

Rational Design of D- π -D Hole-Transporting Materials for Efficient Perovskite Solar Cells

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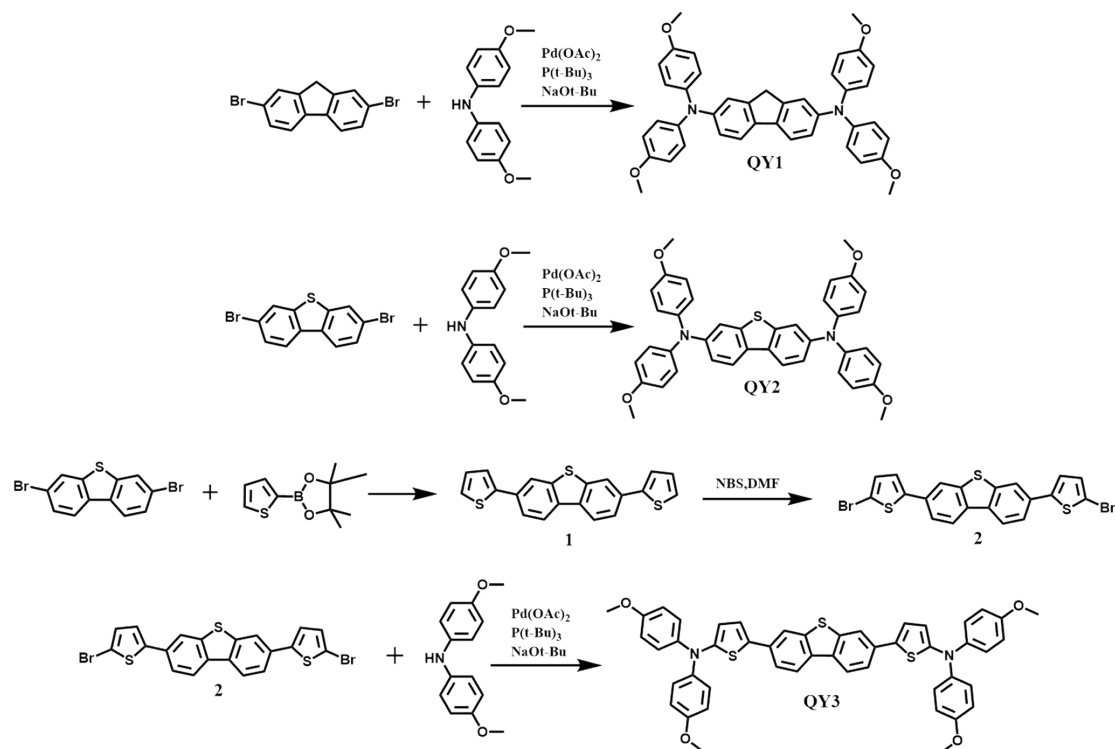
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Experimental section

1. Synthesis:

Materials were all available commercially and used without further purification if not mentioned specially. The synthetic routes of QY1, QY2 and QY3 are shown in Scheme S1 and the details are described.



Scheme S1. Synthetic route to QY1, QY2 and QY3, respectively.

QY1: In a 25 mL two-necked flask, a mixture of 2,7-dibromo-9H-fluorene (0.65 mmol, 210 mg), bis(4-methoxyphenyl)amine (1.37 mmol, 314 mg) and sodium tert-butoxide (3.90 mmol, 375 mg) in anhydrous toluene (10 mL) was stirred for 30 minutes under N₂ atmosphere to remove oxygen, then added palladium (II) acetate (0.013 mmol, 3 mg), tri-tert-butylphosphine (0.039 mmol, 8 mg), the reaction mixture was stirred overnight at 110 °C until the reaction was complete by (thin layer chromatography) TLC analysis. After cooling, the reaction was quenched by deionized water, and then followed by product extraction with ethyl acetate. At last, the organic layer was dried over anhydrous Mg₂SO₄ and evaporated under vacuum. The collected residue was further purified by silica gel column chromatography (hexane/EtOAc, v/v, 5:1) to give

QY1 (yield 85%). ^1H NMR (400 MHz, CDCl_3 , δ), δ/ppm : 7.96-7.90 (d, 2H), 7.75 (s, 2H), 7.25-7.08 (d, 10H), 6.84-6.79 (d, 8H), 4.09 (s, 2H), 3.75 (s, 12H). ^{13}C NMR (400 MHz, CDCl_3 , δ), 156.18, 147.99, 140.61, 133.84, 126.95, 125.65, 123.42, 120.61, 118.83, 114.85, 60.39, 55.49. MALDI-TOF-MS (m/z): calculated for $[\text{M}-\text{H}]$ $\text{C}_{41}\text{H}_{36}\text{N}_2\text{O}_4$: 620.2675, found: 620.2653.

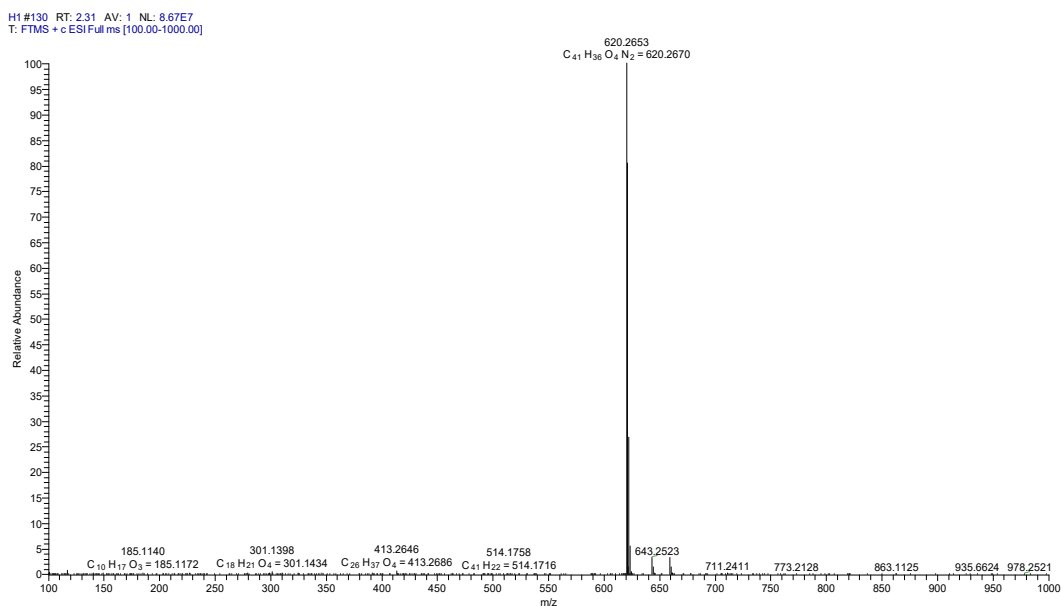


Fig. S1. Mass spectrum of QY1.

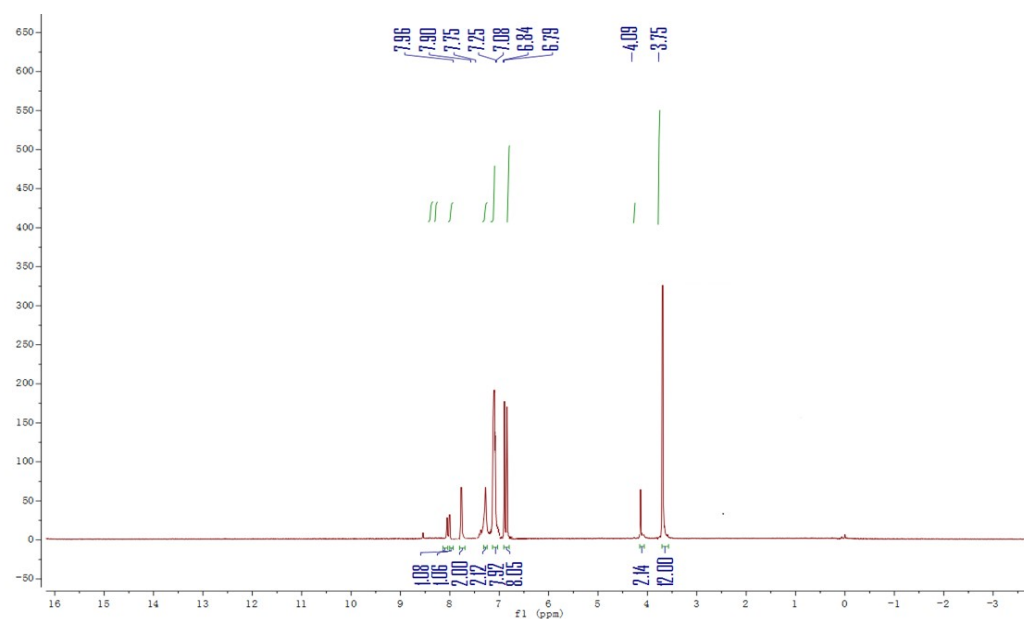


Fig. S2. ^1H NMR spectra of QY1.

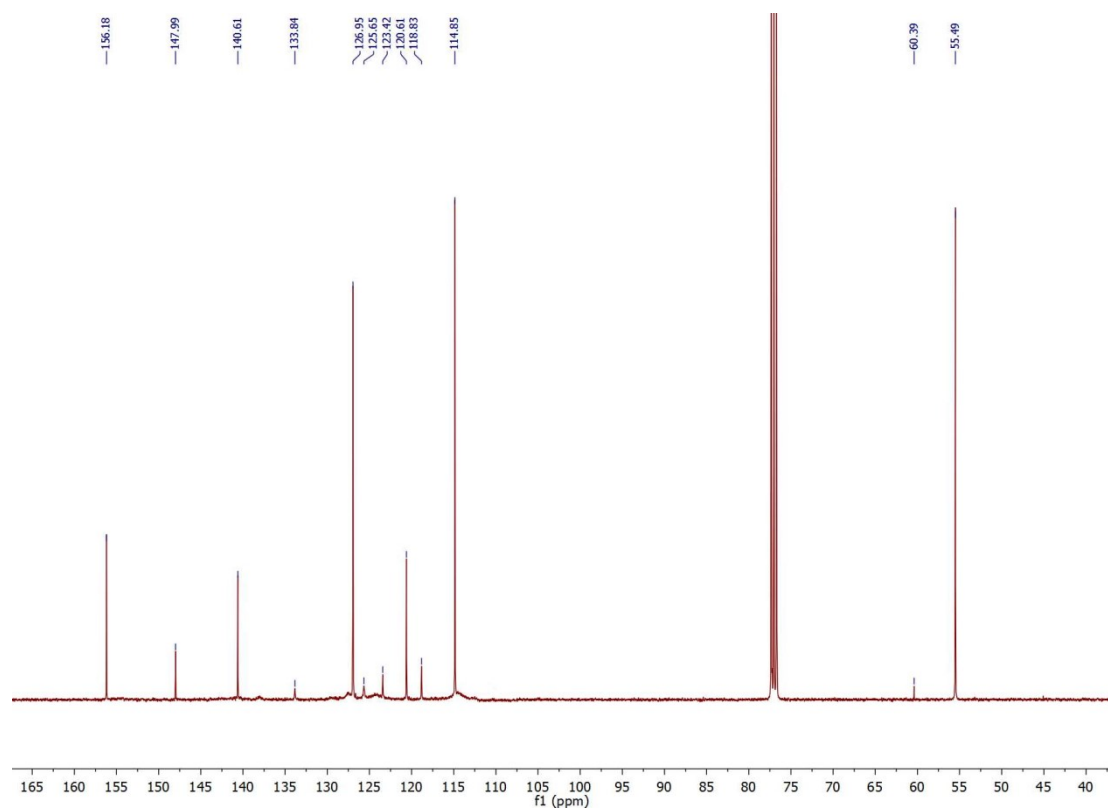


Fig. S3. ^{13}C NMR spectra of QY1.

QY2: In a 25 mL two-necked flask, a mixture of 3,7-dibromodibenzo[b,d]thiophene (0.65 mmol, 221 mg), bis(4-methoxyphenyl)amine (1.37 mmol, 314 mg) and sodium tert-butoxide (3.90 mmol, 375 mg) in anhydrous toluene (10 mL) was stirred for 30 minutes under N_2 atmosphere to remove oxygen, then added palladium (II) acetate (0.013 mmol, 3 mg) and tri-tert-butylphosphine (0.039 mmol, 8 mg), the reaction mixture was stirred overnight at 110 °C until the reaction was complete by TLC analysis. After cooling, the reaction was quenched by deionized water, and then followed by product extraction with ethyl acetate. The organic layer was dried over anhydrous Mg_2SO_4 and evaporated under vacuum. The collected residue was further purified by silica gel column chromatography (hexane/EtOAc, v/v, 3:1) to give QY2 (yield 83%). ^1H NMR (400 MHz, CDCl_3), δ /ppm: 7.97 (s, 2H), 7.77 (s, 2H), 7.52 (s, 2H), 7.31-7.19 (d, 8H), 6.95-6.89 (d, 8H) 3.70 (s, 12H). ^{13}C NMR (400 MHz, CDCl_3 ,

δ), 158.73, 133.86, 128.47, 125.72, 123.44, 118.85, 115.04, 114.31, 109.95, 55.50.
MALDI-TOF-MS (m/z): calculated for [M-H] C₄₀H₃₄N₂O₄S: 638.2239, found:
638.2204.

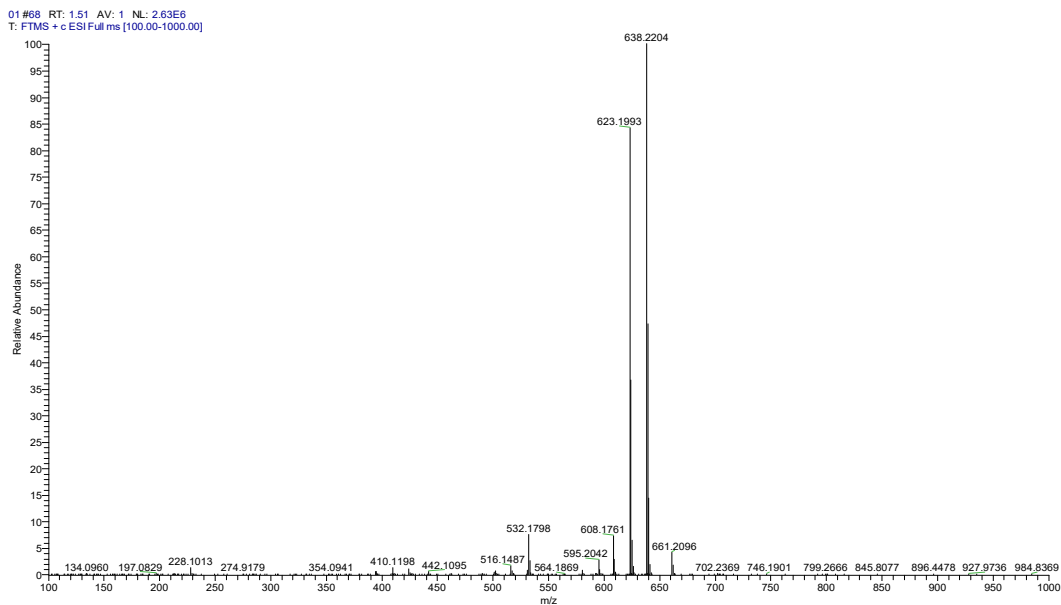


Fig. S4. Mass spectrum of QY2.

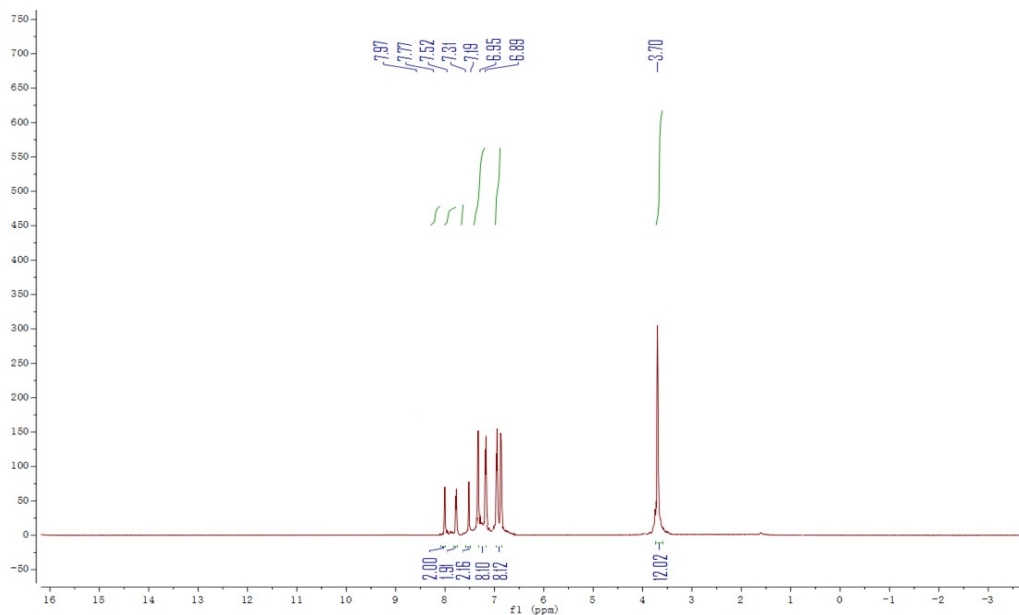


Fig. S5. ¹H NMR spectrum of QY2.

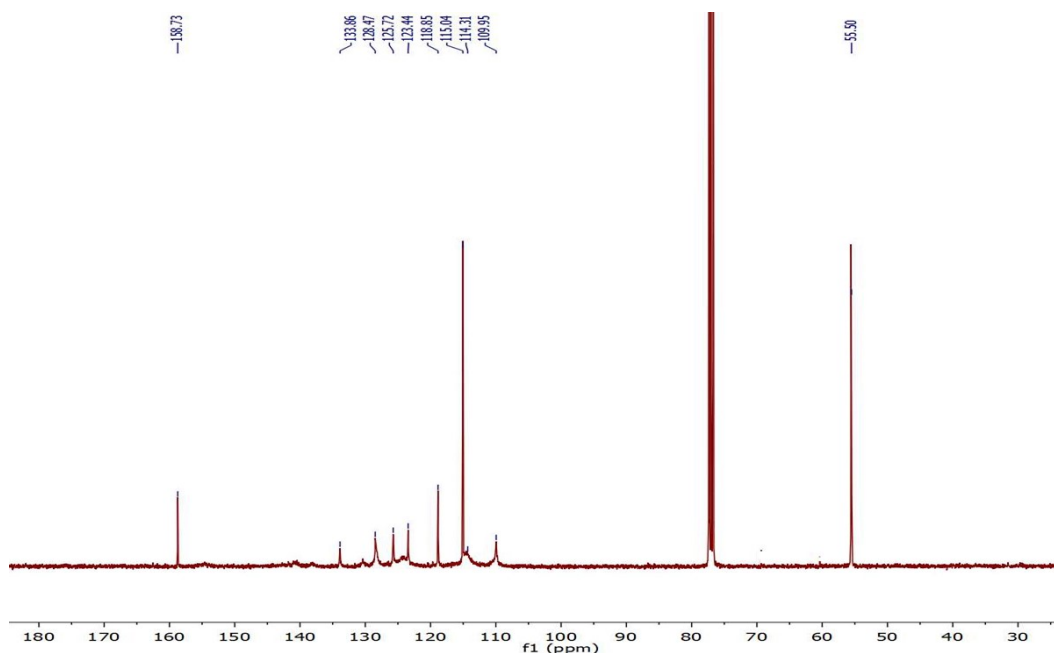


Fig. S6. ^{13}C NMR spectra of QY2.

Compound 1: In a 50 mL two-necked flask, a mixture of 3,7-dibromodibenzo[b,d]thiophene (0.80 mmol, 272 mg), 4,4,5,5-tetramethyl-2-(thiophen-2-yl)-1,3,2-dioxaborolane (1.68 mmol, 353 mg) in anhydrous toluene (15 mL) was stirred for 30 minutes under N_2 atmosphere. Then 1.5 mol L^{-1} potassium carbonate aqueous solution (2 mL), tetrabutylammonium bromide (0.30 mmol, 97 mg) and tetrakis(triphenylphosphine)palladium (0.0163 mmol, 19 mg) were added. And the mixture was stirred three days at $120 \text{ }^\circ\text{C}$ and then cooled to $25 \text{ }^\circ\text{C}$. The organic layer evaporated under vacuum and the residue was further purified by silica gel column chromatography (hexane/ CH_2Cl_2 , v/v, 3:1) to give compound 1 (yield 84%). ^1H NMR (400 MHz, *d*-DMSO), δ/ppm : 8.83 (d, 2H), 8.27 (s, 2H), 7.79 (d, 2H), 7.61 (d, 2H), 7.56 (d, 2H), 7.23-7.15 (m, 2H).

Compound 2: In a 25 mL two-necked flask, compound 1 (0.68 mmol, 237 mg) was added to *N,N*-Dimethylformamide (10 mL) and stirred for 5 minutes. Then *N*-bromobutanamide (1.43 mmol, 255 mg) was added four times and the mixture was stirred four hours at 0°C . The organic solvent evaporated under vacuum and the residue was further purified by silica gel column chromatography (hexane/ CH_2Cl_2 , v/v, 1:1) to give compound 2 (yield 92%). ^1H NMR (400 MHz, *d*-DMSO), δ/ppm : 8.39-8.29 (d,

2H), 8.23 (s, 2H), 7.77 (dd, 2H), 7.42 (d, 2H), 7.35 (d, 2H).

QY3: In a 25 mL two-necked flask, a mixture of compound 2 (0.43 mmol, 217 mg), bis(4-methoxyphenyl)amine (0.91 mmol, 209 mg) and sodium tert-butoxide (2.58 mmol, 248 mg) in anhydrous toluene (10 mL) was stirred for 30 minutes under N₂ atmosphere. Then palladium(II)acetate (0.0086 mmol, 2 mg), tri-tert-butylphosphine (0.0258 mmol, 6 mg) were added into the mixture and then stirred overnight at 110 °C. After cooling, the reaction was quenched with water, and then extracted with ethyl acetate. The organic solvent was evaporated under vacuum and the residue was purified by silica gel column chromatography (hexane/EtOAc, v/v, 2:1) to give QY3 (yield 78%). ¹H NMR (400 MHz, DMSO-d₆), δ/ppm: 8.02-8.00 (d, 2H), 7.94-7.91 (d, 2H), 7.78-7.76 (d, 2H), 7.16-7.15 (d, 8H), 6.82-6.62 (d, 2H), 6.49-6.48 (d, 8H), 6.07-6.01 (d, 2H), 3.75 (s, 12H). ¹³C NMR (400 MHz, CDCl₃, δ) 156.04, 153.70, 141.27, 140.30, 134.01, 133.74, 133.33, 124.87, 122.25, 121.78, 121.47, 118.38, 116.76, 114.59, 55.52. MALDI-TOF-MS (m/z): calculated for [M-H] C₄₈H₃₈N₂O₄S₃: 802.1994, found: 802.1969.

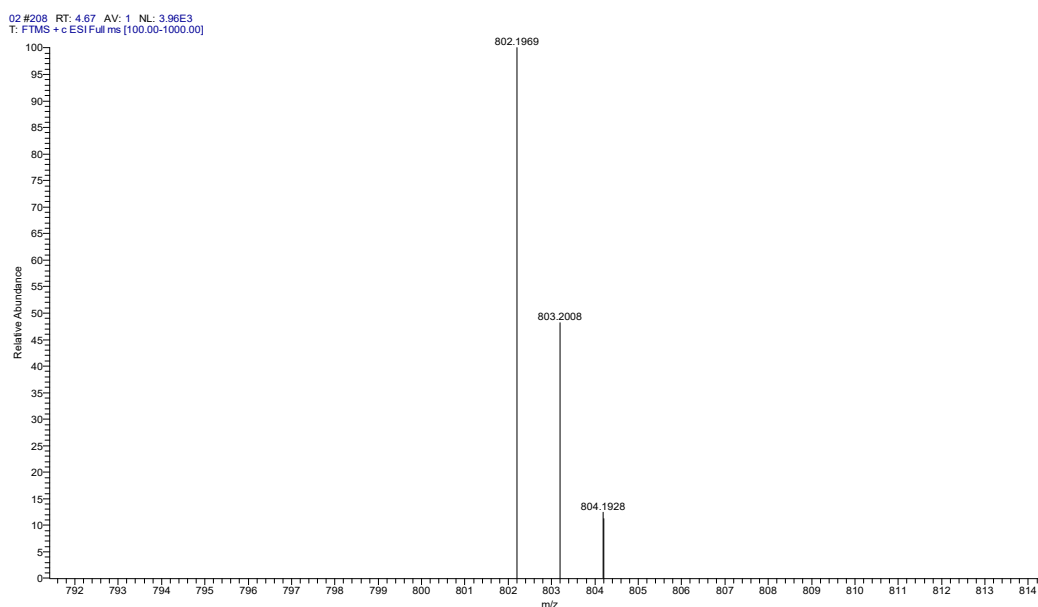


Fig. S7. Mass spectrum of QY3.

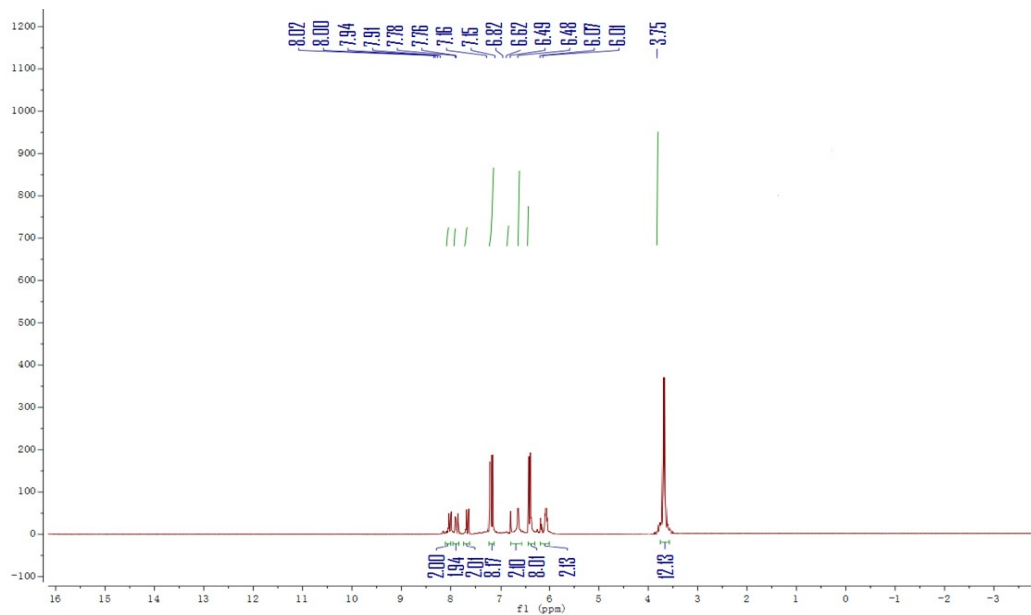


Fig. S8. ^1H NMR spectrum of QY3.

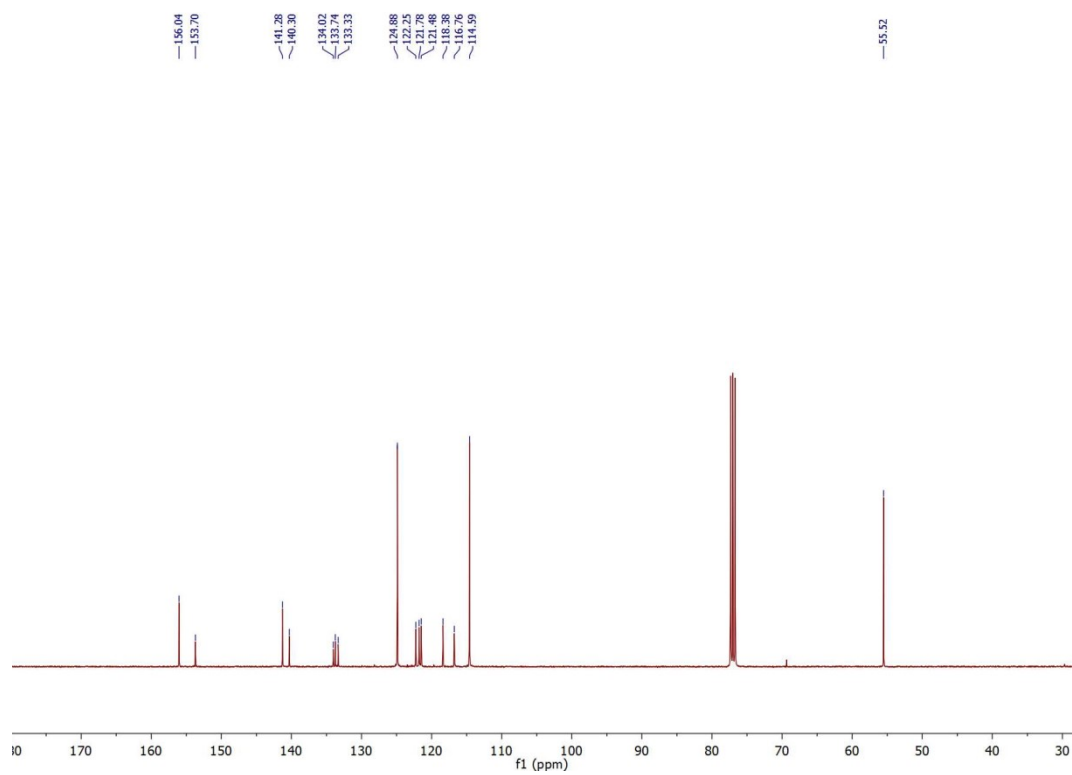


Fig. S9. ^{13}C NMR spectrum of QY3.

2. Materials cost for synthesis of QY1, QY2 and QY3

Table S1. Materials cost for synthesis of QY1

Materials	Amount/mg	Amount/mL	Price USD /g or mL	Total price/ USD
2,7-dibromo-9H-fluorene	210	-	0.92	0.19
bis(4-methoxyphenyl)amine	314	-	4.62	1.45
sodium tert-butoxide	375	-	0.18	0.07
palladium(II)acetate	3	-	61.66	0.18
tri-tert-butylphosphine	8	-	1.31	0.01
toluene	-	10	0.12	1.20
ethyl acetate	-	400	0.003	1.20
hexane	-	1000	0.0038	3.80
total cost	7.91 USD			
amount QY1	445 mg			
cost for QY1	17.77 USD g ⁻¹			

Table S2. Materials cost for synthesis of QY2

Materials	Amount/mg	Amount/mL	Price USD /g or mL	Total price/ USD
3,7-dibromodibenzo[b,d] thiophene	221	-	480.84	106.26
bis(4- methoxyphenyl)amine	314	-	4.62	1.45
sodium tert-butoxide	375	-	0.18	0.07
palladium(II)acetate	3	-	61.66	0.18
tri-tert-butylphosphine	8	-	1.31	0.01
toluene	-	10	0.12	1.20
ethyl acetate	-	500	0.003	1.50
hexane	-	900	0.0038	3.42
total cost	114.09 USD			
amount QY2	444 mg			
cost for QY2	256.95 USD g ⁻¹			

Table S3. Materials cost for synthesis of compound 1

Materials	Amount/ mg	Amount/ mL	Price USD/g or mL	Total price/USD
3,7-dibromodibenzo[b,d] thiophene	272	-	480.84	130.78
4,4,5,5-tetramethyl-2-(thiophen-2-yl)- 1,3,2-dioxaborolane	353	-	4.62	1.63
toluene	-	15	0.12	1.80
potassium carbonate	415	-	0.009	0.003
tetrabutylammonium bromide	97	-	0.18	0.017
tetrakis(triphenylphosphine)palladium	19	-	15.41	0.29
dichloromethane	-	500	0.002	1.00
hexane	-	900	0.0038	3.42
total cost	138.94 USD			
Amount compound 1	525 mg			
cost for compound 1	264.64 USD g ⁻¹			

Table S4. Materials cost for synthesis of compound 2

Materials	Amount/mg	Amount/mL	Price USD /g or mL	Total price/ USD
compound 1	237	-	264.64	62.71
N-bromobutanamide	255	-	0.18	0.04
N,N-Dimethylformamide	-	10	0.04	0.40
dichloromethane	-	700	0.002	1.40
hexane	-	500	0.0038	1.9
total cost	66.45 USD			
Amount compound 2	452 mg			
cost for compound 2	147.01 USD g ⁻¹			

Table S5. Materials cost for synthesis of QY3

Materials	Amount/mg	Amount/mL	Price USD /g or mL	Total price/ USD
compound 2	217	-	147.01	31.90
bis(4-methoxyphenyl)amine	209	-	4.62	0.96
sodium tert-butoxide	248	-	0.18	0.04
palladium(II)acetate	2	-	61.66	0.12
tri-tert-butylphosphine	6	-	1.31	0.007
toluene	-	10	0.12	1.20
ethyl acetate	-	500	0.003	1.50
hexane	-	600	0.0038	2.28
total cost	38.00 USD			
amount QY3	332 mg			
cost for QY3	114.45 USD g ⁻¹			

3. Electrochemical Measurements

Electrochemical experiments were performed with a CH Instruments electrochemical workstation (model 660A) using a conventional three-electrode electrochemical cell. A glassy carbon electrode (diameter 3 mm) was used as the working electrode, a platinum wire as the counter electrode, Ag/AgCl as the reference electrode and 0.1 M of tetrabutylammoniumhexafluorophosphate ($n\text{-Bu}_4\text{NPF}_6$) in dichloromethane solution as supporting electrolyte. The cyclic voltammetric scan rates were 50 mV s^{-1} .

4. Mobility Measurements

Indium Tin Oxide (ITO) coated glass substrates (Pilkington TEC15) were patterned by etching with zinc powder and 2 M hydrochloric acid. The substrates were carefully cleaned in ultrasonic baths of detergents, deionized water, acetone and ethanol successively. The remaining organic residues were removed with 10 min by airbrush. A 40 nm thick PEDOT: PSS layer was spin-coated onto the substrates, which were then annealed at $120 \text{ }^\circ\text{C}$ for 30 min in air. The substrates were then transferred into a glovebox for further fabrication steps. The HTMs were dissolved in anhydrous chlorobenzene. J - V characteristics of the devices have been measured with a Keithley 2400 Source-Measure unit, interfaced with a computer. Device characterization was carried out in air.

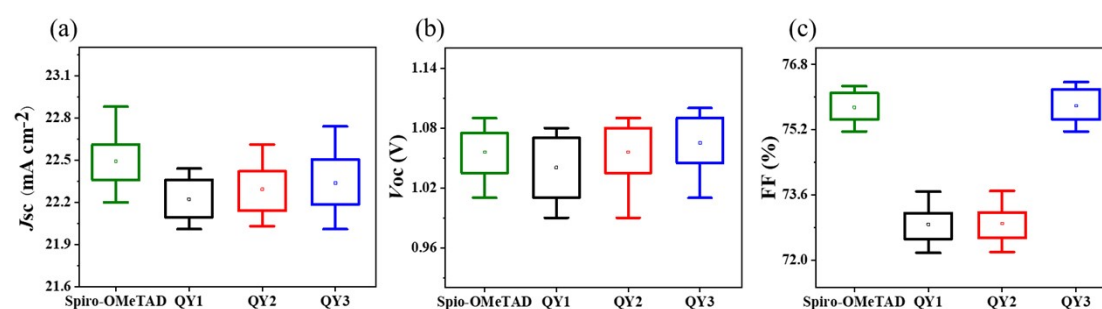


Fig. S10. Statistics of photovoltaic parameters for 36 solar cell devices each for the QY1, QY2, QY3 (a) J_{sc} , (b) V_{oc} , and (c) FF.

Table S6. Fitted results of TRPL decay curves in Figure 5b using a biexponential decay function of $y = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) + y_0$, where τ_1 and τ_2 represent fast and slow decay time, respectively. $\tau_{ave} = (A_1\tau_1^2 + A_2\tau_2^2)/(A_1\tau_1 + A_2\tau_2)$

Sample	perovskite		QY1		QY2		QY3	
τ (ns)	τ_1	τ_2	τ_1	τ_2	τ_1	τ_2	τ_1	τ_2
	2.95	43.22	1.72	17.10	1.23	10.96	0.89	7.14
A%	98.601	1.3989	99.9976	0.0024	99.9951	0.0048	99.9892	0.0108
	1							
τ_{Ave} (ns)	9.88		1.72		1.23		0.89	