Electronic Supplementary Information (ESI)

Low cost and stable quinoxaline-based hole-transporting materials with a D-A-D molecular configuration for efficient perovskite solar cells

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Materials and reagents

All chemicals and solvents used for synthesis were of reagent grade and were obtained from J&K Scientific, Adamas Reagent Co Ltd and so on. The TiO_2 nanoparticle paste were purchased from Dyesol. Other materials and solvents used for perovskite solar cell fabrication were purchased from TCI and Sigma-Aldrich.
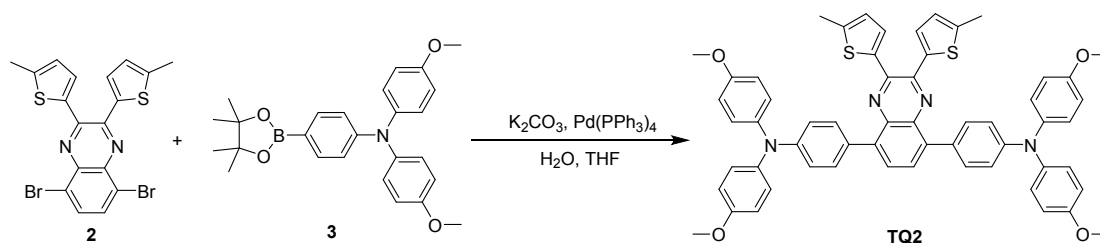
Synthesis

The starting materials, 5,8-dibromo-2,3-diphenyl-quinoxaline (**1**), 5,8-dibromo-2,3-bis(5-methyl-2-thienyl)-quinoxaline (**2**) and *N,N*-Bis(4-methoxyphenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzenamine (**3**) were synthesized according to published procedures.[S1-S3] We note that these materials are also commercially available. All other chemicals and solvents were purchased from commercial sources and were used without further purification.
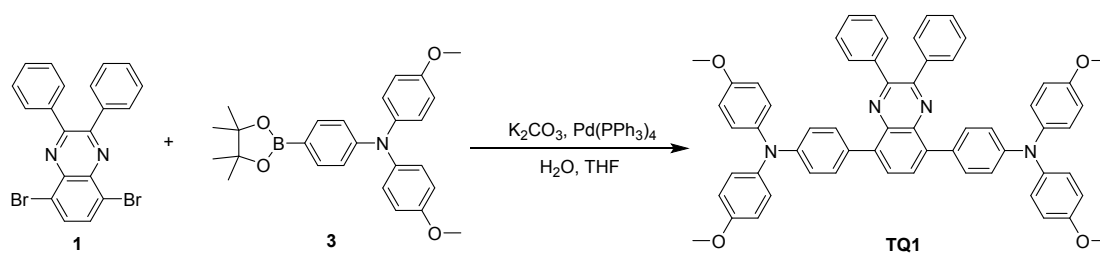
Sythesis of TQ1. In a three-neck round-bottom flask, **1** (0.96 g, 2.18 mmol) and **3** (2.35 g, 5.45 mmol) was dissolved in THF(45 mL). Then, 2 M K_2CO_3 aqueous solution (15 mL) and $Pd(PPh_3)_4$ (200 mg, 0.16 mmol) was added. The mixed solution was heated at 80 °C under nitrogen atmosphere and stirred for 12 h. After cooling to the room temperature, the organic phase were separated with a separatory funnel.

Then, the solvent (THF) was evaporated and the residue was dissolved in CH_2Cl_2 and washed with brine. The organic phases were combined together, dried over anhydrous Na_2SO_4, and purified by column chromatography on silica gel (petroleum ether : CH_2Cl_2 = 1 : 1). The crude product was then recrystallized with a mixed solution of chloroform and methanol (V/V: 1/1.5) to afford an orange-red solid **TQ1** (1.70 g, yield 77.6%). ^{1}H NMR (400 MHz, CDCl$_3$, δ, ppm): 7.85 (s, 2H), 7.73 (d, J = 8.7 Hz, 4H), 7.59-7.61(m, 4H), 7.29-7.33 (m, 6H), 7.16 (d, J = 9.0 Hz, 8H), 7.07 (d, J = 8.7 Hz, 4H), 6.87 (d, J = 9.0 Hz, 8H), 3.82 (s, 12H). ^{13}C NMR (100 MHz, CDCl$_3$, δ, ppm): 155.93, 150.89, 148.22, 140.97, 139.25, 138.61, 138.23, 131.51, 130.12, 129.28, 128.69, 128.14, 126.86, 119.71, 114.71, 55.53. HRMS-ESI (m/z): [M + H]$^+$ Calcd. For ($C_{60}H_{49}N_4O_4$), 889.3754, found: 889.3756.

Sythesis of TQ2. Compound **TQ2** was obtained as a red powder (0.75 g, yield 81.2%) by using a similar procedure to that of compound **TQ1**. ^{1}H NMR (400 MHz, CDCl$_3$, δ, ppm): 7.76 (s, 2H), 7.70 (d, J = 8.6 Hz, 4H), 7.29 (d, J = 3.6, 2H), 7.17 (d, J = 8.5 Hz, 8H), 7.09 (d, J = 8.1 Hz, 4H), 6.86 (d, J = 8.9 Hz, 8H), 6.65 (dd, J_1 = 3.7 Hz, J_2 = 1.0 Hz, 2H), 3.82 (s, 12H), 2.53 (s, 6H). ^{13}C NMR (100 MHz, CDCl$_3$, δ, ppm): 155.81, 148.09, 144.05, 141.09, 140.46, 137.87, 137.54, 131.57, 130.19, 129.20, 128.86,

126.65, 125.82, 120.01, 114.66, 55.52, 15.68. HRMS-ESI (m/z): [M + H]$^+$ Calcd. For

($C_{58}H_{49}N_4O_4S_2$), 929.3195, found: 929.3200.

Perovskite solar cells fabrication

Fluorine-doped tin oxide (FTO) glass was etched with zinc powder and hydrochloric acid (2M). The substrates were rinsed with deionized water and ethanol, then washed in acetone for 30 min with sonication and finally cleaned with ultraviolet ozone treatment for 15 min. A thin layer of the TiO_2 blocking layer was deposited onto the FTO substrates via spray pyrolysis at 500 ^{o}C from a precursor solution of titanium diisopropoxide bis(acetylacetonate) in anhydrous ethanol. Then, the TiO_2 nanoparticle (30-NRT) paste diluted in ethanol (1:6, weight ratio) was spin coated onto the substrate at 4000 rpm for 20 s and annealed at 500 ^{o}C for 30 min to achieve a 150–200 nm mesoporous TiO_2 layer. Perovskite films were deposited onto the mesoporous TiO_2 by one step "anti-solvent" method from a precursor solution containing PbI_2 (1.2 M) and MAI (1.2 M) dissolved in anhydrous mixed solvent DMF: DMSO (4:1,volume ratio). The substrates were then annealed at 100 °C for 30 min. Subsequently, the substrates were cooled down for a few minutes. The HTMs were applied from a 60 mM solution in chlorobenzene for *spiro*-OMeTAD and 40 mM solution for **TQ1** and **TQ2** respectively. *Tert*-butylpyridine (TBP, 330 mol%), and tris(bis(trifluoromethylsulfon-yl)imide) (Li-TFSI, 30-60% molar ratio to HTMs) were added as additives for new HTMs. Upon preliminary optimization, we found that the addition of 50% Li-TFSI (molar ratio to HTM) is the optimum doping concentration. Then, the HTM solutions were deposited onto the perovskite layers by spin-coating at 3000 rpm for 30 s. Finally, 80 nm thick film of Au was thermally evaporated under high vacuum on top of the hole transporting layer.

Characterization and measurements

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM 400 spectrometer with tetramethylsilane (TMS) as an internal standard. High resolution mass spectrometry (HRMS) was performed using a Waters LCT Premier XE spectrometer. Single crystal X-ray crystallographic data was collected by Bruker SMART APEX II X-ray diffractometer and was analyzed by Bruker SHELXTL software. Compound purity was measured by a Agilent 1100 Series high performance liquid chromatograph. The UV-vis absorption spectra were recorded with a Varian Cary 100 spectrophotometer. Fluorescence spectra were measured with a Horiba Fluoromax-4 fluorescence spectrometer. Photoluminescence lifetimes were determined with the single photon counting technique by means of Edinburgh FLS890 spectrometer. SEM images were obtained by using a TESCAN VEGA 3 SBH scanning electron microscope. AFM images were obtained by using Veeco IIIa MultiMode AFM scanning probe microscope. Photocurrent density$-$voltage ($J-V$) curves of devices were measured by Keithley 2400 Source meter Instruments under standard AM 1.5 simulated solar irradiation (WXS-155S-10) with using a black metal mask, with aperture area of 0.09 or 1.02 cm^2. The IPCE spectra were measured by Newport-74125 system (Newport Instruments).

The cyclic voltammograms were measured by using a CHI660E electrochemical workstation (Chenhua Co. Ltd, Shanghai, China) in a three-electrode cell. The working electrode was a glassy carbon electrode, used in conjunction with a Pt wire

counter electrode and a saturated calomel reference electrode. An amount of 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF$_6$) was used as the supporting electrolyte in CH$_2$Cl$_2$. The ferrocene/ferrocenium (Fc/Fc$^+$) redox couple was used as an external potential reference. The scan rate was 100 mV/s.

The thermal decomposition temperature (T_d) was confirmed by thermogravimetric analysis (TGA) from PerkinElmer Pyris 1 instruments at a heating rate of 10 °C min^{-1}. The differential scanning calorimetry (DSC) was performed on NETZSCN DSC 200 PC instruments and the DSC data were recorded in the temperature range from 25 to 350 °C at a heating rate of 10 °C min^{-1}.

Hole mobility of the new HTMs was measured by the space-charge-limited current (SCLC) method with hole only device utilizing the configuration of ITO/PEDOT: PSS/HTM/Au. The dark current in the range of 0-5 V was recorded by Keithley 2400 Source meter Instruments. The results were fitted to a space charge limited form, based on the following equation:

$$J = 9\mu\varepsilon_0\varepsilon_r V^2 / 8d^3$$

where J is the current density, μ is the hole mobility, ε_0 is the vacuum permittivity (8.85 × 10^{-12} F m^{-1}), ε_r is the dielectric constant of the material (normally taken to approach 3 for organic semiconductors), V is the applied bias, d is the film thickness of the active layer determined through AFM measurement.

The conductivity of the new HTM films were investigated using Keithley 4200 semiconductor parameter analyzer with sandwich devices composed by ITO/HTM(70

nm)/Au. The direct current conductivity can be determined from the slope of *I-V* plot

based on the following equation (A is the sample area and d is the sample thickness):
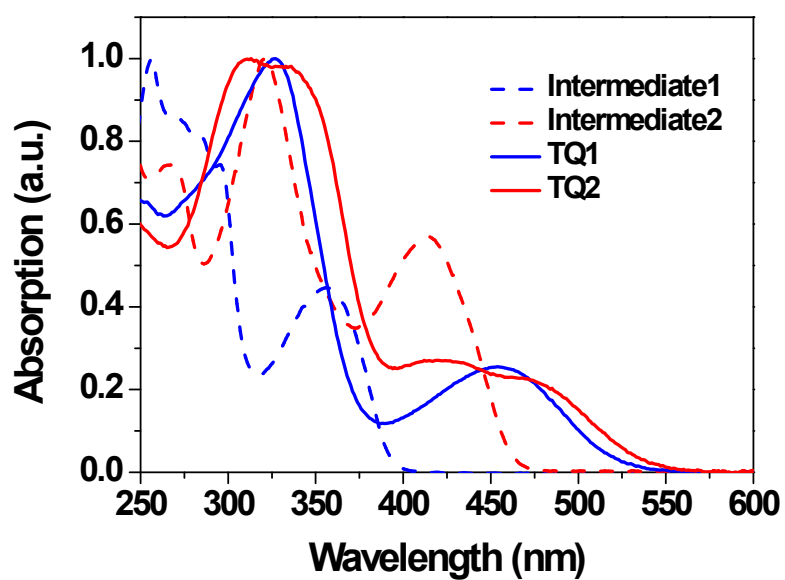
$$I = \sigma_0 A d^{-1} V$$

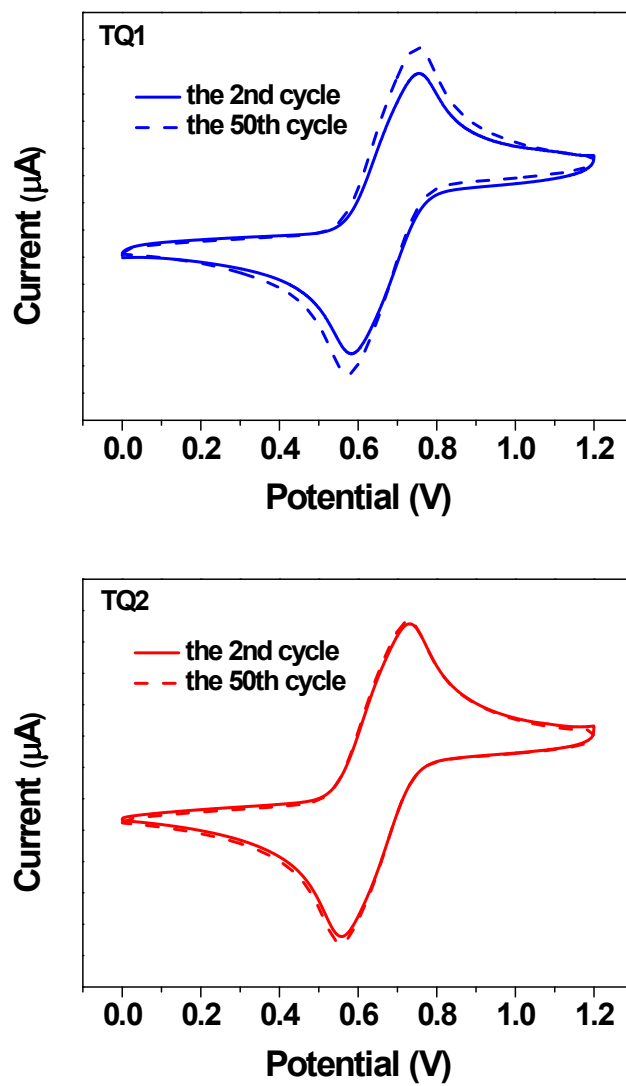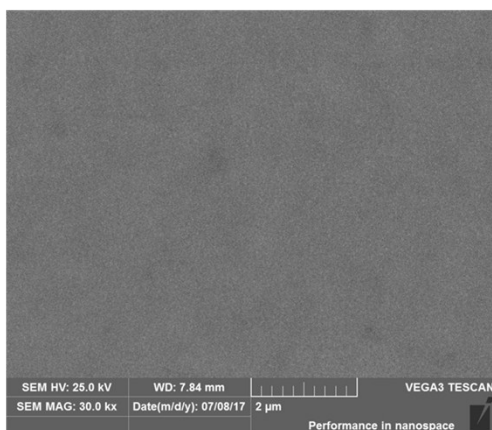**Fig. S1** Absorption spectra of synthetic intermediates **1** and **2**.

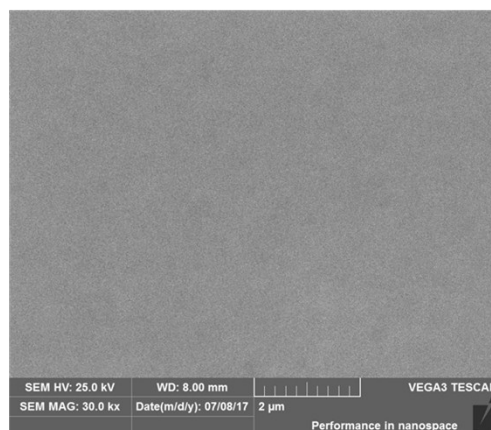**Fig. S2** The second and fiftieth cycle CV trace of **TQ1** (top) and **TQ2** (bottom).

(a) (b)

Fig. S3 Top-view SEM images of (a) **TQ1** and (b) **TQ2** thin films deposited on perovskite layer.
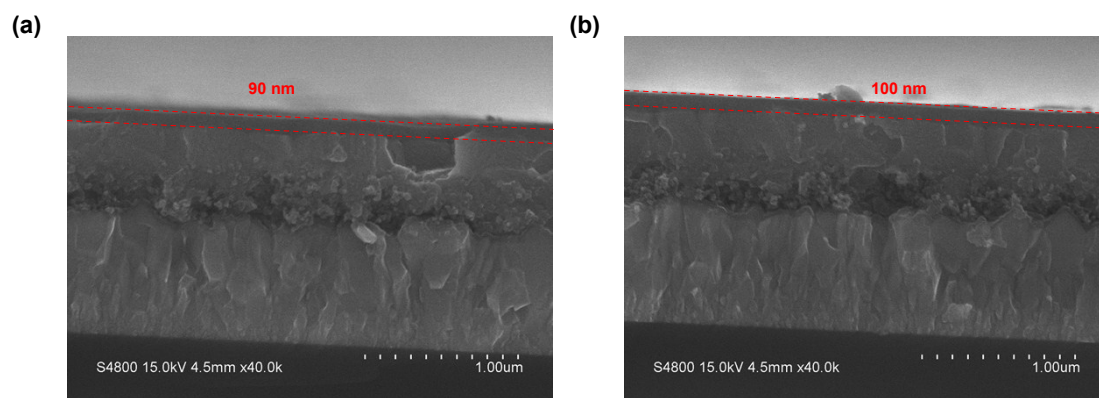
Fig. S4 Cross section SEM images of PSCs devices based on (a) **TQ1** and (b) **TQ2**.
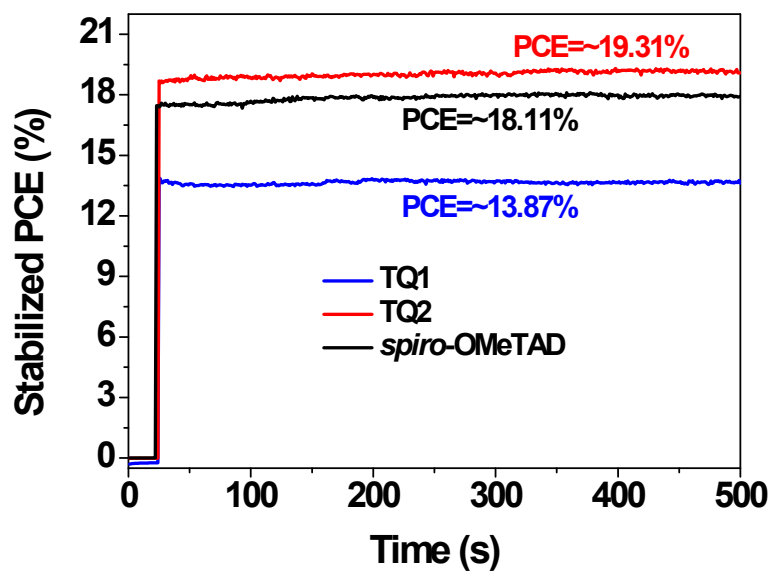
Fig. S5 The steady state power output as a function of time measured at a bias voltage of 0.77, 0.94, and 0.90 V for the devices based on **TQ1**, **TQ2**, and *spiro*-OMeTAD respectively.
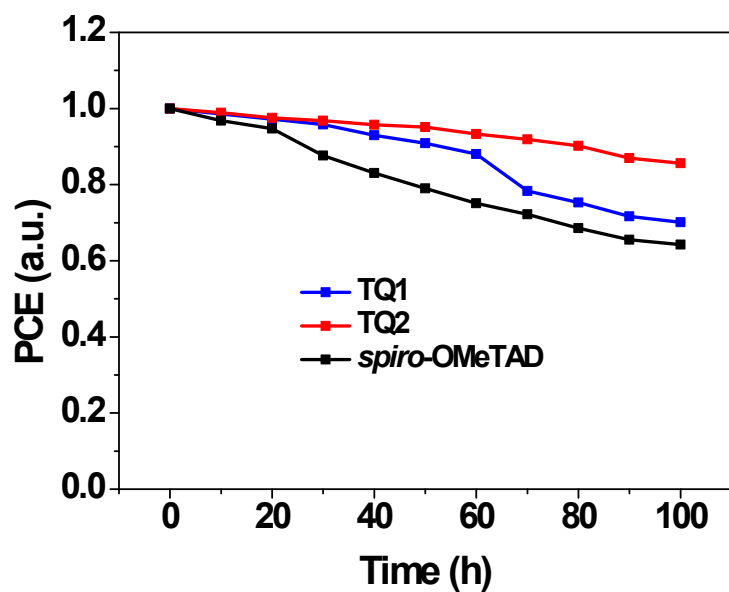
Fig. S6 The operation stability test of PSCs based on **TQ1**, **TQ2** and *spiro*-OMeTAD

under continuous one sun illumination under controlled environmental conditions

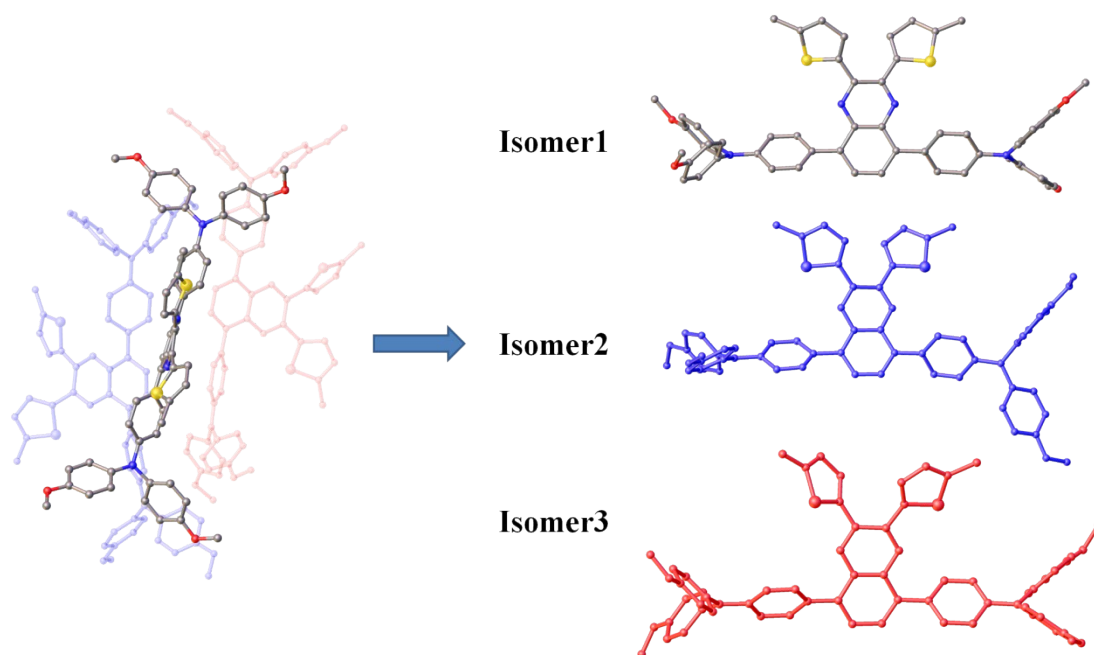(relative humidity of 30% and temperature of 25 °C).

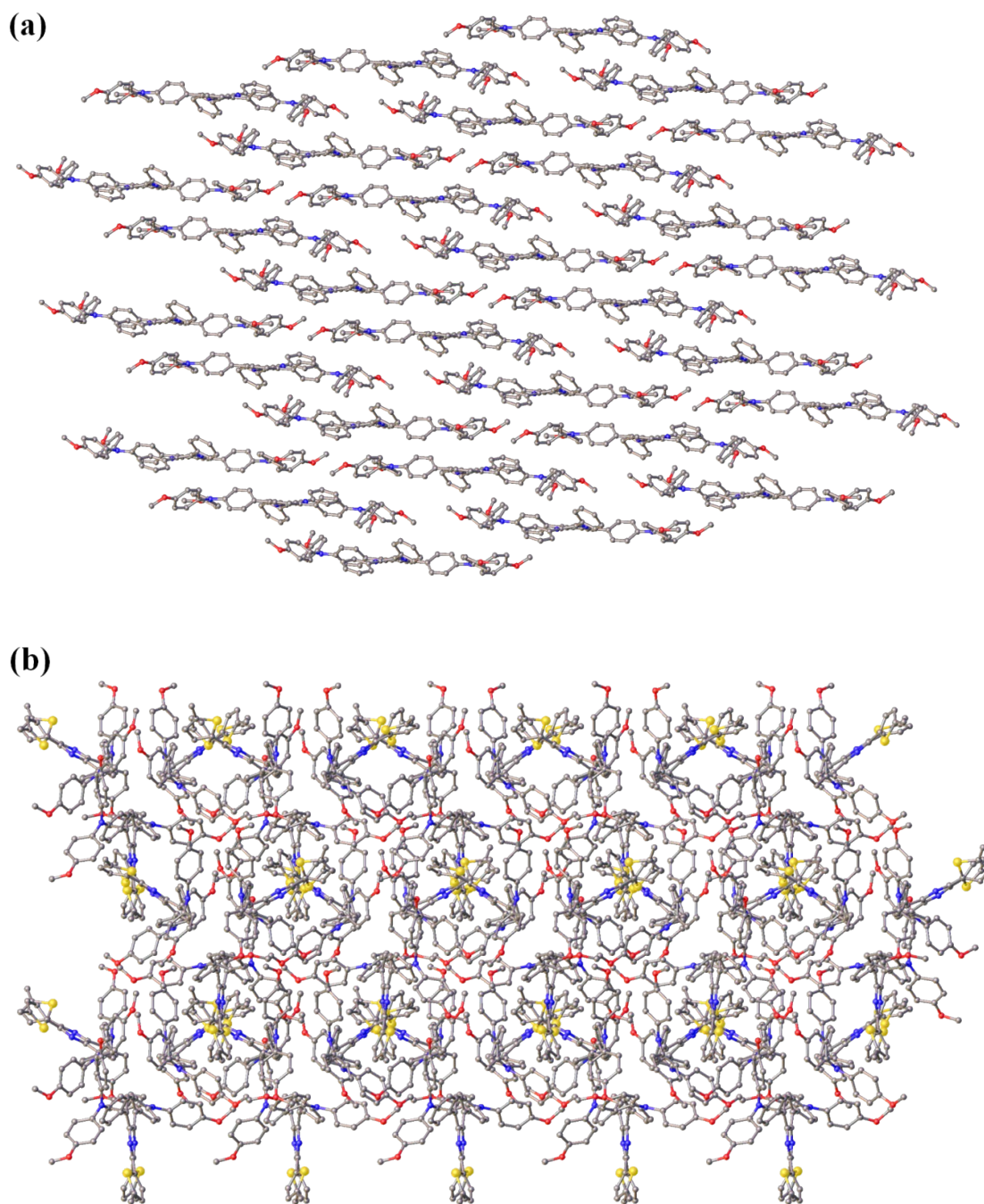**Fig. S7** Three conformational isomers for **TQ2**.

(a)

(b)

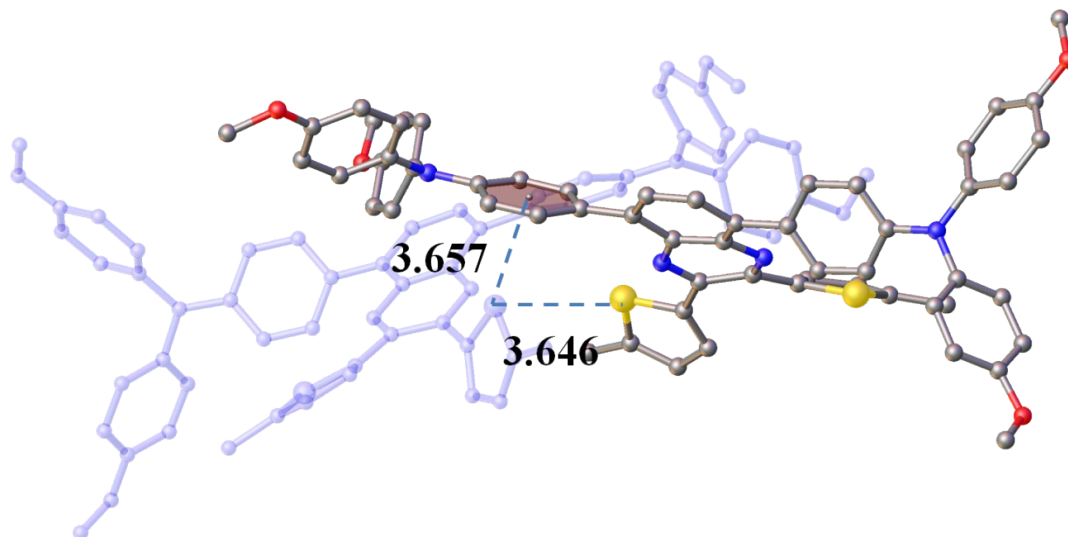**Fig. S8** Molecular packing in the crystal structure of (a) **TQ1** and (b) **TQ2**.

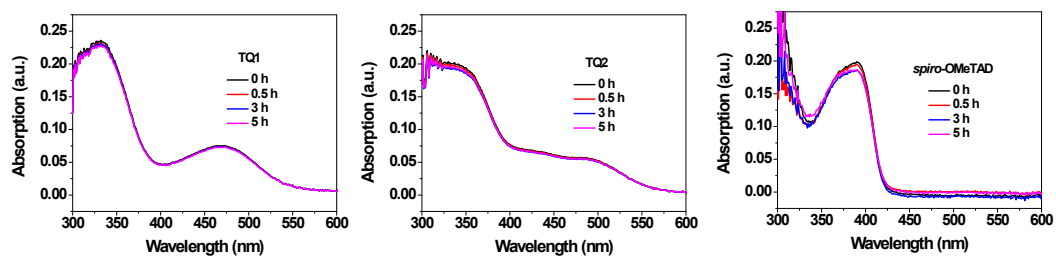**Fig. S9** The presence of S-S, and S-π interactions between two adjacent molecules of **TQ2** stack.

Fig. S10 Absorption spectra of **TQ1**, **TQ2** and *spiro*-OMeTAD films upon continuous light irradiation under simulated AM 1.5.
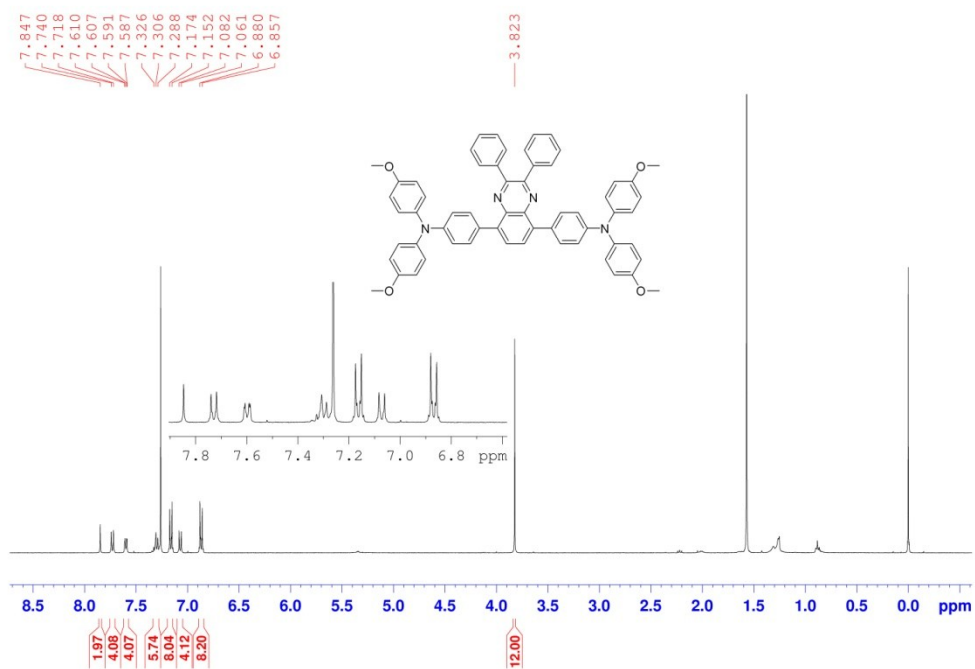
Fig. S11 ^{1}H NMR of hole-transporting material **TQ1** recorded in CDCl$_3$.
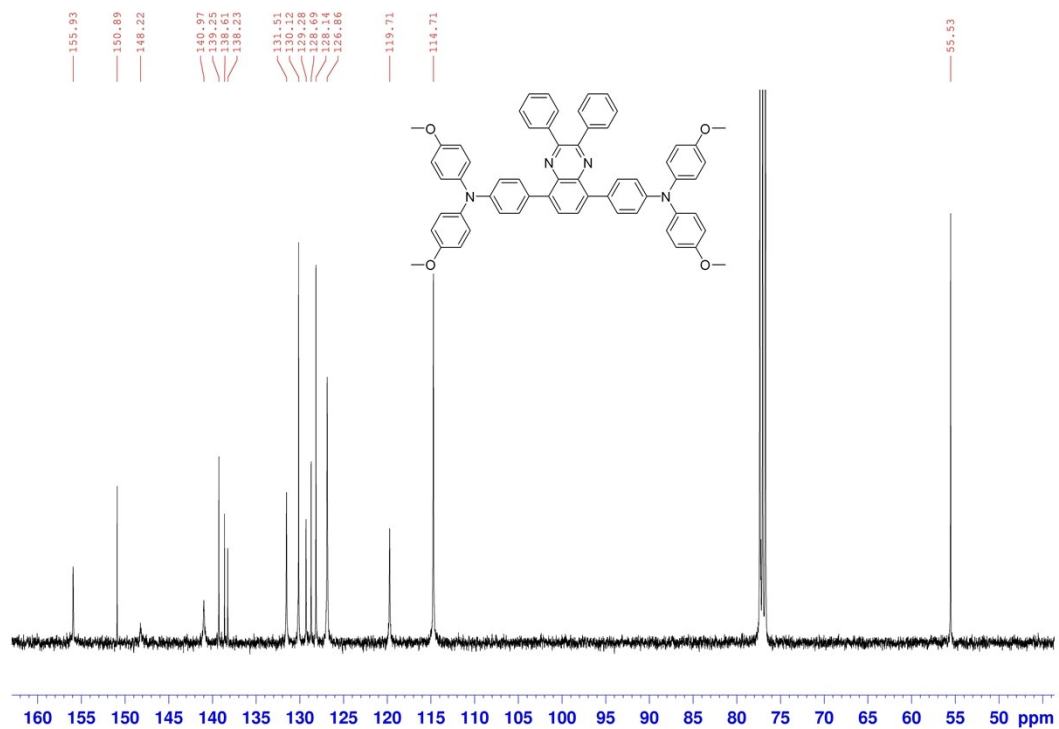
Fig. S12 ^{13}C NMR of hole-transporting material **TQ1** recorded in CDCl$_3$.

Elemental Composition Report   Page 1

Single Mass Analysis
Tolerance = 50.0 PPM   /   DBE: min = -1.5, max = 100.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions
7 formula(e) evaluated with 1 results within limits (up to 1 closest results for each mass)
Elements Used:
C: 0-60   H: 0-49   N: 0-4   O: 0-4
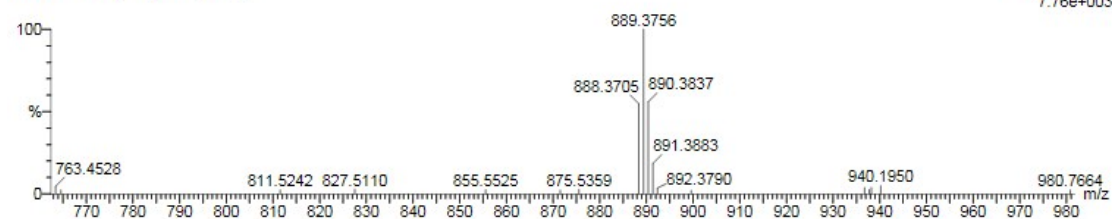WH-ZHU   ECUST institute of Fine Chem   12-Oct-2015
                                                                                        18:25:37
ZW-ZH-09 62 (0.472) Cm (60:66)   1: TOF MS ES+
                                                                                      7.76e+003

Minimum: -1.5
Maximum: 300.0   50.0   100.0

Mass   Calc. Mass   mDa   PPM   DBE   i-FIT   i-FIT (Norm) Formula

889.3756   889.3754   0.2   0.2   38.5   17.7   0.0   C60 H49 N4 O4

Fig. S13 High resolution mass spectrometry of hole-transporting material **TQ1**.
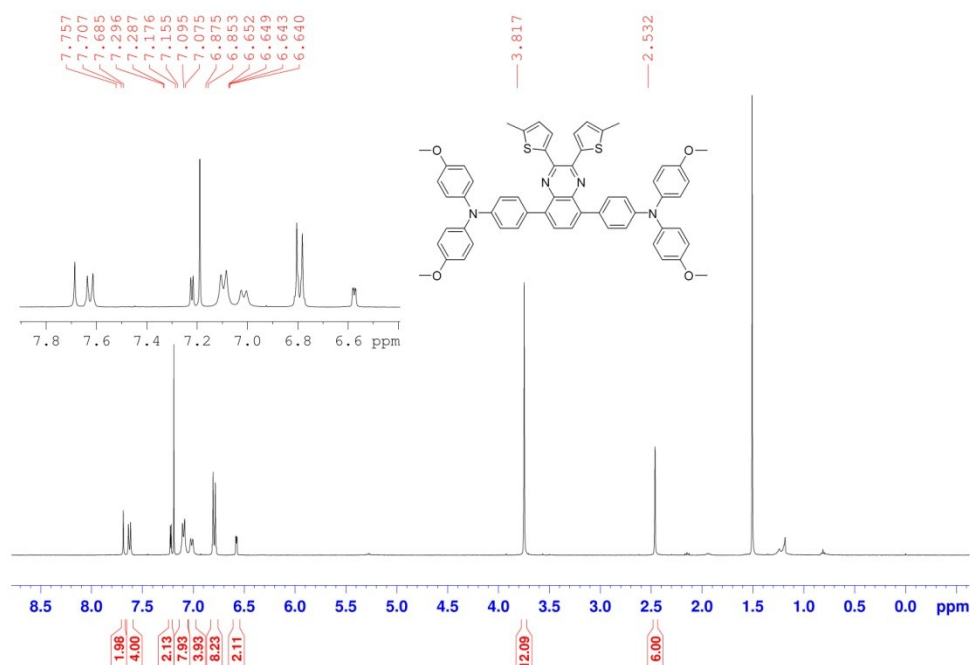
Fig. S14 ^1H NMR of hole-transporting material **TQ2** recorded in CDCl$_3$.
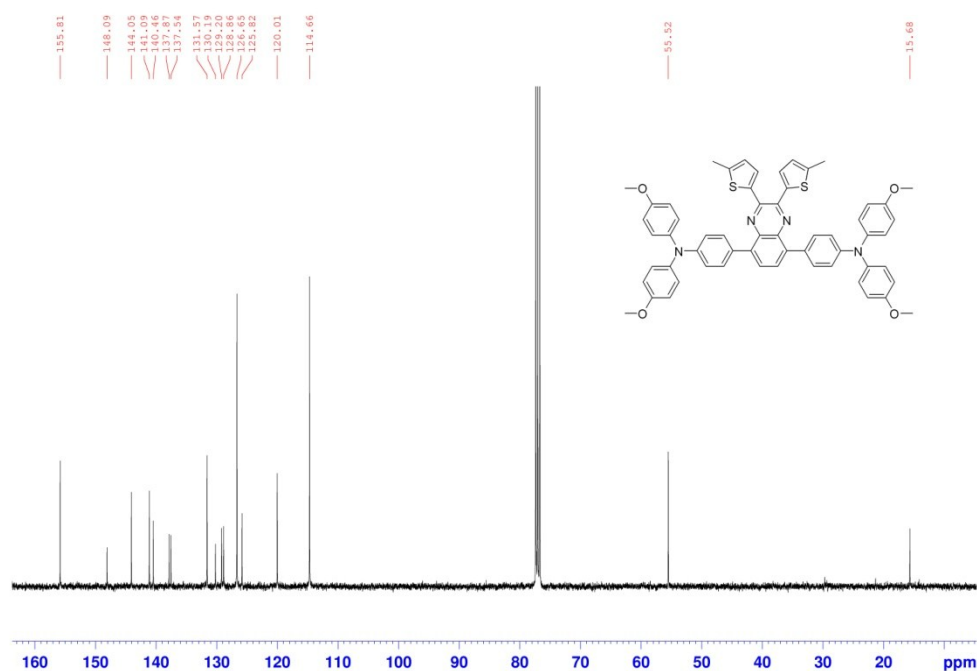
Fig. S15 ^{13}C NMR of hole-transporting material **TQ2** recorded in CDCl$_3$.

Fig. S16 High resolution mass spectrometry of hole-transporting material **TQ2**.
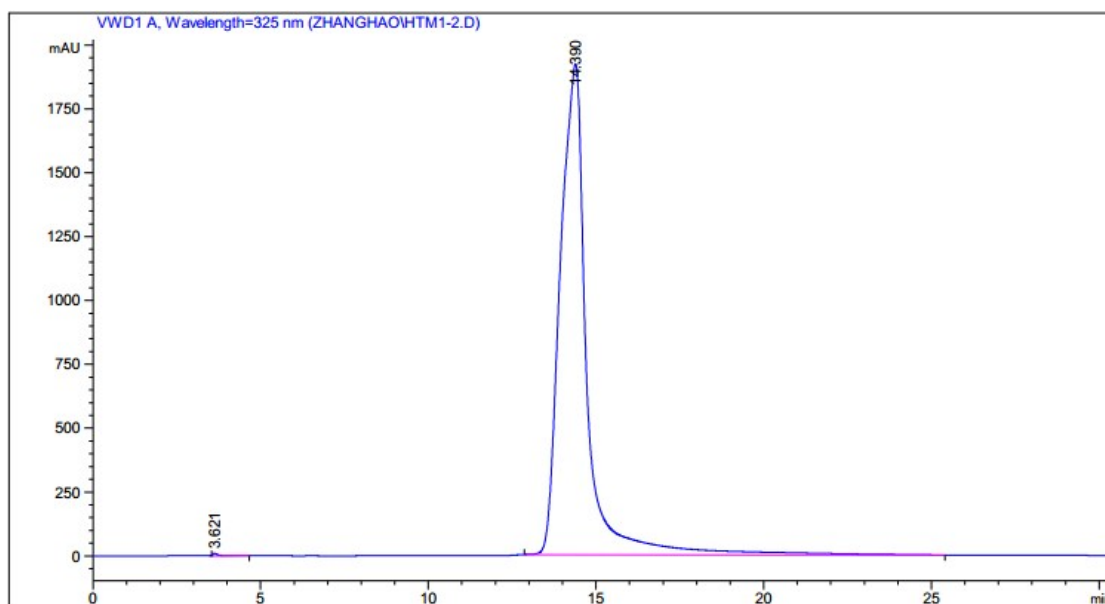
Fig. S17 High performance liquid chromatography (HPLC) analysis of hole-tran sporting material **TQ1**.
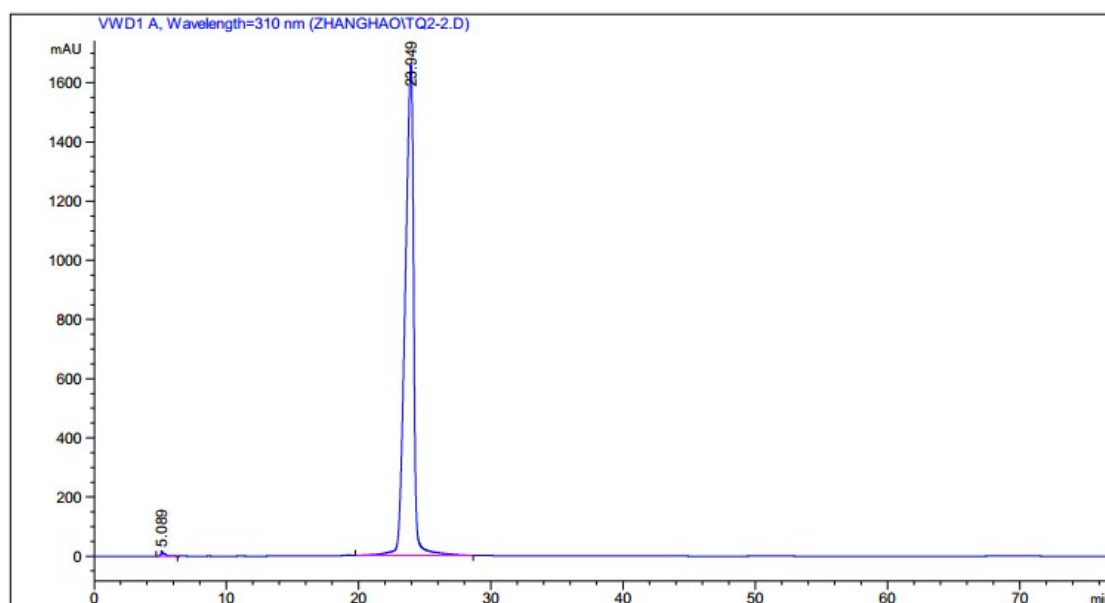
Fig. S18 High performance liquid chromatography (HPLC) analysis of hole-transporting material **TQ2**.

Cost analysis

We roughly estimated the synthesis cost of 1 gram of **TQ1** and **TQ2** according to the cost model that were reported previously. The prices of the used chemicals and solvents have been collected from major chemical suppliers (Energy-Chemical etc.). The estimated synthetic cost of **TQ1** and **TQ2** is 14.7 and 16.7 $/g, respectively, which is only 1/30 of the high purity *spiro*-OMeTAD (500 $/g).

3: 1.38 g
K$_2$CO$_3$: 4.67 g
Water: 10 g
Pd[PPh$_3$]$_4$: 0.14 g

THF: 30 g

Extraction
Dichloromethane: 60 g
water: 20 g
Na$_2$SO$_4$: 1 g
Column
Dichloromethane: 200 g
petroleum ether: 100 g
SiO$_2$: 120 g
Recrystalization
CHCl$_3$:22 g
methanol:18 g

0.63 g
1.44 mmol
1
Molecular Weight: 440.1380

77.6%

1.00 g
1.12 mmol
TQ1
Molecular Weight: 889.0680

→ Reagants
→ Solvents
→ Work materials

Table S1 Materials quantities and cost for the synthesis of hole-transporting material **TQ1**.

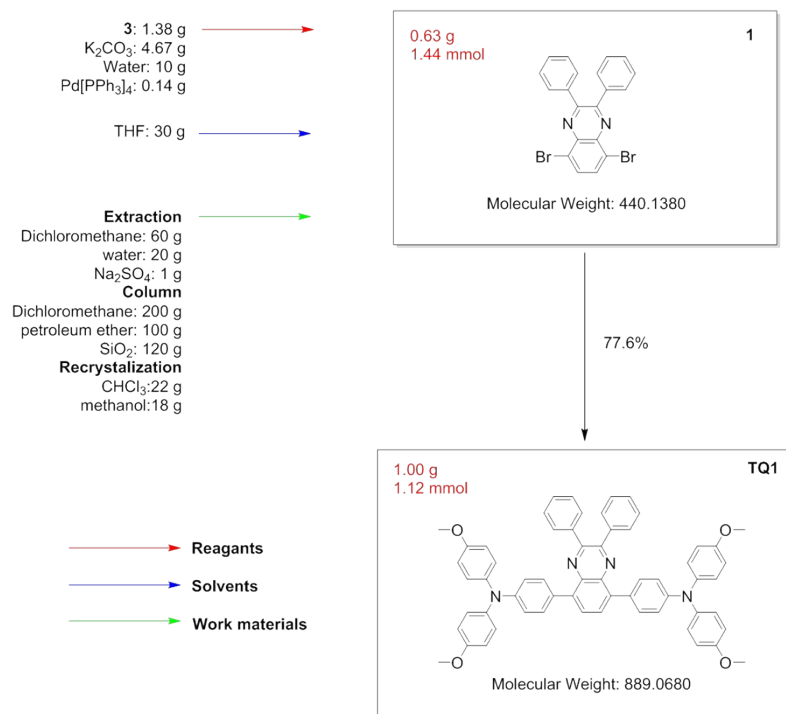| Chemical name	Weight reagent (g/g)	Weight solvent (g/g)	Weight workup (g/g)	Price of Chemical (¥/kg)	Material cost (¥/g product)	Cost per step (¥/step)
3	1.38			37000.00	51.06	97.71
1	0.63			47160.00	29.71	
K$_2$CO$_3$	4.67			33.00	0.16	
water		10		-	-	
Pd[PPh$_3$]$_4$	0.14			36142.00	5.06	
Tetrahydrofuran		30		52.00	0.29	
Dichloromethane			60.00	11.00	0.66	
Water			20.00	-	-	
Na$_2$SO$_4$			1.00	68.25	0.07	
Dichloromethane			200	11.00	2.20	
Petroleum ether			100	15.30	1.53	
Silica gel			120	50.00	6.00	
chloroform			22.00	30.50	0.67	
Methanol			18.00	16.70	0.30	
Total	**6.82**	**40.00**	**541.00**			**97.71**
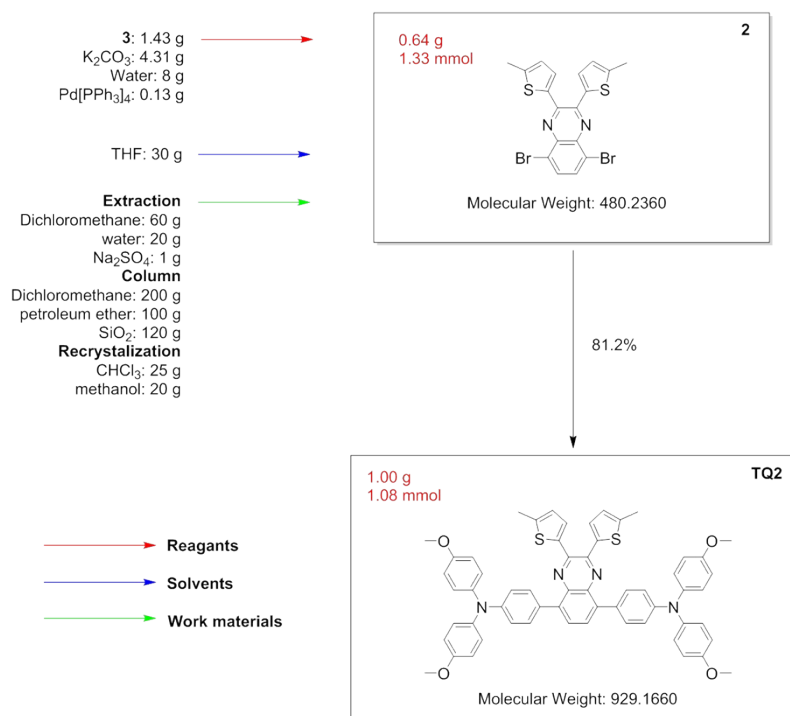
Table S2 Materials quantities and cost for the synthesis of hole-transporting material **TQ2**.

Chemical name	Weight reagent (g/g)	Weight solvent (g/g)	Weight workup (g/g)	Price of Chemical (¥/kg)	Material cost (¥/g product)	Cost per step (¥/step)
3	1.43			37000.00	52.91	110.82
2	0.72			57250.00	41.22	
K_2CO_3	4.31			33.00	0.15	
water		8		-	-	
$Pd[PPh_3]_4$	0.13			36142.00	4.70	
Tetrahydrofuran		30		52.00	0.29	
Dichloromethane			60.00	11.00	0.66	
Water			20.00	-	-	
Na_2SO_4			1.00	68.25	0.07	
Dichloromethane			200	11.00	2.20	
Petroleum ether			100	15.30	1.53	
Silica gel			120	50.00	6.00	
chloroform			25.00	30.50	0.76	
Methanol			20.00	16.70	0.33	
Total	**6.59**	**38.00**	**546.00**			**110.82**

Table S3 Crystallographic data and structure refinement for hole-transporting material **TQ1** (Data CCDC No. 1823702).

Identification code	mo_d8v17152_0m
Empirical formula	C60 H48 N4 O4
Formula weight	889.02
Temperature	173.01 K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 12.0014(12) Å α = 88.379(4)°
	b = 13.0411(12) Å β = 81.381(4)°
	c = 17.0476(15) Å γ = 74.642(4)°
Volume	2543.6(4) Å^3
Z	2
Density (calculated)	1.161 Mg/m^3
Absorption coefficient	0.073 mm^{-1}
F(000)	936
Crystal size	0.15 x 0.03 x 0.02 mm^3
Theta range for data collection	2.514 to 25.500°
Index ranges	-14<=h<=14, -14<=k<=15, -20<=l<=20
Reflections collected	33930
Independent reflections	9238 [R(int) = 0.1287]
Completeness to theta = 25.242°	97.4 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.5361
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9238 / 44 / 647
Goodness-of-fit on F^2	1.012
Final R indices [I>2sigma(I)]	R1 = 0.0990, wR2 = 0.2315
R indices (all data)	R1 = 0.1954, wR2 = 0.2991
Extinction coefficient	0.024(3)
Largest diff. peak and hole	0.267 and -0.303 e.Å^{-3}

Table S4 Crystallographic data and structure refinement for hole-transporting material **TQ2** (Data CCDC No. 1823703).

Identification code	d8v17256
Empirical formula	C177 H150 Cl6 N12 O12 S6
Formula weight	3042.14
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	P n a 21
Unit cell dimensions	a = 25.387(2) Å α = 90°
	b = 27.537(3) Å β = 90°
	c = 21.8595(19) Å γ = 90°
Volume	15282(2) Å^3
Z	4
Density (calculated)	1.322 Mg/m^3
Absorption coefficient	0.262 mm^{-1}
F(000)	6360
Crystal size	0.20 x 0.16 x 0.12 mm^3
Theta range for data collection	1.767 to 25.499°
Index ranges	-30<=h<=30, -33<=k<=33, -24<=l<=26
Reflections collected	176985
Independent reflections	26922 [R(int) = 0.1731]
Completeness to theta = 25.242°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.6700
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	26922 / 26 / 1937
Goodness-of-fit on F^2	1.035
Final R indices [I>2sigma(I)]	R1 = 0.0873, wR2 = 0.1854
R indices (all data)	R1 = 0.1711, wR2 = 0.2351
Absolute structure parameter	0.08(3)
Extinction coefficient	0.00072(12)
Largest diff. peak and hole	0.953 and -0.888 e.Å^{-3}

Table S5 Time-resolved PL decay fitting parameters.

Sample	A_1 (%)	Life time τ_1 (ns)	A_2 (%)	Life time τ_2 (ns)
Perovskite	0.74	4.25	99.26	118.14
Pero/TQ1	50.47	3.34	49.53	30.09
Pero/TQ2	65.30	1.17	34.70	7.45
Pero/spiro-OMeTAD	57.06	2.22	42.94	18.70

References

[S1]D. W. Chang, H. J. Lee, J. H. Kim, S. Y. Park, S. Park, L. Dai and J. Baek, *Org. Lett.*, 2011, **13**, 3880.

[S2]H. Zhu, B. Liu, J. Liu, W. Zhang and W. Zhu, *J. Mater. Chem. C*, 2015, **3**, 6882.

[S3]H. D. Pham, Z. Wu, L. K. Ono, S. Manzhos, K. Feron, N. Motta, Y. Qi and P. Sonar, *Adv. Electron. Mater.*, 2017, **3**, 1700139.