

Highly Efficient Phenothiazine 5, 5-Dioxide-Based Hole Transport Materials for Planar Perovskite Solar Cells with PCE Exceeding 20%

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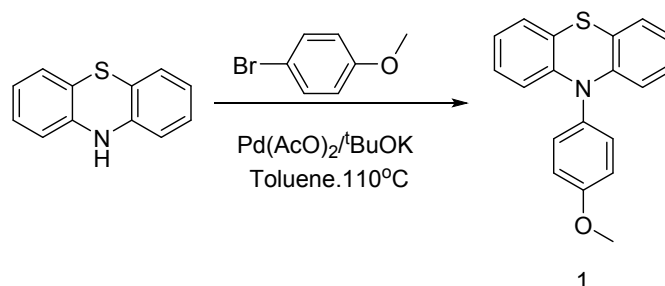
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Synthesis method

Chemicals: All of the solvents and chemicals were used as received unless specially stated.

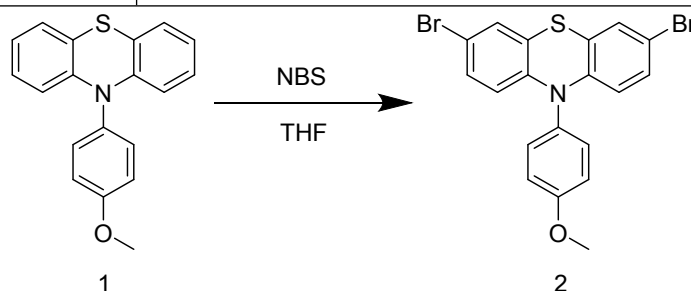


10-(4-Methoxyphenyl)-10H-phenothiazine (1). A mixture of 4-bromoanisole (0.823 g, 4.40 mmol), phenothiazine (0.797 g, 4.00 mmol), catalyst palladium diacetate (0.018 g, 0.08 mmol), tri-tert-butylphosphonate (0.05 mmol) and potassium *tert*-butoxide (0.577 g, 6.00 mmol) in toluene (50 mL) was stirred at 110 °C for 24 h. After cooling down the reaction to room temperature, 50 mL dichloromethane was added into reaction solution, and then wash three times with 150mL water. The organic layer was collected and evaporated under reduced pressure. The crude product was purified by column chromatography (petroleum ether/dichloromethane = 4:1 vol/vol) to obtain **1** (0.991 g, yield: 81.16%) as an off-white solid. ¹H-NMR (CDCl₃): δ 7.34 (d, J = 8.7 Hz, 2H); 7.14 (d, J = 8.7 Hz, 2H); 7.02 (dd, J = 7.5, 1.6 Hz, 2H); 6.88-6.85 (m, 2H); 6.83-6.80 (m, 2H); 6.22 (dd, J = 8.2, 1.2 Hz, 2H); 3.93 (s, 3H) ppm. HR-MS: calculated: C₁₉H₁₅NOS, 305.0874, found:305.0870.

Table S1 Synthesis cost of intermediate **1**

Reagent	Amount /g	Amount /ml	Price (RMB/g or RMB/mL)	Total price (RMB)
Phenothiazine	0.797		0.316	0.251
4-bromoanisole	0.823		0.590	0.486
Palladium diacetate	0.018		180.000	3.240

Tri-tert-butylphosphonate		0.116	7.450	0.865
Potassium tert-butoxide	0.577		0.396	0.228
Toluene		50.00	0.041	2.050
Silica gel	100.00		0.292	29.230
Petroleum ether		400.00	0.119	47.400
Dichloromethane		150.00	0.182	27.250
Total cost	111.000 RMB			
Amount intermediate 1	0.990 g			
COST for intermediate 1	112.121 RMB/g			
Exchange rate	1\$=6.930 RMB			

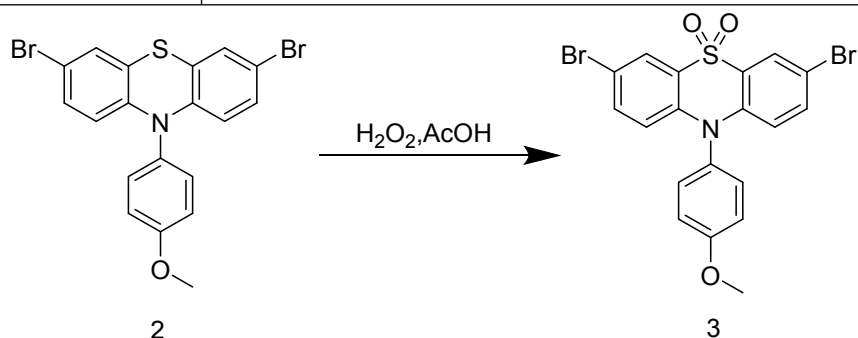


3,7-dibromo-10-(4-methoxyphenyl)-10H-phenothiazine (2). *N*-Bromo-succinimide (1.957 g, 11.00 mmol) was added in small portions to a solution of **1** (1.540 g, 5.00 mmol) in THF (100 mL) and the obtained mixture was stirred for 6h at 0-5 °C. The reaction mixture was then poured into water and the obtained solid was filtered, washed with water and dried under vacuum. The collected crude product was purified by elution through a short silica plug (petroleum ether/dichloromethane = 2:1 vol/vol) to afford **2** (1.76 g, yield: 76.3%) as a yellow solid. ¹H NMR (400 MHz, Acetone) δ 7.47 – 7.29 (m, 2H), 7.27 – 7.13 (m, 4H), 7.06 (dd, J = 8.8, 2.2 Hz, 2H), 6.11 (d, J = 8.8 Hz, 2H), 3.92 (s, 3H) ppm. HR-MS: calculated: C₁₉H₁₃Br₂NOS, 460.9085, found: 462.9077.

Table S2 Synthesis cost of intermediate 2

Reagent	Amount	Amount	Price (RMB/g)	Total price
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	/g	/ml	or RMB/mL)	(RMB)
1	1.540g		112.121	172.666
THF		100.00	0.063	6.250
NBS	1.967		0.395	0.779
Silica gel	100.00		0.292	29.200
Petroleum ether		300.00	0.119	35.550
Dichloromethane		200.00	0.182	36.340
Total cost	280.611 RMB			
Amount intermediate 2	1.760 g			
COST for intermediate 2	159.430 RMB/g			
Exchange rate	1\$=6.930 RMB			

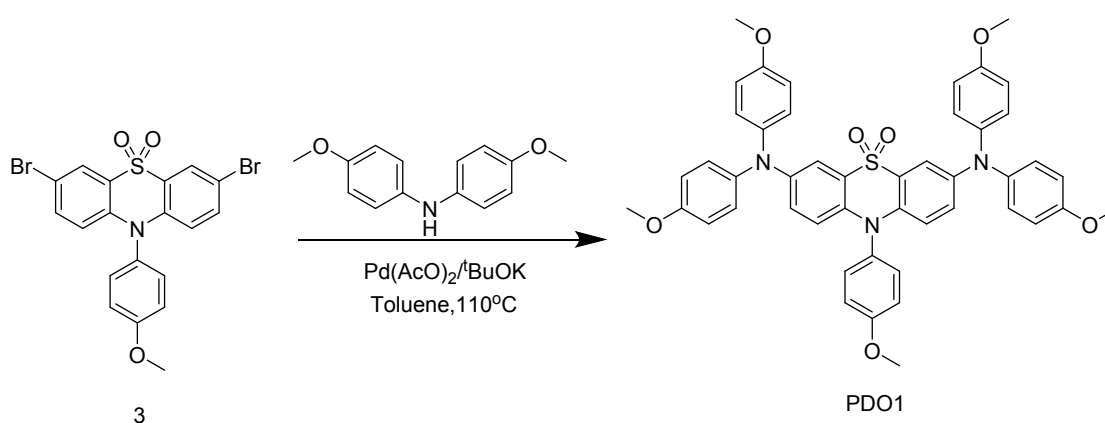


3,7-dibromo-10-(4-methoxyphenyl)-10H-phenothiazine 5,5-dioxide (3). Hydrogen peroxide (25 mL) was slow added in small portions to a solution of **2** (1.760 g, 3.800 mmol) in acetic acid (50 mL) and the obtained mixture was stirred for 6h at 120-130 °C. After cooling down the reaction to room temperature, the mixture was washed with water several times. The organic layer was collected and evaporated under reduced pressure. The collected crude product was purified by elution through a short silica plug (petroleum ether/dichloromethane = 2:1 vol/vol) to afford **3** (1.130 g, yield: 60.1%) as a yellow solid. ¹H-NMR (400 MHz, CDCl₃) δ 8.23 (d, J = 2.3 Hz, 2H), 7.46 (dd, J = 9.2, 2.3 Hz, 2H), 7.24 (dt, J = 5.3, 3.1 Hz, 2H), 7.19 – 7.14 (m, 2H), 6.57 (d, J = 9.2 Hz, 2H), 3.94 (s, 3H) ppm. HR-MS: calculated: C₁₉H₁₃Br₂NO₃S, 492.8983, found:

494.8963.

Table S3 Synthesis cost of intermediate 3

Reagent	Amount /g	Amount /ml	Price (RMB/g Or RMB/mL)	Total price (RMB)
2	1.760		159.430	280.611
H ₂ O ₂		25.00	0.030	0.750
AcOH		50.00	0.069	3.425
Silica gel	100.00		0.292	29.200
Petroleum ether		200.00	0.119	23.700
Dichloromethane		250.00	0.182	45.425
Total cost	383.111 RMB			
Amount intermediate 3	1.130 g			
COST for intermediate 3	339.030 RMB/g			
Exchange rate	1\$=6.930 RMB			



3,7-bis(bis(4-methoxyphenyl)amino)-10-(4-methoxyphenyl)-10H-phenothiazine

5,5-dioxide (PDO1). A mixture of **3** (0.493 g, 1.00 mmol), 4,4-Dimethoxydiphenylamine (0.560 g, 2.20 mmol), palladium acetate (0.012 g, 0.05 mmol), tri-tert-butylphosphonate (0.10 mmol) and potassium tertiary butanol (0.339 g, 3.00 mmol) in toluene (100 mL) was stirred at 110 °C for 24 h. After cooling down the reaction to room temperature, the mixture was diluted with dichloromethane and washed with water. The organic layer was collected and evaporated under reduced pressure. The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 2:1 vol/vol) to obtain PDO1 (0.560 g, yield: 70.8%) as a yellow solid. ¹H-NMR (400 MHz, Acetone) δ 7.41 (d, J = 2.7 Hz, 2H), 7.37 (d, J = 8.9 Hz, 2H), 7.25 (d, J = 8.9 Hz, 2H), 7.10 – 7.00 (m, 10H), 6.96 – 6.86 (m, 8H), 6.59 (d, J = 9.3 Hz, 2H), 3.91 (s, 3H), 3.78 (d, J = 5.0 Hz, 12H) ppm. ¹³C-NMR (101 MHz, Acetone): 205.41, 205.22, 205.01, 163.27, 159.78, 156.41, 144.16, 143.48, 142.33, 140.41, 140.26, 135.26, 134.57, 131.61, 131.52, 128.20, 126.25, 125.93, 122.69, 121.32, 118.37, 116.20, 114.91, 112.57, 55.14, 54.82, 29.51, 29.32, 29.12, 28.93, 28.74, 28.55, 28.35 ppm. HR-MS: calculated: C₄₇H₄₁N₃O₇S, 791.2665, found: 791.2654.

Table S4 Synthesis cost of **PDO1**

Reagent	Amount /g	Amount /mL	Price(RMB/g orRMB/mL)	Total price(RMB)
3	0.493		339.030	167.142
4,4-Dimethoxydiphenylamine	0.560		38.400	21.504
Palladium diacetate	0.012		180.000	2.160
Tri-tert-butylphosphonate		0.232	7.450	1.728
Potassium Tert-butoxide	0.339		0.396	0.134
Toluene		100.00	0.041	4.100
Silica gel	50.00		0.292	14.600

Petroleum ether		200.00	0.119	23.700
Ethyl acetate		100.00	0.063	6.250
Total cost	241.318 RMB			
Amount PDO1	0.560 g			
COST for PDO1	430.920 RMB/g			
Exchange rate	1\$=6.930 RMB			

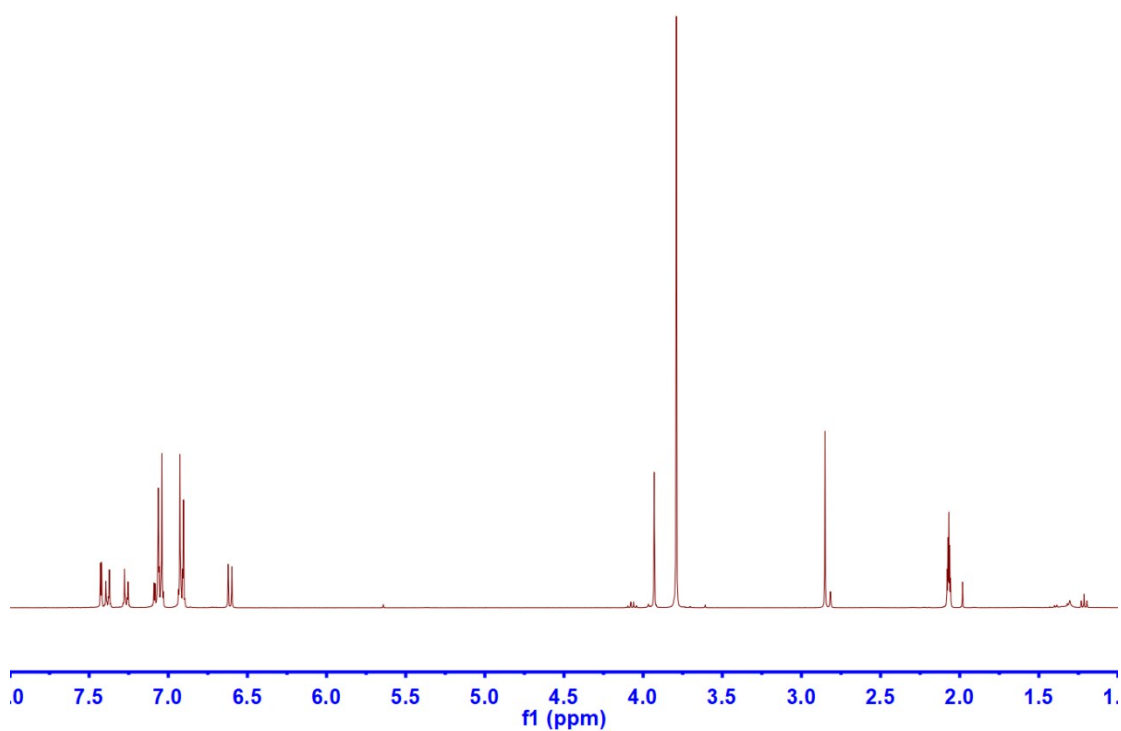


Figure S1. ¹H-NMR spectrum of PDO1 recorded in acetone

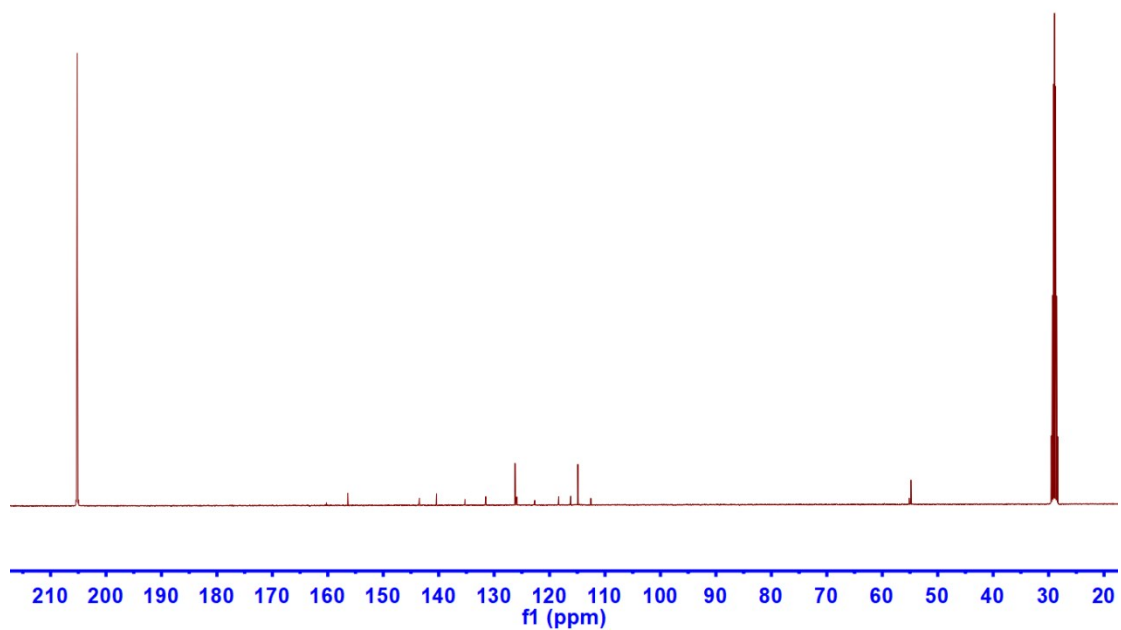


Figure S2. ^{13}C -NMR spectrum of PDO1 recorded in acetone

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yx180531-4 576 (9.585) Cm (576:577-105:129)

TOF MS EI+
662

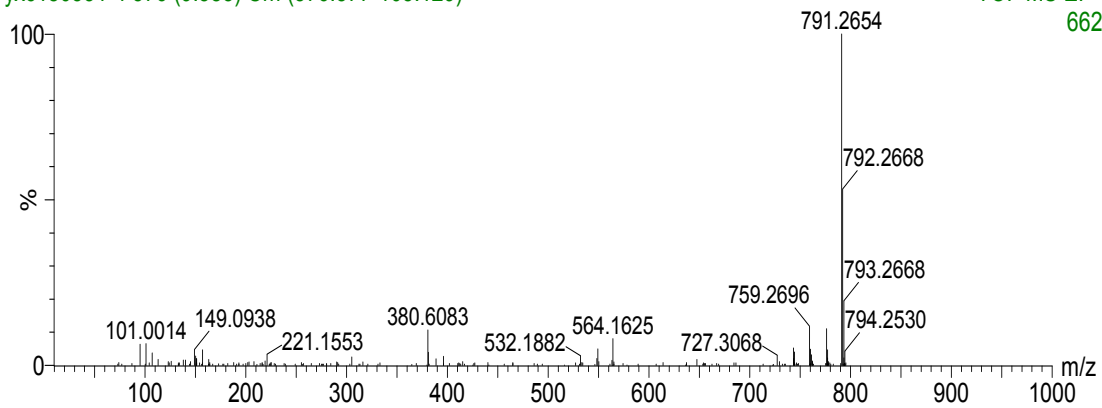
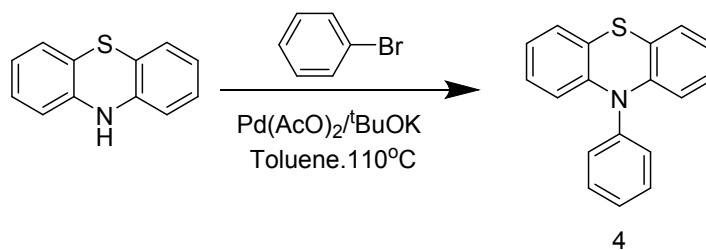


Figure S3 HR-MS of PDO1

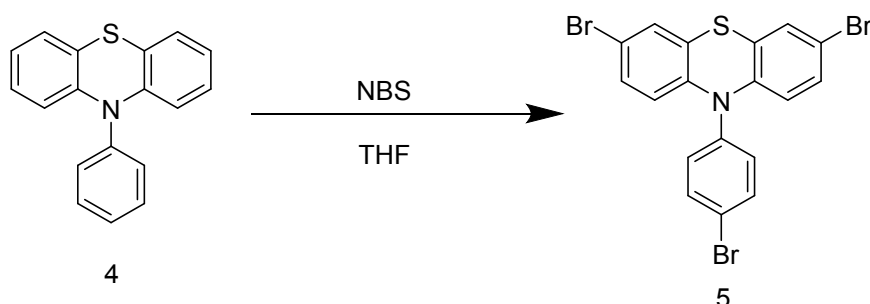


10-phenyl-10H-phenothiazine (4). A mixture of phenothiazine (5g, 25.00mmol) bromobenzene (4.137 g, 26.25 mmol), catalyst palladium acetate (0.300 g, 1.25 mmol), tri-tert-butylphosphine (5.000 g, 2.50 mmol) and tert-butyl Potassium alkoxide (8.475 g, 75.00 mmol) in toluene (100 mL) was stirred at 110 °C for 24 h. After cooling down the reaction to room temperature, the mixture was diluted with dichloromethane and washed with water. The organic layer was collected and evaporated under reduced pressure. The crude product was purified by column chromatography (petroleum ether/dichloromethane = 10:1 vol/vol) to obtain **4** (5.300 g, yield: 77.0%) as an off-white solid. ¹H-NMR (400 MHz, CDCl₃) δ 7.62 (d, J = 16.8 Hz, 2H), 7.47 (t, J = 7.4 Hz, 1H), 7.39 (d, J = 7.1 Hz, 2H), 7.01 (t, J = 8.4 Hz, 3H), 6.95 – 6.73 (m, 3H), 6.30 – 6.10 (m, 2H) ppm. HR-MS: calculated: C₁₈H₁₃NS, 275.0769, found: 275.0781.

Table S5 Synthesis cost of intermediate **4**

Reagent	Amount /g	Amount /ml	Price(RMB/g orRMB/mL)	Total price(RMB)
Phenothiazine	5.000		0.316	1.580
Bromobenzene	4.137		0.216	0.932
Palladium diacetate	0.300		180.000	54.00
Tri-tert-butylphosphonate		5.80	7.450	43.210
Potassium Tert-butoxide	8.475		0.396	3.356
Toluene		100.00	0.041	4.100
Silica gel	200.00		0.292	58.400
Petroleum ether		1000.00	0.119	118.500
Dichloromethane		100.00	0.182	18.170

Ethyl acetate		50.00	0.063	3.125
Total cost	305.373 RMB			
Amount intermediate 4	5.300 g			
COST for intermediate 4	57.618 RMB/g			
Exchange rate	1\$=6.930 RMB			

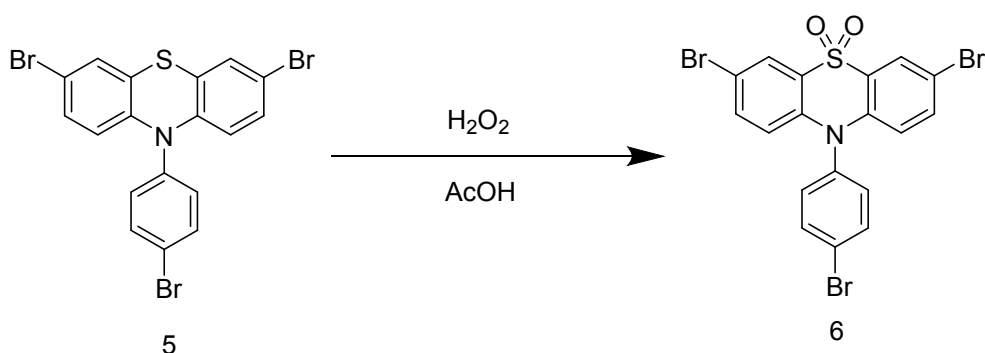


3,7-dibromo-10-(4-bromophenyl)-10H-phenothiazine (5). *N*-Bromo-succinimide (11.000 g, 61.70 mmol) was added in small portions to a solution of **4** (5.300 g, 19.30 mmol) in THF (100 mL) and the obtained mixture was stirred for 6h at 0-5 °C. The reaction mixture was then poured into water and the obtained solid was filtered, washed with water and dried under vacuum. The collected crude product was purified by elution through a short silica plug (petroleum ether/dichloromethane = 2:1 vol/vol) to obtain **5** (4.500 g, yield: 45.6%) as a white solid. ¹H-NMR (400 MHz, CDCl₃) δ 7.80 – 7.66 (m, 2H), 7.26 – 7.16 (m, 2H), 7.11 (d, J = 2.3 Hz, 2H), 6.94 (dd, J = 8.8, 2.3 Hz, 2H), 6.02 (d, J = 8.8 Hz, 2H). HR-MS: calculated: C₁₈H₁₀Br₃NS, 508.8084, found: 510.8071.

Table S6 Synthesis cost of intermediate **5**

Reagent	Amount /g	Amount /ml	Price(RMB/g or RMB/mL)	Total price(RMB)
4	5.300		57.618	305.373
THF		100.00	0.063	6.250
NBS	11.000		0.395	4.345

Silica gel	150.000		0.292	43.800
Petroleum ether		400.00	0.119	47.400
Dichloromethane		200.00	0.188	36.340
Total cost	443.508 RMB			
Amount intermediate 5	4.500 g			
COST for intermediate 5	98.557 RMB/g			
Exchange rate	1\$=6.930 RMB			

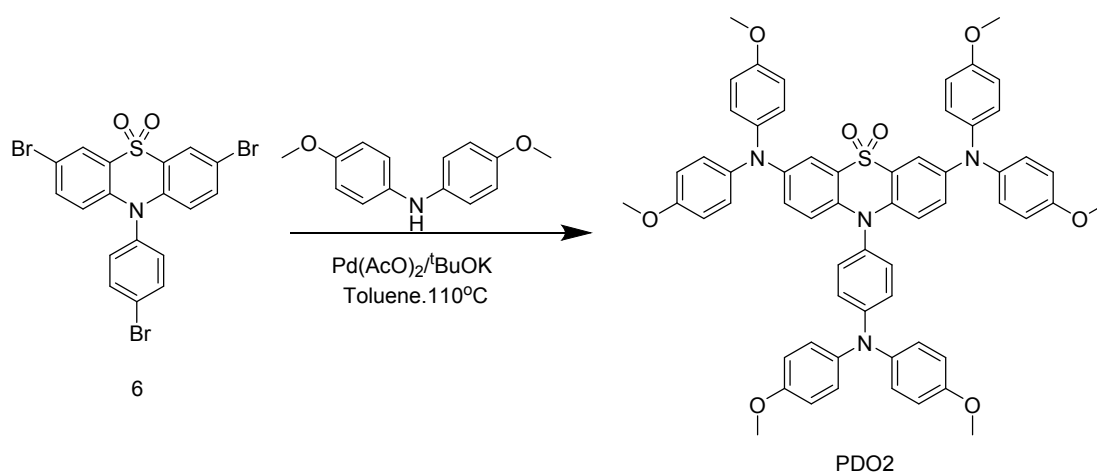


3,7-dibromo-10-(4-bromophenyl)-10H-phenothiazine 5,5-dioxide (6). hydrogen peroxide (25 mL) was slow added in small portions to a solution of **5** (2.27 g, 4.44 mmol) in acetic acid (50 mL) and the obtained mixture was stirred for 6h at 120-130°C, After cooling down the reaction to room temperature, the mixture was washed with water several times, The organic layer was collected and evaporated reduced pressure. The collected crude product was purified by elution through a short silica plug (petroleum ether/dichloromethane = 1:1 vol/vol) to obtain **6** (2.8 g, yield: 96.5%) as a yellow solid. ¹H-NMR (400 MHz, CDCl₃) δ 8.25 (d, J = 2.3 Hz, 2H), 7.89 – 7.83 (m, 2H), 7.49 (dd, J = 9.1, 2.3 Hz, 2H), 7.30 – 7.23 (m, 2H), 6.52 (d, J = 9.1 Hz, 2H). HR-MS: calculated: C₁₈H₁₀Br₃NS, 540.7982, found: 544.7947.

Table S7 Synthesis cost of intermediate 6

Reagent	Amount /g	Amount /ml	Price(RMB/g or RMB/mL)	Total price(RMB)
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5	2.270		98.557	223.725
H ₂ O ₂		25.00	0.030	0.750
AcOH		100.00	0.069	6.850
Silica gel	100.00		0.292	29.200
Petroleum ether		350.00	0.119	41.475
Dichloromethane		350.00	0.182	63.595
Total cost	365.595 RMB			
Amount intermediate 6	2.800 g			
COST for intermediate 6	130.569 RMB/g			
Exchange rate	1\$=6.930 RMB			



3,7-bis(bis(4-methoxyphenyl)amino)-10-(4-(bis(4-methoxyphenyl)amino)phenyl)-10H-phthalazine 5,5-dioxide (PDO2). A mixture of **6** (1.210 g, 2.20 mmol), 4,4-Dimethoxydiphenylamine (1.690 g, 7.40 mmol), palladium acetate (0.026 g, 0.11 mmol), tertiary butyl phosphine (0.445 g, 0.22 mmol) and potassium tertiary butanol (0.746 g, 6.60 mmol) in toluene (100 mL) was stirred at 110°C for 24 h. After cooling down the reaction to room temperature, the mixture was diluted with dichloromethane and washed with water. The organic layer was collected and evaporated reduced

pressure. The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 2:1 vol/vol) to obtain PDO2 (0.94 g, yield: 43.2%) as a yellow solid. ¹H-NMR (400 MHz, CDCl₃) δ 7.26 (s, 2H), 7.19 – 7.10 (m, 5H), 7.04 (dd, J = 17.4, 8.6 Hz, 12H), 6.92 – 6.85 (m, 5H), 6.81 (s, 8H), 6.59 (s, 2H), 3.89 – 3.66 (m, 18H) ppm. ¹³C-NMR (101 MHz, CDCl₃): 156.69, 156.59, 154.01, 149.52, 148.30, 139.99, 137.84, 133.10, 128.87, 127.41, 126.99, 126.63, 126.00, 124.61, 122.05, 121.50, 120.35, 119.26, 118.21, 116.68, 115.02, 106.07, 77.37, 77.25, 77.05, 76.73, 73.25, 55.52, 55.50, 31.92, 31.45, 30.23, 29.69, 29.35, 22.68, 14.21, 14.11 ppm. HR-MS: calculated: C₆₀H₅₂N₄O₈S, 988.3506, found [M+H]:989.3552.

Table S8 Synthesis cost of PDO2

Reagent	Amount /g	Amount /ml	Price(RMB/g or RMB/mL)	Total price(RMB)
6	1.210		130.569	157.989
4,4-Dimethoxydiphenylamine	1.690		38.400	64.896
Palladium diacetate	0.026		180.000	4.752
Tri-tert-butylphosphonate		5.10	7.450	38.025
Potassium tert-butoxide	0.746		0.396	0.295
Toluene		100.00	0.041	41.000
Silica gel	100.00		0.292	29.200
Petroleum ether		400.00	0.119	47.400
Ethyl acetate		250.00	0.063	15.625
Total cost	399.182 RMB			
Amount PDO2	0.940 g			
COST for PDO2	424.662 RMB/g			
Exchange rate	1\$=6.930 RMB			

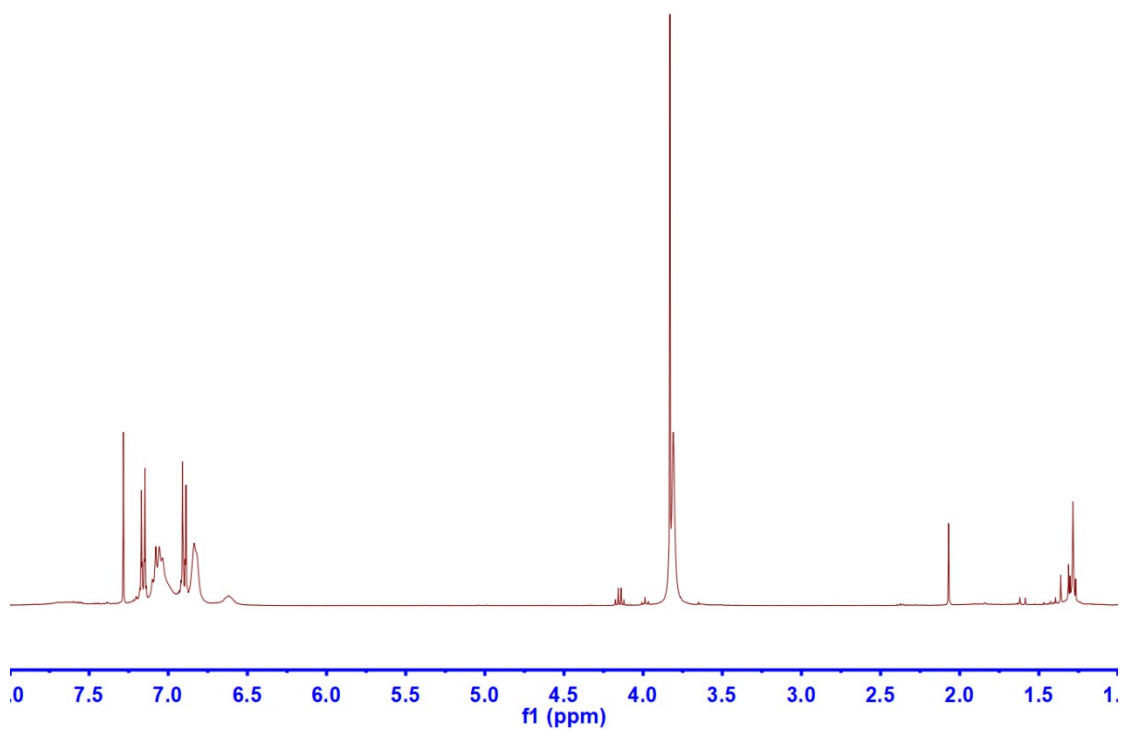


Figure S4. ^1H -NMR spectrum of PDO2 recorded in CDCl_3

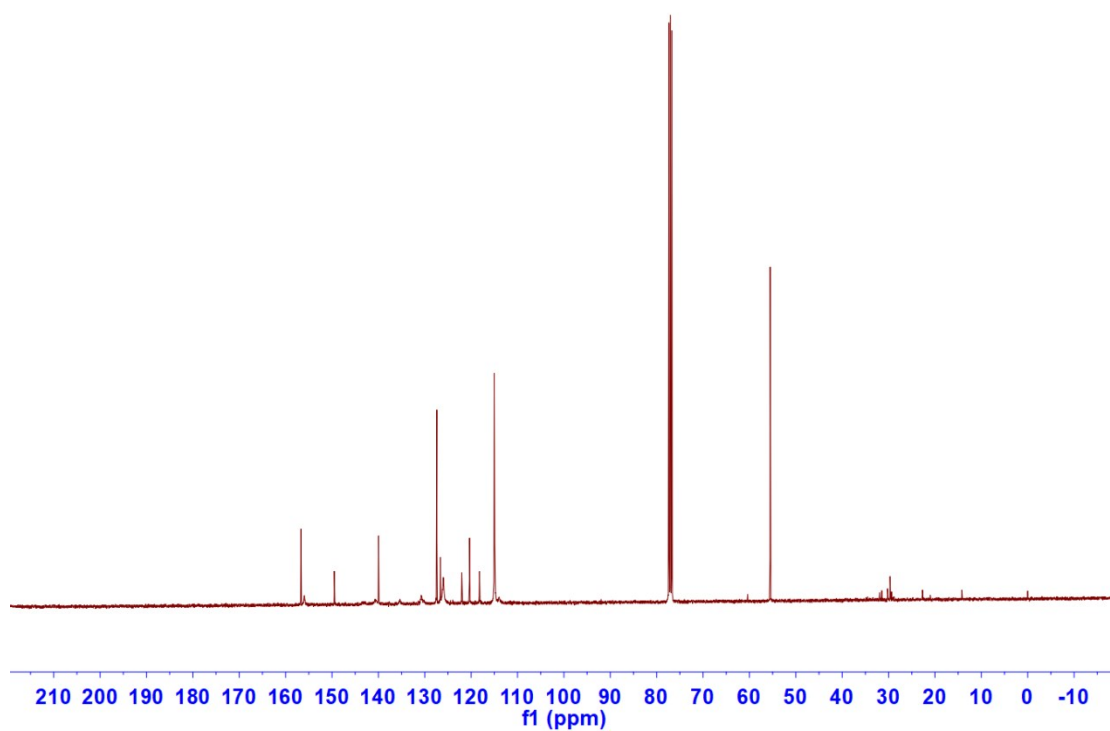


Figure S5. ^{13}C -NMR spectrum of PDO2 recorded in CDCl_3

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T: FTMS + p ESI Full ms [200.00-1200.00]

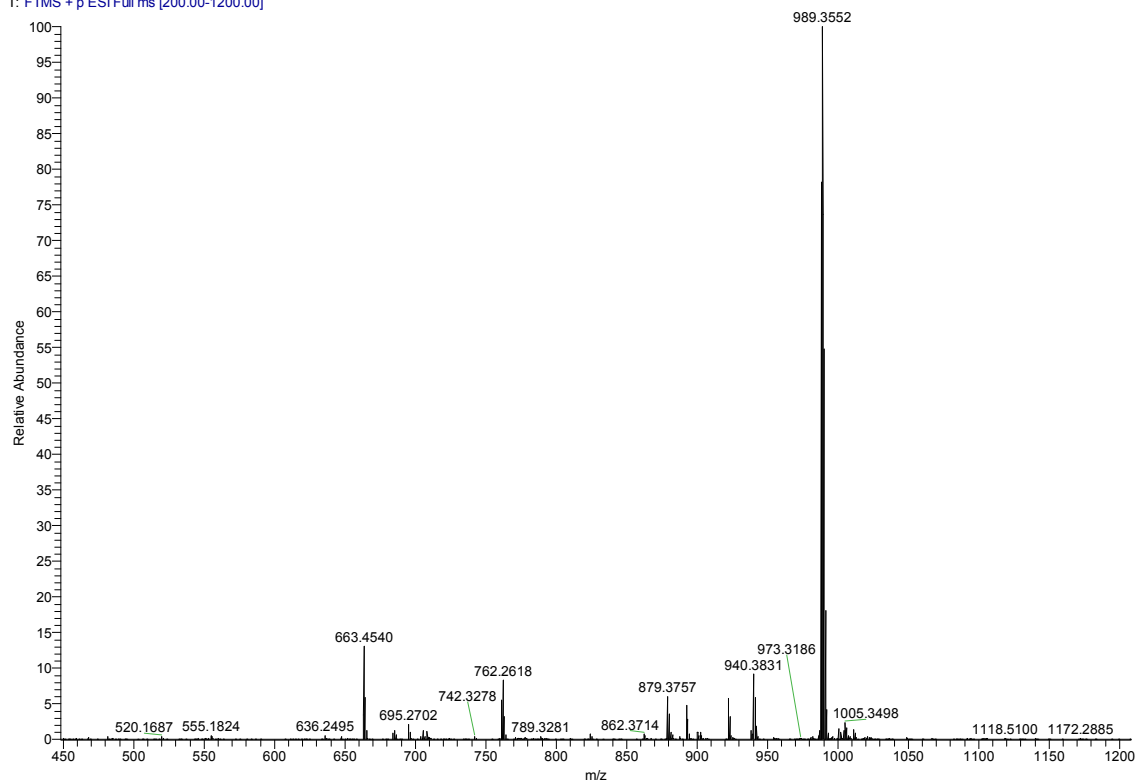


Figure S6 HR-MS of PDO2

Computational Details

In the simulation for this publication optimization and single point energy calculations are performed using the B3LYP and the 6-31G* basis set for all atoms, without any symmetry constraints. All reported calculations were carried out by means of Gaussian 09.

Measurement

The absorption spectra were recorded on an Agilent 8453 spectrophotometer using a 1 cm cuvette. Cyclic voltammetry (CV) was performed in dichloromethane with 0.1 M TBAPF₆ as the supporting electrolyte, a Ag⁺/AgNO₃ electrode as the reference electrode, a carbon-glass electrode as the working electrode, a Pt electrode as the counter electrode and ferrocene/ferrocenium (*Fc/Fc*⁺) as an internal reference with a Zahner electrochemical workstation. The SEM images were taken on a JEOL JSM-7800. Light source for the photocurrent-voltage (*J-V*) measurement is an AM 1.5G solar simulator. The incident light intensity was 100 mW·cm⁻² calibrated with a standard Si solar cell. The tested solar cells were masked to a working area of 0.126

cm². The photocurrent-voltage (J - V) curves were obtained by the linear sweep voltammetry (LSV) method using a Keithley 2400 source-measure unit. The measurement of the incident-photon-to-current conversion efficiency (IPCE) was performed with CEL-QPCE3000 photoelectric chemical quantum efficiency testing and analysis system. For the steady-state PL decay, the excitation wavelength is 438 nm. NMR spectra were recorded on a Bruker AVANCE 400 MHz spectrometer. Hole mobility was measured by using the space-charge-limited current (SCLC) method with the device structure of FTO/PEDOT:PSS/HTM/Au. Two devices (eight groups of data) are tested and the data shown in Figure is an average data. Space-charge-limited current can be described by equation below:

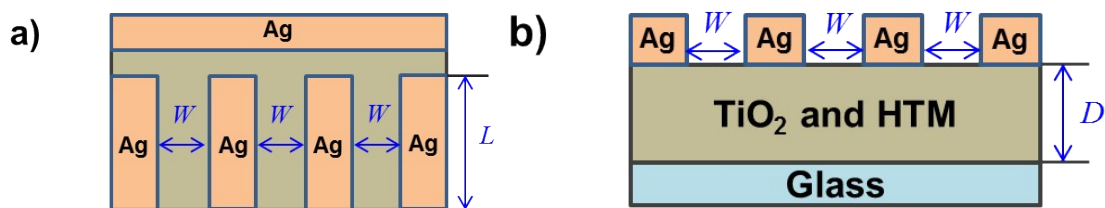
$$J = \frac{9}{8} \mu \epsilon_0 \epsilon_r \frac{V^2}{D^3}$$

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

For conductivity, two devices (six groups of data) are tested and the data shown in Figure is also an average data. The electrical conductivities of the HTM films were determined by using two-probe electrical conductivity measurements. The electrical conductivity (σ) was calculated by using the following equation:

$$\sigma = \frac{W}{R L D}$$

where L is the channel length 10 mm, W is the channel width 2 mm, D is the film thickness of the TiO₂ and HTM, and R is the film resistance calculated from the gradients of the curves.



Scheme S1 Schematic illustrations of the conductivity device: (a) top-sectional view;
(b) cross-sectional view

Single crystal X-ray diffraction data of PDO1 and PDO2 were collected on a Rigaku XtaLAB PRO 007HF(Mo) diffractometer with Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$), at 180 K and 290 K respectively. Data reduction and empirical absorption correction were performed using the CrysAlisPro program. The structure was solved by a dual-space algorithm using SHELXT program. All non-hydrogen atoms could be located directly from the difference Fourier maps. Framework hydrogen atoms were placed geometrically and constrained using the riding model to the parent atoms. Final structure refinement was done using the SHELXL program by minimizing the sum of squared deviations of F^2 using a full-matrix technique.

Table S9 Crystal data and structure refinement for PDO1

Identification code	a_a
Empirical formula	$C_{20}H_{20}N_2O_{10}S_2$
Formula weight	512.50
Temperature/K	293(2)
Crystal system	monoclinic
Space group	C2/c
a/ \AA	40.4587(8)
b/ \AA	11.7583(2)
c/ \AA	17.7354(3)
$\alpha/^\circ$	90
$\beta/^\circ$	105.271(2)
$\gamma/^\circ$	90
Volume/ \AA^3	8139.3(3)
Z	16
$\rho_{\text{calc}}/\text{g/cm}^3$	1.673
μ/mm^{-1}	0.328
F(000)	4256.0
Crystal size/ mm^3	? \times ? \times ?

Radiation	MoK α ($\lambda = 0.71073$)
2 Θ range for data collection/ $^{\circ}$	4.174 to 50.052
Index ranges	$-43 \leq h \leq 48$, $-13 \leq k \leq 13$, $-21 \leq l \leq 21$
Reflections collected	24108
Independent reflections	7171 [$R_{\text{int}} = 0.0231$, $R_{\text{sigma}} = 0.0249$]
Data/restraints/parameters	7171/0/528
Goodness-of-fit on F^2	1.048
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0486$, $wR_2 = 0.1477$
Final R indexes [all data]	$R_1 = 0.0581$, $wR_2 = 0.1557$
Largest diff. peak/hole / e \AA^{-3}	1.53/-0.54

Table S10 Crystal data and structure refinement for PDO2

Identification code	i2a_a
Empirical formula	$\text{C}_{60}\text{H}_{52}\text{N}_4\text{O}_8\text{S}$
Formula weight	989.12
Temperature/K	298
Crystal system	monoclinic
Space group	I2/a
a/ \AA	12.9140(7)
b/ \AA	22.0318(14)
c/ \AA	17.9982(14)
$\alpha/^{\circ}$	90.00
$\beta/^{\circ}$	97.635(6)
$\gamma/^{\circ}$	90.00
Volume/ \AA^3	5075.4(6)
Z	4
$\rho_{\text{calc}}/\text{g/cm}^3$	1.294
μ/mm^{-1}	0.126
F(000)	2080.0
Crystal size/ mm^3	$0.1 \times 0.06 \times 0.05$
Radiation	MoK α ($\lambda = 0.71073$)
2 Θ range for data collection/ $^{\circ}$	7.1 to 50.06
Index ranges	$-14 \leq h \leq 15$, $-25 \leq k \leq 26$, $-21 \leq l \leq 14$
Reflections collected	14800
Independent reflections	4463 [$R_{\text{int}} = 0.0566$, $R_{\text{sigma}} = 0.0612$]
Data/restraints/parameters	4463/0/345
Goodness-of-fit on F^2	1.074
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0808$, $wR_2 = 0.2294$
Final R indexes [all data]	$R_1 = 0.1123$, $wR_2 = 0.2549$

Largest diff. peak/hole / e \AA^{-3} 0.66/-0.63

Perovskite Solar Cell Fabrication

The perovskite and hole-transport material solutions were prepared inside an Argon glovebox. Conducting $\text{SnO}_2:\text{F}$ glass substrates (Pilkington, TEC15) were cut (25 mm x 15 mm) and patterned by chemical etching using zinc powder and hydrochloric acid. The substrates were washed by sonication in deionized water, acetone and ethanol for 15 minutes each. A thin and dense layer of TiO_2 (bl- TiO_2) was applied on the glass using spray-pyrolysis at 500°C from a solution of 0.2 M titanium (IV) tetraisopropoxide (Aldrich) and 2 M acetylacetonate (Aldrich) in isopropanol (Aldrich). The 15% Tin Oxide colloid precursor was diluted to 2.67% by deionized water. And the solution was spun onto the glass/compact TiO_2 substrate surface at 3000 r.p.m for 30 s, and then baked on a hotplate in ambient atmosphere at 120°C for 20 min. To yield a $(\text{FAPbI}_3)_{0.85}(\text{MAPbBr}_3)_{0.15}$ perovskite solution we mixed PbI_2 (Xi'an Polymer Light Technology Corp.), FAI (Xi'an Polymer Light Technology Corp.), PbBr_2 (Xi'an Polymer Light Technology Corp.), MABr (Xi'an Polymer Light Technology Corp.) in molar concentrations of 1.1, 1, 0.2, 0.2, respectively, in 4:1 DMF:DMSO (anhydrous, Aldrich). The solutions were heated to dissolve the inorganic salts but otherwise kept at room temperature at all times. 75 μl of the perovskite solution spread onto the SnO_2 . The substrate was the spin-coated at 2000 rpm for 10 seconds and 6000 rpm for 30 seconds with a ramp speed of 2000 rpm/s. During the second spin-coating step an anti-solvent was injected onto the film after 15 seconds using 200 μl of chlorobenzene (anhydrous, Aldrich). The perovskite films were then annealed at 100°C for 30 minutes on a hotplate. Subsequently, the HTM layer was then spin coated on top of the perovskite film. The PDO1 and PDO2-based HTL was deposited by spin coating at 4000 rpm for 30 s with a chlorobenzene containing 40 mg PDO1 or PDO2, 30 mM LiTFSI and 200 mM TBP. Finally, a layer of 100 nm Au was deposited sequentially under high vacuum ($<4 \times 10^{-4}$ Pa) by thermal evaporation through a shadow mask to

form an active area of $\sim 20 \text{ mm}^2$.

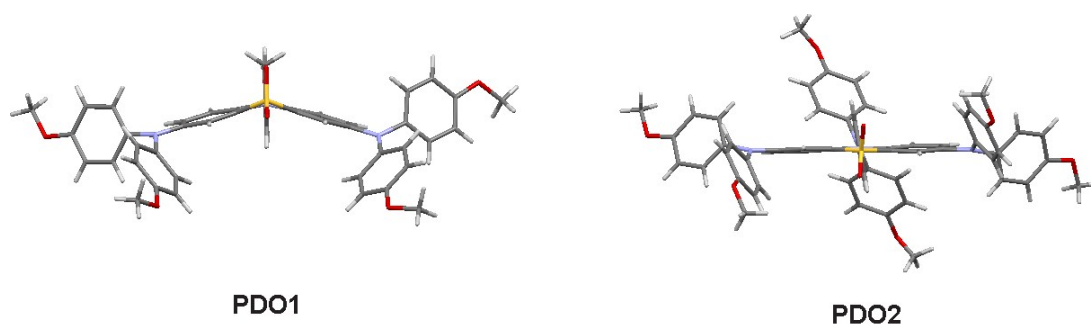


Figure S7 Top-view of PDO1 and PDO2 crystal structures

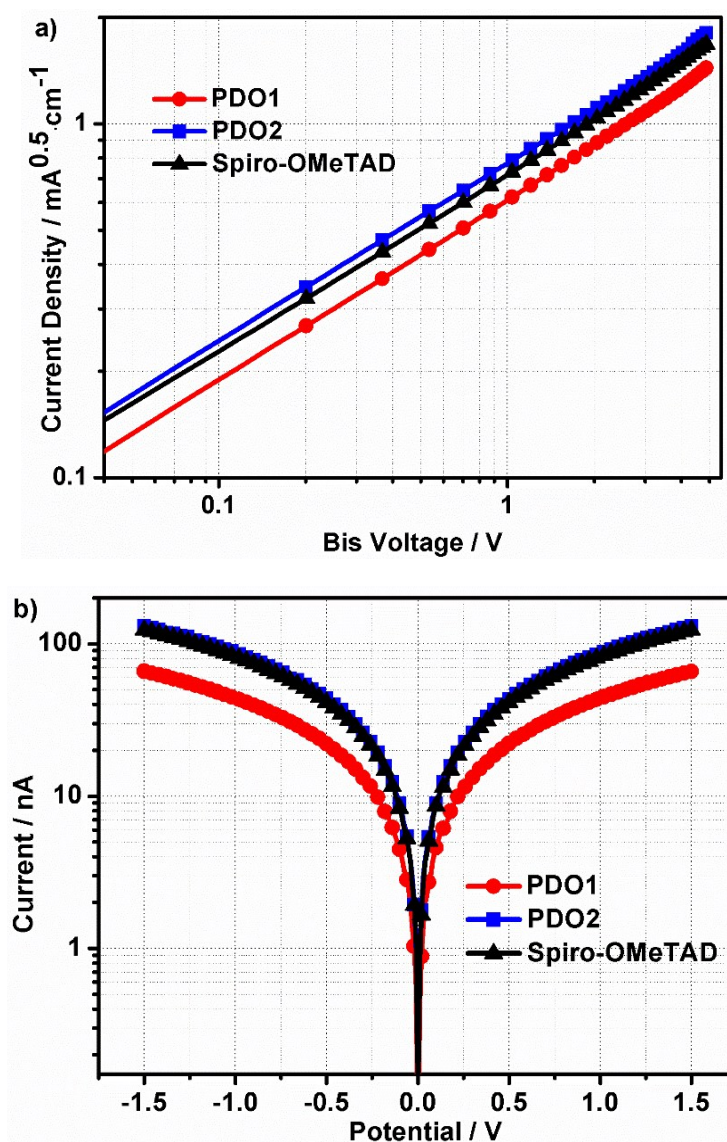


Figure S8 a) hole mobility test result of PDO1, PDO2 and Spiro-OMeTAD, b)

Conductivity of PDO1, PDO2 and Spiro-OMeTAD

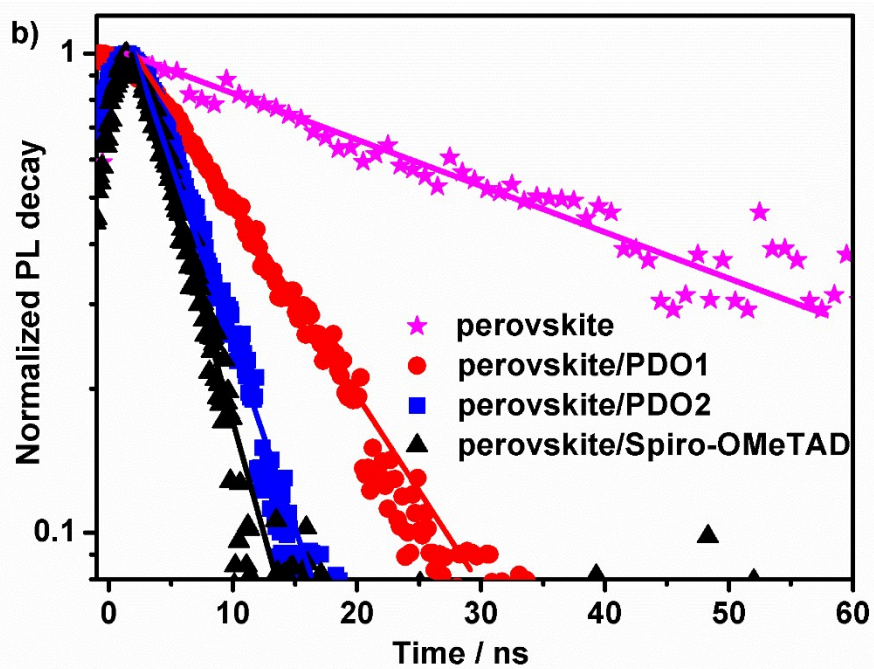
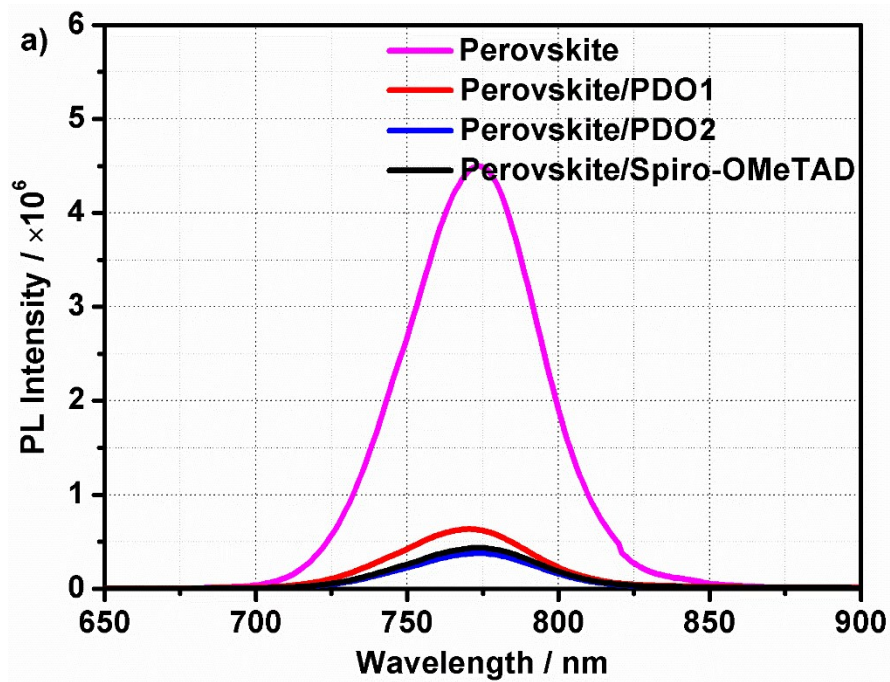


Figure S9 Steady-state PL decay of perovskite, perovskite/PDO1 and perovskite/PDO2 systems

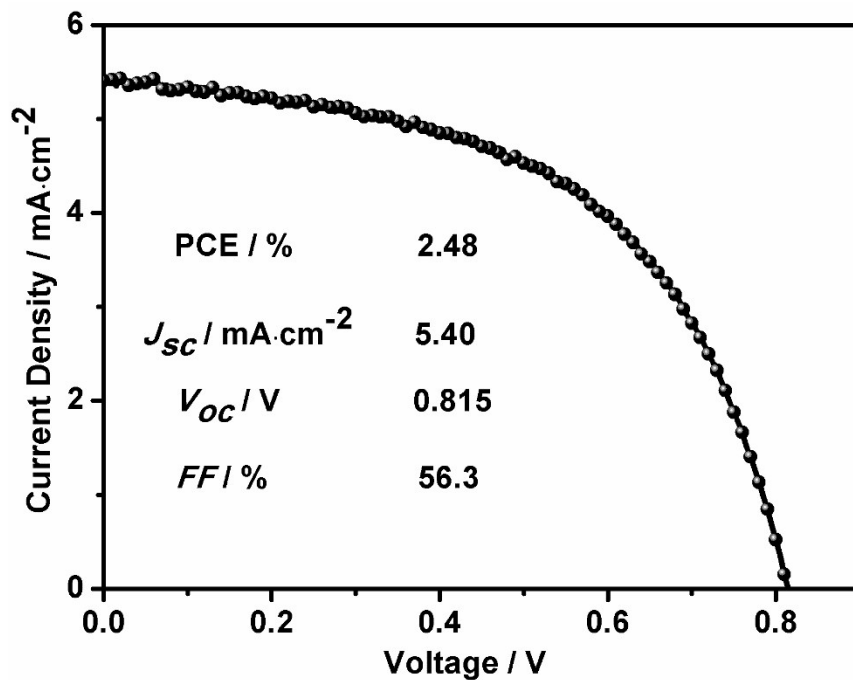


Figure S10 J - V characteristic curves of the PSCs containing PTZ1 as HTM

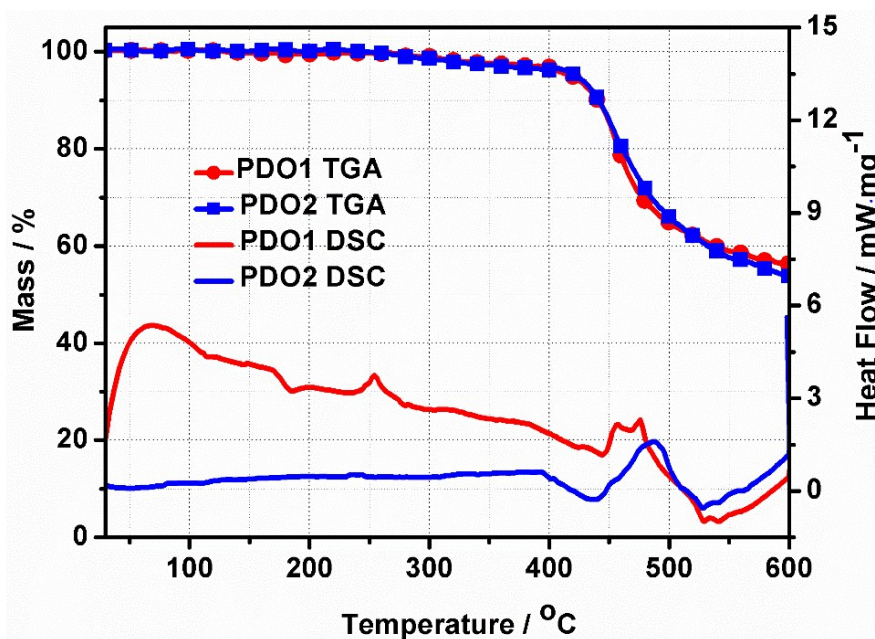


Figure S11 Thermogravimetric analysis and DSC heating traces of PDO1 and PDO2 measured with a heating rate of 10 °C min⁻¹ under nitrogen atmosphere.