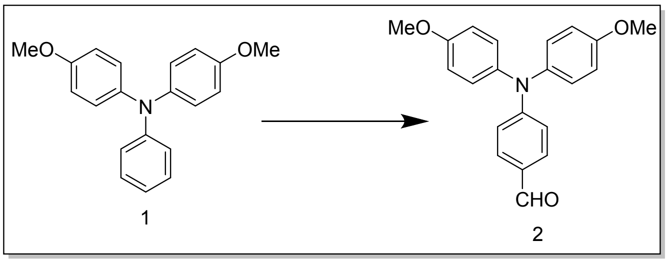
The cost estimation for synthesis of 1 g of material was carried out using previously published material cost model.[2-4] The material prices were taken from various chemical companies (Sigma-Aldrich, Alfa aesar, SD Fine-Chem limited, TCI chemicals and Avra) using the largest available package on their websites. The synthetic flow charts and material cost calculation are shown below.



Scheme S1. Synthesis of **1**

Table S4. Cost calculation for the synthesis of **1**.

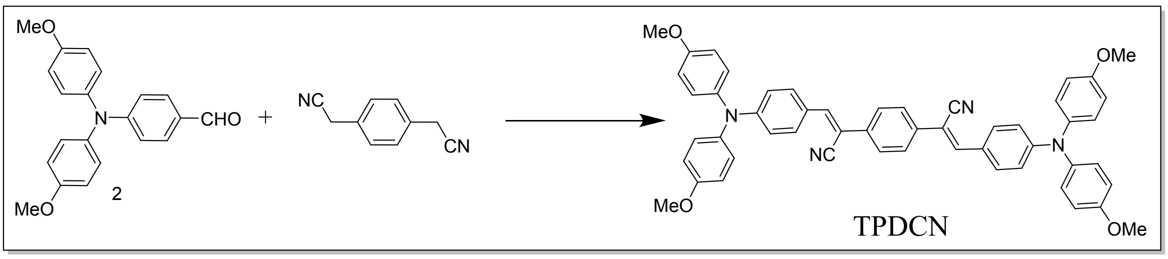
Chemical	Weight Reagent (g/g)	Weight Solvent (g/g)	Price of Chemical ($/kg)	Chemical Cost ($)
Aniline	0.591		224.85	0.13
4-iodoanisole	3.12		563.30	1.75
Copper iodide	0.217		237.20	0.051
1,10-phenanthroline monohydrate	0.226		126.74	0.028
Potassium tert-butoxide	5		71.82	0.01
Toluene		19	7.04	0.13
Dichloromethane		40	11.16	0.44
$MgSO_4$	2		4.22	0.008
Hexane		200	2.25	0.45
Ethyl acetate		80	2.14	0.171
Total cost	3.16			
Amount of product 1	1 g			



Scheme S2. Synthesis of **2**

Table S5. Cost calculation for the synthesis of **2.**

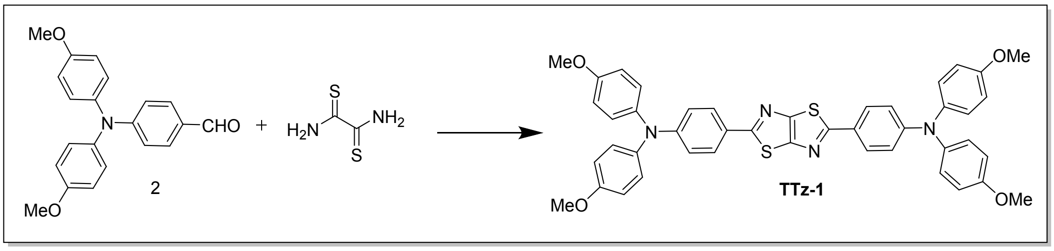
Chemical	Weight Reagent (g/g)	Weight Solvent (g/g)	Price of Chemical ($/kg)	Chemical Cost ($)
1	1.45		3168	4.59
DMF	0.92		5.09	0.01
$POCl_3$	0.78		70.35	0.08
1,2-dichloroethane		20	9.96	0.28
NaOH	1		5.38	0.01
DCM		30	11.16	0.33
MgSO4	1		4.22	0.01
Hexane		216	2.25	0.48
Ethyl acetate		59	2.14	0.12
Total cost	5.91			
Amount of product 2	1 g			



Scheme S3. Synthesis of **TPDCN**

Table S6. Evaluation of cost for **TPDCN.**

Chemical	**Weight Reagent (g/g)**	**Weight Solvent (g/g)**	**Price of Chemical ($/kg)**	**Chemical Cost ($)**
2	1.20		5910	7.09
1,4-Phenylenediacetonitrile	0.267		2534	0.67
ethanol		120	3.12	0.37
Potassium tert-butoxide	0.035		71.82	0.002
Hexane		60	2.25	0.13
DCM		20	2.14	0.042
Total cost	8.64			
Amount of product	1 g			



Scheme S4. Synthesis of **TTz-1**

Table S7. Evaluation of cost for **TTz-1.**

Chemical	**Weight Reagent (g/g)**	**Weight Solvent (g/g)**	**Price of Chemical ($/kg)**	**Chemical Cost ($)**
2	4		5910	23.34
Dithiooxamide	0.656		704	0.45
DMF		50	5.09	0.25
MgSO4	1		4.22	0.01
Hexane		150	2.25	0.33
Ethyl acetate		70	2.14	0.14
Total cost	24.82			
Amount of product	1 g			

The estimated materials cost was compared with estimated materials cost of Spiro-OMeTAD and commercial price of Spiro-OMeTAD. The estimated materials cost for Spiro-OMeTAD was taken from previous reported literature.[2]

Table S8. Comparison of the estimated materials cost for the synthesis of HTMs.

HTM	**Steps**	**Cost ($/g)**	**Commercial Price ($/g)**
TPDCN	3	8.64	n/a
TTz-1	3	24.82	n/a
Spiro-OMeTAD	6	91.67	170-475

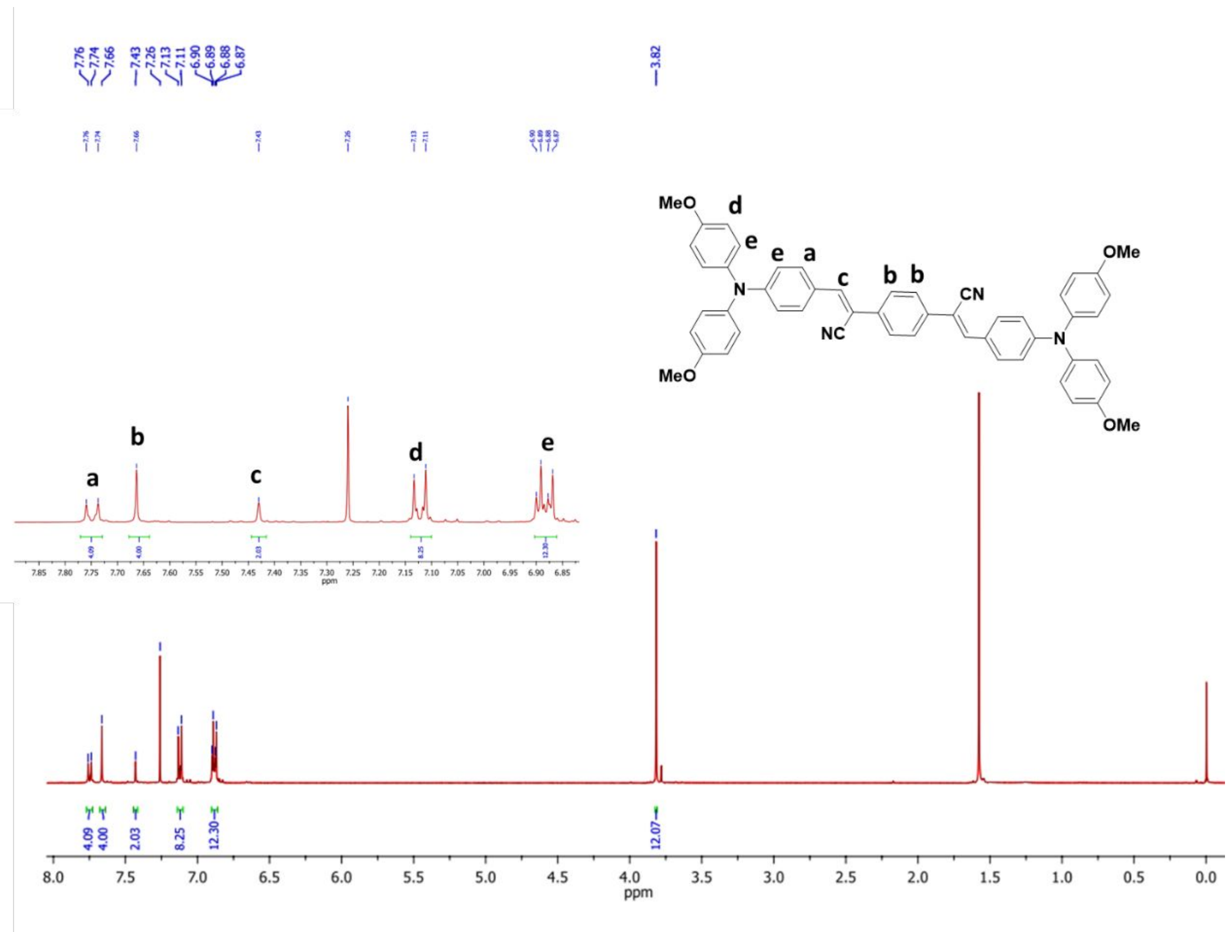


Figure S6. ^{1}HNMR Spectra of TPDCN

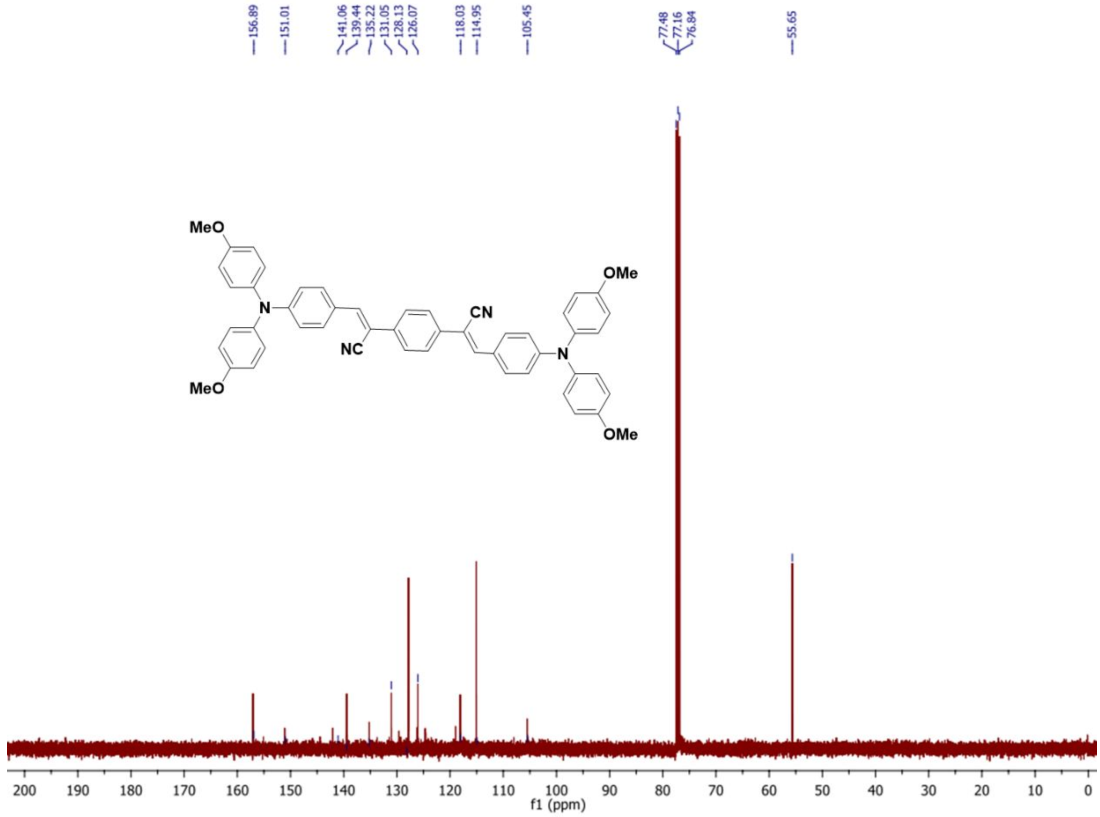


Figure S7. ^{13}CNMR Spectra of TPDCN

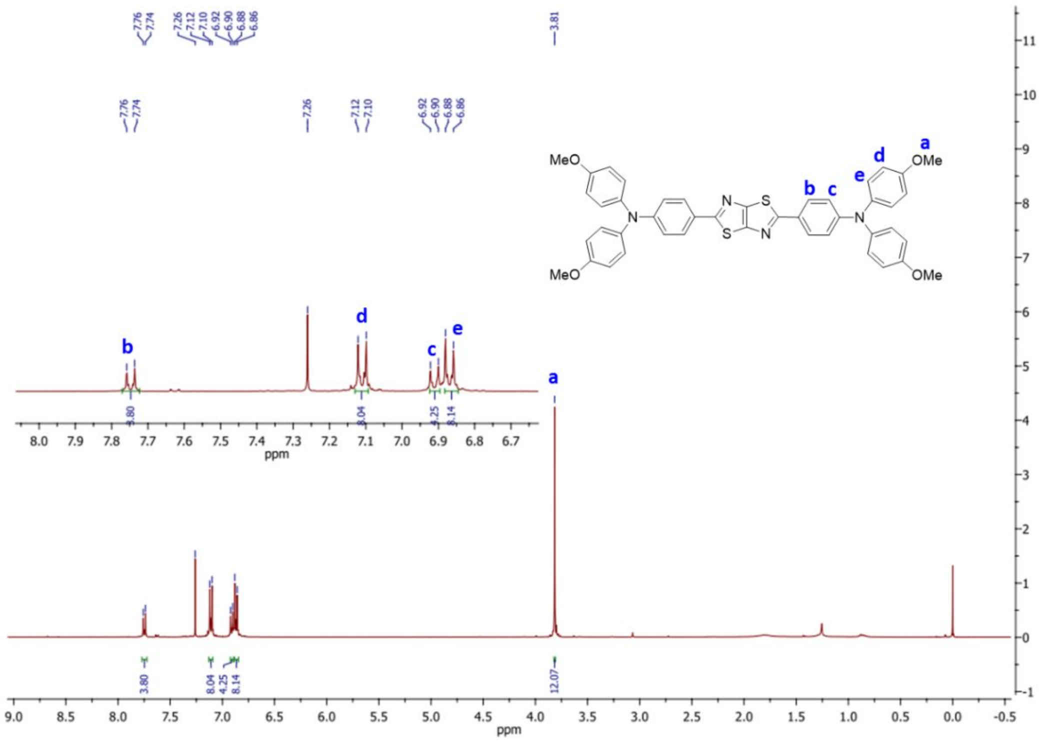


Figure S8. ^{1}H-NMR spectrum of TTz-1 in $CDCl_3$ solvent

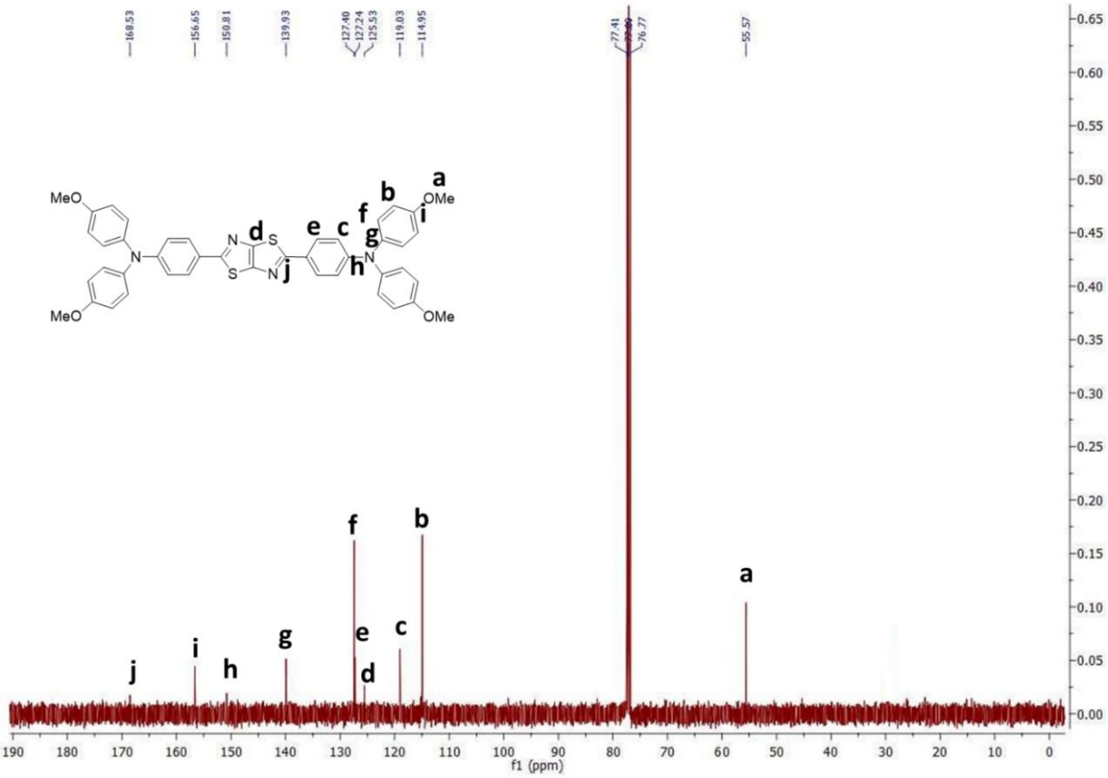


Figure S9. ^{13}C-NMR spectrum of TTz-1 in $CDCl_3$ solvent

References

(1) Petrus, Michiel L.; Music, A.; Closs, A. C.; Bijleveld, J. C.; Sirtl, M. T.; Hu, Y.; Dingemans, T. J.; Bein, T.; Docampo, P., Design rules for the preparation of low-cost hole transporting materials for perovskite solar cells with moisture barrier properties. *J. Mater. Chem. A* **2017,** *5* (48), 25200-25210.

(2) Petrus, M. L.; Bein, T.; Dingemans, T. J.; Docampo, P., A low cost azomethine-based hole transporting material for perovskite photovoltaics. *J. Mater. Chem. A* **2015,** *3* (23), 12159-12162.

(3) Guan, L., Yin, X., Zhao, D., Wang, C., An, Q., Yu, J., Shrestha, N., Grice, C.R., Awni, R.A., Yu, Y. and Song, Z., Cost-effective hole transporting material for stable and efficient perovskite solar cells with fill factors up to 82%. *J. Mater. Chem. A* **2017**, 5(44), 23319-23327.

(4) Cui, B.B., Zhu, C., Yang, S., Han, Y., Yang, N., Zhang, L., Wang, Y., Jia, Y., Zhao, L. and Chen, Q., Two Low-Cost and Efficient Hole-Transporting Materials for n–i–p Type Organic–Inorganic Hybrid Perovskite Solar Cells. Acs Omega, 2018, 3(9), 10791-10797.