

Electronic Supplementary Material

Arm modulation of triarylamine to fine-tune the properties of linear D- π -D HTMs for robust higher performance perovskite solar cells

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1. Base Characterization

1.1 NMR, UV-vis and fluorescence.

^1H NMR and ^{13}C NMR spectra were recorded with a Bruker-400MHz spectrometer. The absorption spectra of the solution of **M140-141** (dissolve in DCM) were measured by a SHIMADZU UV-2600 spectrophotometer. Same samples of fluorescence measurements were obtained on a HITACHI F-4500 fluorescence spectrophotometer.

1.2 DPV, DSC and TGA measurements

Differential pulse voltammetric (DPV) of **M140-141** were measured on a CHI660D electrochemical workstation, with a platinum electrode (counter electrode), Ag/AgCl electrode (reference electrode) and a glassy carbon disk (working electrode) at a scan rate of 0.05 mV s^{-1} in DCM solution of containing 0.1 M of $n\text{-Bu}_4\text{NPF}_6$ and all potentials were reported against the ferrocene/ferrocenium (Fc/Fc^+) reference. Differential scanning calorimetry (DSC) was conducted on NETZSCH DSC 200 F3 differential scanning calorimeter at heating rate of $10\text{ }^\circ\text{C min}^{-1}$ under nitrogen atmosphere within temperature range of $20\text{ }^\circ\text{C}$ to $300\text{ }^\circ\text{C}$. Thermogravimetric analysis (TGA) was conducted on NETZSCH TG209F3 thermogravimetric apparatus within temperature range of $40\text{ }^\circ\text{C}$ to $600\text{ }^\circ\text{C}$ at heating rate of $10\text{ }^\circ\text{C min}^{-1}$.

1.3 Mobility Measurements

Hole mobilities of **M140-141** were measured by the space-charge-limited-current (SCLC) method with a device structure of ITO/PEDOT:PSS/HTMs/Ag. PEDOT:PSS was spin-coated onto the ITO substrates and then annealed on a hotplate at $120\text{ }^\circ\text{C}$ for 30 min. Then, doped **M140-141** (30 mM in anhydrous chlorobenzene) was deposited

via spin-coating at 2000 rpm for 20 s. Finally, a 80 nm thick Ag back contact was deposited onto the HTM layer. The thicknesses of the HTMs were measured by using a Dektak profilometer. Devices were measured in the dark under bias from 0 V to 5 V using a CHI660D electrochemical workstation. The classic Mott-Gurney equation (1) was used to determine the mobility.

$$J = 9\mu\epsilon_0\epsilon_r V^2 / (8d^3) \quad (1)$$

Here, J is the current density, ϵ_r is the average dielectric constant of the film (normally taken to approach 3 for organic semiconductors), ϵ_0 is the permittivity of the free space (8.85×10^{-12} F/m), μ is the carrier mobility, d is the thickness of the film, and V is the applied voltage.

1.4 Conductivity Measurements

The conductivities of doped **M140-141** were determined by a two-contact electrical conductivity set-up. **M140-141** films were prepared by spin-coating a chlorobenzene solution onto ITO glass substrate via a spin speed of 1000 rpm for 20 s at room temperature. Then, 80 nm thick Ag back contact was deposited by thermal evaporation. The thicknesses of the HTMs were measured by using a Dektak profilometer. The following equation (2) was used to determine the conductivity.

$$\sigma = d / (RS) \quad (2)$$

Here, S is the area of metal mask, R is the area of resistance, d is the thickness of HTM film.

2. Device Fabrication

2.1 Materials

FAI, MABr, and FK209 were purchased from Dyesol. Indium tin oxide (ITO) coated glass, PbI_2 (99.999%), PbBr_2 (99.999%) and thiocarbamide were purchased from TCI. Spiro-OMeTAD (99.5%) and PEDOT:PSS (Heraeus, Clevios PVP Al 4083) were purchased from p-OLED (China). Lithiumbis-(trifluoromethylsulfonyl)imide (Li-TFSI, 99%), 4-(tert-Butyl)pyridine (TBP, 99%) and CsI (99%) were purchased from Energy Chemicals (China). $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (98%) was purchased from Alfa Aesar. Anhydrous DMSO (99.8%), DMF (99.8%) and chlorobenzene (99.8%) were purchased from Sigma Aldrich.

2.2 Devices Fabrication

We fabricated n-i-p PSCs with a structure of ITO/ SnO_2 / $\text{Cs}_{0.05}(\text{FA}_{0.83}\text{MA}_{0.17})_{0.95}\text{Pb}(\text{Br}_{0.17}\text{I}_{0.83})_3$ /HTMs/Au to measure the photovoltaic performance of PSCs. The ITO substrates were etched by diluted HCl solution and little of zinc powder. Then ultrasonic cleaning 15 min in detergent, deionized water acetone and ethanol, respectively. After drying with hot air, the glass was further cleaned by UV-ozone for 30min.

SnO_2 QD electron transporting layer was prepared according the reported literature [1]. The precursor solution of SnO_2 QD was spin-coated onto the substrate at a speed of 1000 rpm for 3 s and then 3200 rpm for 20 s. Then the substrates were annealed under ambient atmosphere at 170 °C for 1 h. After the film was cooled to room temperature, the glass was further cleaned by UV-ozone for 15 min. Then KCl aqueous solution (1 mg mL^{-1}) was spin-coated onto the substrate at a speed of 1000 rpm for 3 s and then 5400 rpm for 20 s.

The preparation method is: 1.30 M PbI₂, 1.19 M FAI, 0.14 M PbBr₂, 0.14 M MABr, and 0.07 M CsI were weighed in a bottle, then quickly transferred to the glove box. Under a nitrogen atmosphere in the glove box, add a mixed solvent with a volume ratio of DMF: DMSO = 4:1. This resulting solution was stirred at 60 °C for 30 min to form (FAPbI₃)_{0.875}(MAPbBr₃)_{0.075}(CsPbI₃)_{0.05}(PbI₂)_{0.03}. The perovskite film was deposited through a two-step spin-coating program (1000 rpm for 10 s and 6000 rpm for 20 s) with dripping of 110 μL chlorobenzene as anti-solvent at the time of 6 s prior to the program end. All the perovskite samples were thermally annealed at 100 °C for 1 h. **M130** (40 mM), **M140** (30 mM), **M141** (30 mM) or *spiro-OMeTAD* (60 mM) in chlorobenzene was spin-coated at 4000 rpm for 20 s to yield films. The hole-transporters were doped with TFSI, *t*-BP and FK209 in a molar ratio of 0.5, 3.3 and 0.03, respectively. In the case of dopant-free PSCs, the concentration of M140-141 was reduced to 25 mg mL⁻¹, and all the dopant-free samples were thermally annealed at 50 °C for 10 min. Finally, 80 nm of gold was then evaporated onto the active layer under high vacuum (less than 10⁻⁴ mbar).

3. Photovoltaic Performance Characterizations

Current-voltage characteristics were measured under 100 mW cm⁻² (AM 1.5 G illumination) using a Newport solar simulator (Keithley 2400). A monocrystalline silicon reference cell (Oriel P/N 91150 V, with KG-5 visible color filter) was used to calibrate the light source for an intensity of 100 mW cm⁻². The cells were masked with a black metal mask limiting the active area to 0.09 cm² and reducing the influence of the scattered light. Incident photon-to-current conversion efficiency (IPCE) spectra

were recorded using a computer-controlled setup consisting of a Xenon light source (Spectral Products ASB-XE-175), a monochromator (Spectra Products CM110), and a potentiostat (LabJack U6 DAQ board), calibrated by a certified reference solar cell (Fraunhofer ISE).

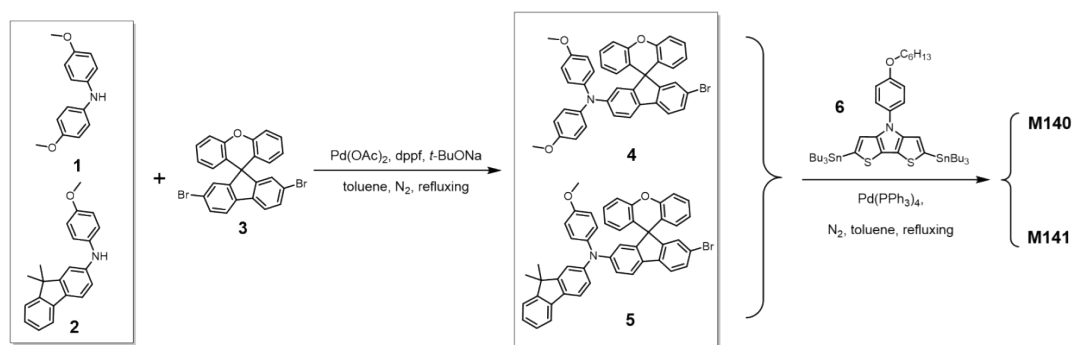
4. Computational Details

In the simulation, optimization and single point energy calculations are performed using the cam-B3LYP₃ and the 6-31G** basis set for all atoms, without any symmetry constraints. All reported calculations were carried out by means of Gaussian 09.

5. Synthesis of HTMs

5.1 Material

Materials were all available commercially and used without further purification if not mentioned specially. Bis(4-methoxyphenyl)amine^[2] (compound **1**), N-(4-methoxyphenyl)-9,9-dimethyl-9H-fluorene-2-amine^[3] (compound **2**), 2,7-dibromospiro[fluorene-9,9'-xanthene]^[4] (compound **3**) and compound **6**^[5] were synthesized according to reported literatures.



Scheme S1. Synthesis routes of the HTMs **M140-141**.

5.2 Synthetic Procedures

Synthesis of 4

To a 100 mL two-neck round bottom flask was charged with compound **1** (500 mg, 2.18 mmol), compound **3** (2138 mg, 4.36 mmol), Pd(OAc)₂ (9.8 mg, 0.044 mmol), dppf (48.3 mg, 0.087 mmol), *t*-BuONa (335 mg, 3.49 mmol) and toluene (50 mL). The reaction mixture was refluxed 8 hours under nitrogen before cooled to room temperature. The mixture was then poured into water and extracted with ethyl acetate. The combined organic layer was dried with anhydrous Na₂SO₄ and evaporated to dryness. The residue was purified by silica gel column chromatography with DCM/PE (1:3 by volume) to give compound **4** as a yellow solid (863 mg, 62%).

Synthesis of 5

A mixture of compound **2** (687 mg, 2.18 mmol), compound **3** (2138 mg, 4.36 mmol), Pd(OAc)₂ (9.8 mg, 0.044 mmol), dppf (48.3 mg, 0.087 mmol) and *t*-BuONa (335 mg, 3.49 mmol) in toluene (50 mL) was heated to reflux for 8 hours under a nitrogen atmosphere. After cooling, the raw product was extracted using ethyl acetate. The organic layers were combined and dried by anhydrous Na₂SO₄. Then the solvent was removed under reduced pressure and the residue was purified by chromatography on a silica gel column with DCM/PE (1:3 by volume) to give compound **5** as yellow solid (899 mg, 57%). ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.87 (d, *J* = 8.4 Hz, 1H), 7.82 (d, *J* = 8.2 Hz, 1H), 7.66 (d, *J* = 6.9 Hz, 1H), 7.59 (d, *J* = 8.2 Hz, 1H), 7.55 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.45 (d, *J* = 7.1 Hz, 1H), 7.30 – 7.21 (m, 4H), 7.18 (d, *J* = 8.1 Hz, 2H), 7.09 (s, 2H), 7.02 (d, *J* = 8.9 Hz, 2H), 6.96 – 6.86 (m, 5H), 6.75 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.68 (d, *J* = 2.1 Hz, 1H), 6.44 (dd, *J* = 7.8, 1.3 Hz, 2H), 3.74 (s, 3H), 1.13 (s, 6H).

HRMS (ESI) calcd for $C_{47}H_{34}BrNO_2$ ($M+H^+$): 723.1173; found: 723.1179.

Synthesis of M140

A mixture of $Pd(PPh_3)_4$ (62 mg, 0.054 mmol), compound **4** (863 mg, 1.35 mmol) and compound **6** (2.49 g, 0.54 mmol) and toluene (30 mL) was stirred at 110 °C overnight under nitrogen before cooled to room temperature. The reaction mixture was then poured into water and extracted with ethyl acetate. The combined organic layer was dried with anhydrous Na_2SO_4 and evaporated to dryness. The crude product was purified by silica gel column chromatography, and a mixed solvent with a volume ratio of DCM/PE = 1/1 was used as an eluent to obtain the product as a yellow solid yield (556 mg, 73%). 1H NMR (400 MHz, CD_2Cl_2) δ 7.70 (d, $J = 7.9$ Hz, 2H), 7.61 (d, $J = 8.4$ Hz, 3H), 7.41 (d, $J = 8.8$ Hz, 2H), 7.32 (s, 2H), 7.22 (dtd, $J = 9.5, 8.2, 1.4$ Hz, 8H), 7.16 (s, 2H), 7.02 (d, $J = 8.9$ Hz, 2H), 6.94 (d, $J = 8.6$ Hz, 8H), 6.90 – 6.84 (m, 6H), 6.78 (s, 2H), 6.75 (d, $J = 8.9$ Hz, 8H), 6.58 (dd, $J = 7.8, 1.2$ Hz, 4H), 4.03 (t, $J = 6.6$ Hz, 2H), 3.77 (s, 12H), 1.88 – 1.79 (m, 2H), 1.41 (dd, $J = 7.2, 3.3$ Hz, 4H), 1.30 (s, 1H), 0.98 (t, $J = 6.9$ Hz, 3H), 0.92 (t, $J = 6.3$ Hz, 1H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 157.84, 156.36, 155.91, 155.69, 151.21, 149.26, 144.65, 142.29, 140.61, 139.05, 134.03, 131.85, 128.15, 127.84, 126.25, 125.14, 124.80, 123.26, 121.55, 120.42, 119.58, 117.39, 116.71, 115.45, 115.24, 114.46, 107.45, 68.43, 55.36, 54.11, 31.62, 29.22, 25.71, 22.67, 13.88. HRMS (ESI) calcd for $C_{98}H_{75}N_3O_7S_2$ ($M+H^+$): 1469.5046; found: 1469.5032.

Synthesis of M141

Synthesis process of **M141** refer to **M140**. Finally we got a light yellow solid (570

mg, 70%). ^1H NMR (400 MHz, CD_2Cl_2) δ 7.61 (d, $J = 8.7$ Hz, 2H), 7.44 (s, 2H), 7.33 (d, $J = 1.9$ Hz, 2H), 7.11 (d, $J = 8.9$ Hz, 8H), 7.06 (dd, $J = 8.7, 2.1$ Hz, 2H), 6.89 (d, $J = 8.9$ Hz, 8H), 4.50 (s, 4H), 3.83 (s, 12H), 1.59 (s, 8H), 1.46 (s, 1H), 1.30 (s, 3H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 157.84, 156.78, 156.35, 154.88, 153.50, 151.05, 148.78, 147.13, 144.67, 142.23, 140.41, 138.89, 134.28, 133.46, 132.77, 131.86, 130.95, 128.74, 128.13, 127.36, 126.87, 126.29, 125.14, 124.80, 124.41, 123.32, 122.41, 122.18, 121.61, 120.59, 120.37, 119.73, 119.19, 118.84, 117.22, 116.78, 115.35, 114.65, 107.52, 68.41, 65.51, 55.41, 46.59, 31.62, 30.56, 29.21, 26.83, 25.71, 22.67, 19.21, 13.89, 13.54. HRMS (ESI) calcd for $\text{C}_{114}\text{H}_{87}\text{N}_3\text{O}_5\text{S}_2$ ($\text{M}+\text{H}^+$): 1641.6087; found: 1641.6056.

6. ^1H NMR ^{13}C NMR spectra of HTMs

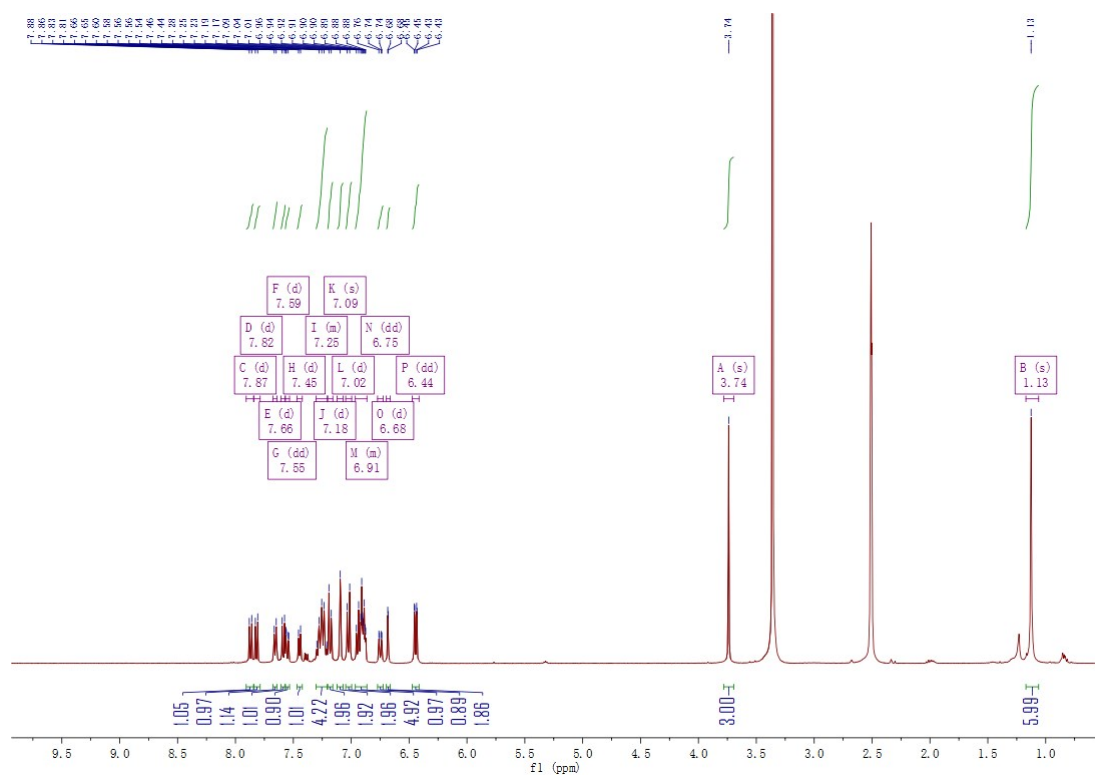


Figure S1. ^1H NMR ($\text{DMSO-}d_6$) spectrum of 5.

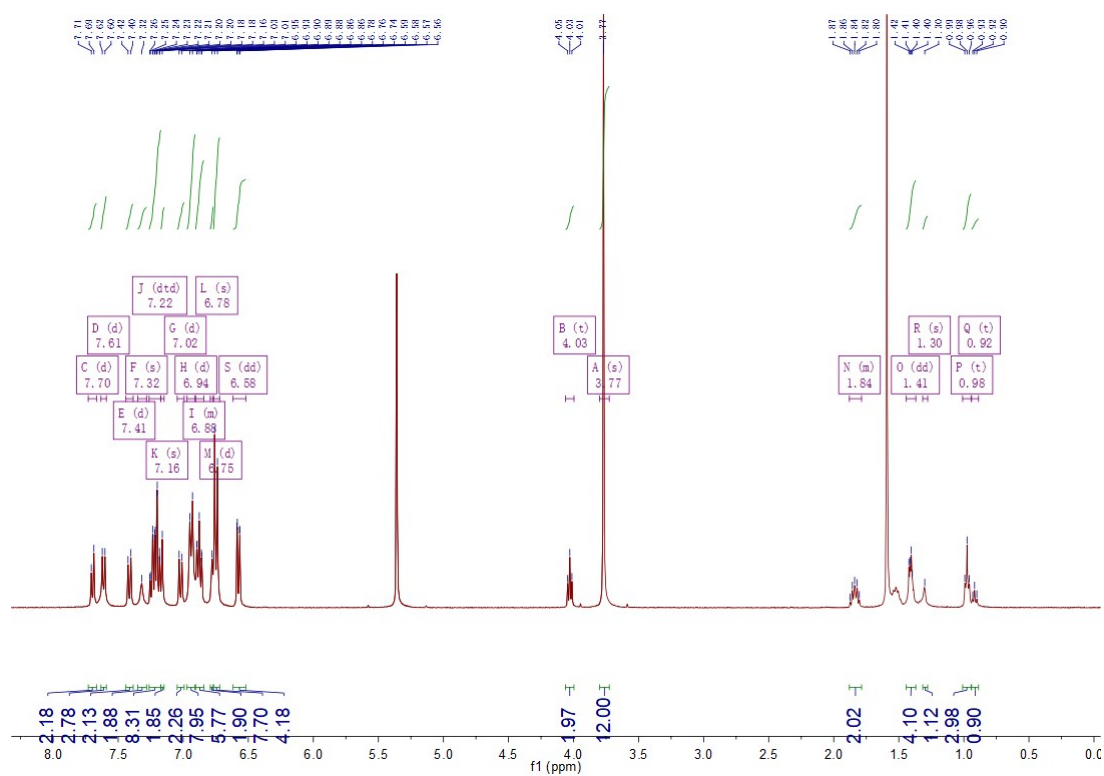


Figure S2. ^1H NMR (CD_2Cl_2) spectrum of **M140**.

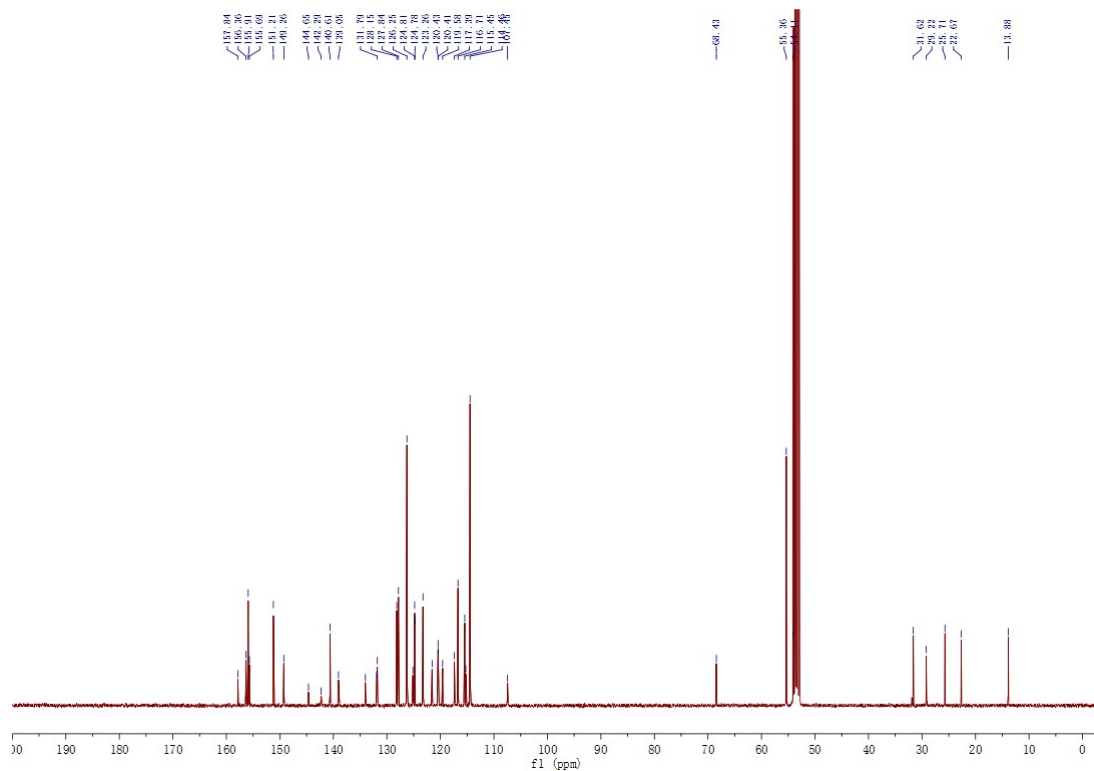


Figure S3. ^{13}C NMR (CD_2Cl_2) spectrum of **M140**.

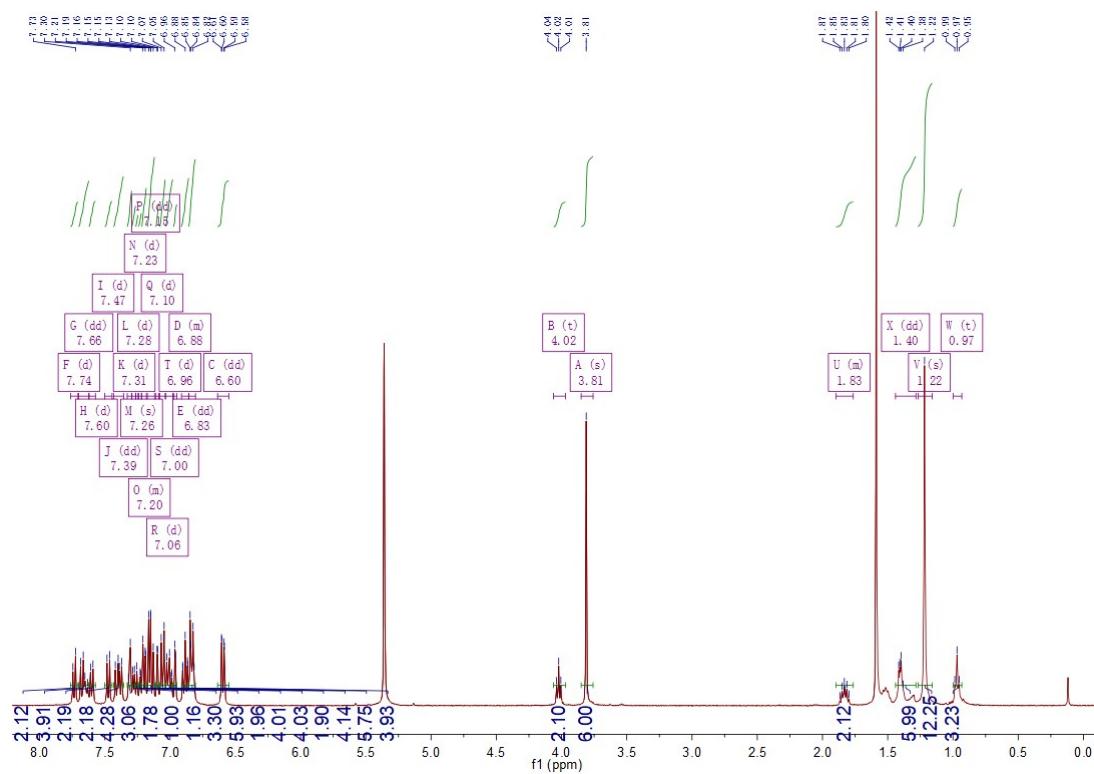


Figure S4. ^1H NMR (CD_2Cl_2) spectrum of **M141**.

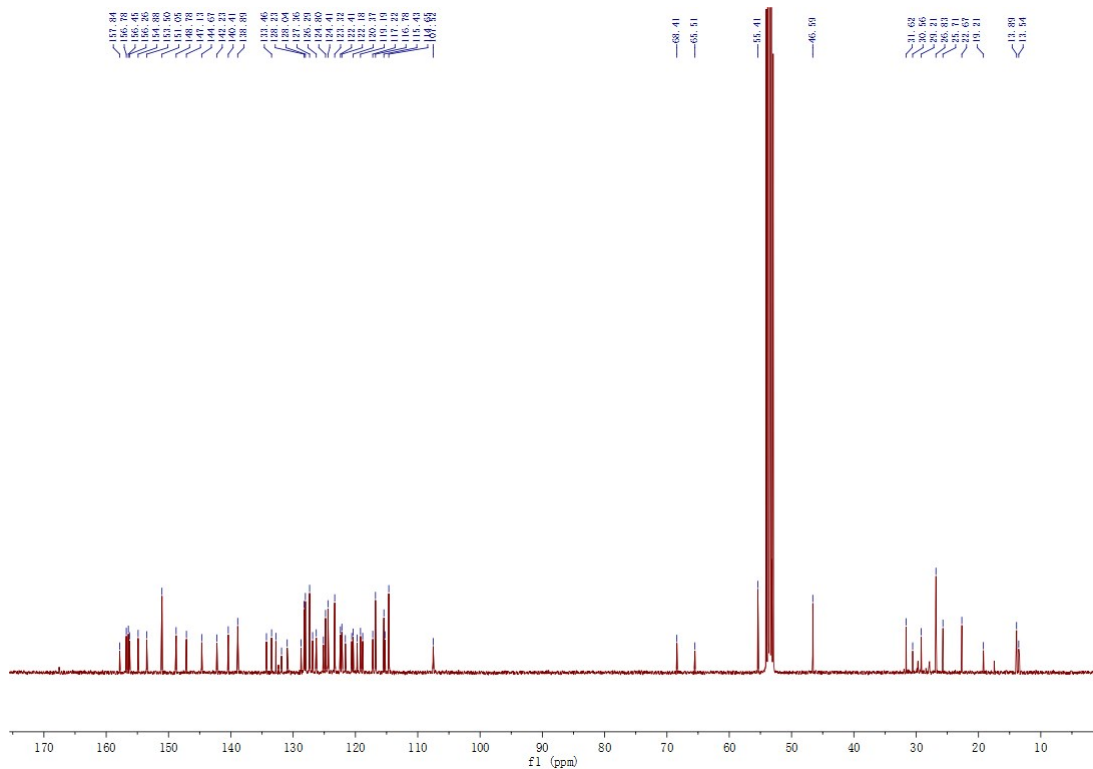


Figure S5. ^{13}C NMR (CD_2Cl_2) spectrum of M141.

7. Figure S6-10

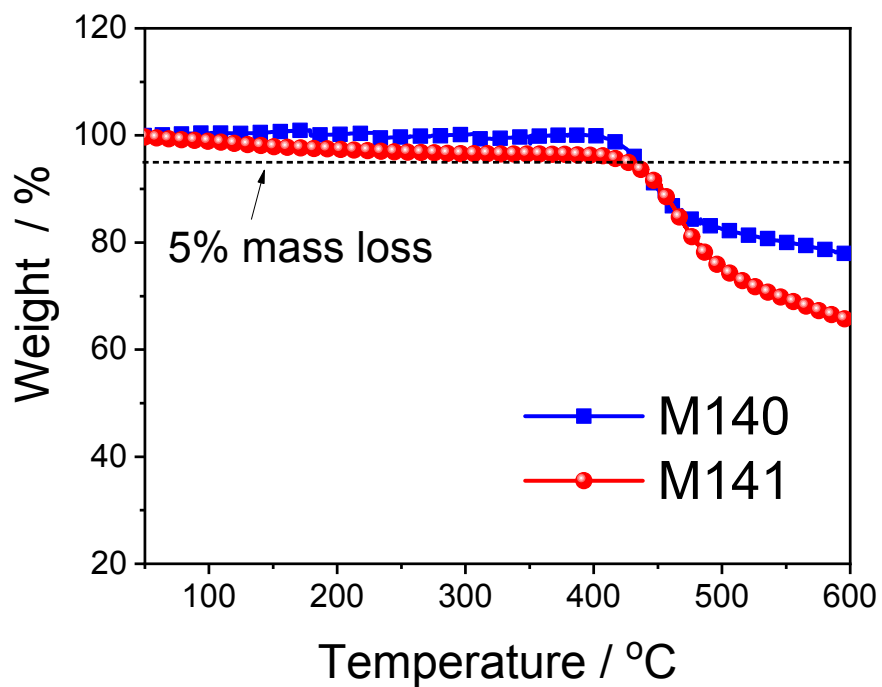


Figure S6. TGA thermograms of the M140-141 at a scan rate of 10 °C/min under N₂ atmosphere.

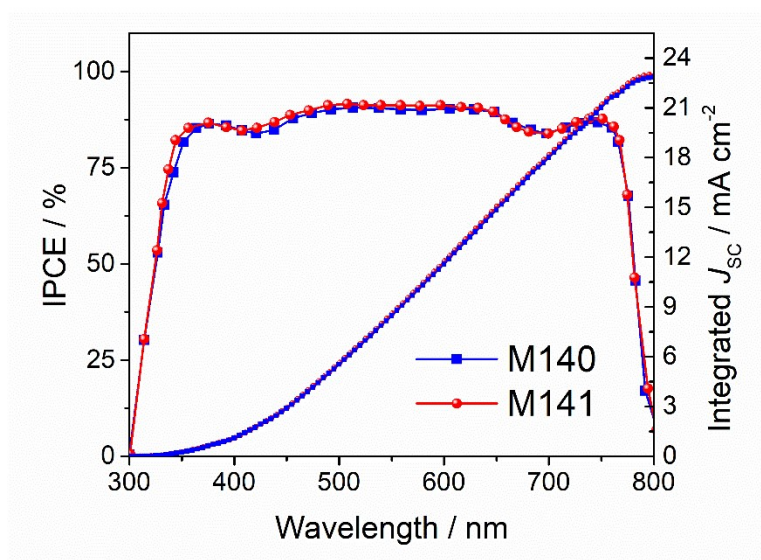


Figure S7. IPCE spectra of PSCs based on doped M140 and M141.

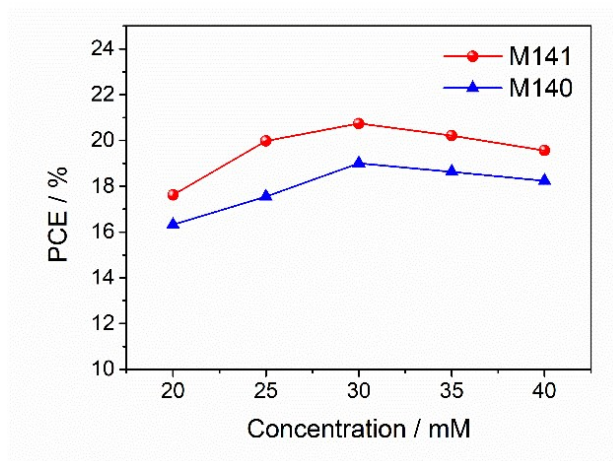


Figure S8. Concentration dependencies of the PCE in devices based on doped M140 and M141.

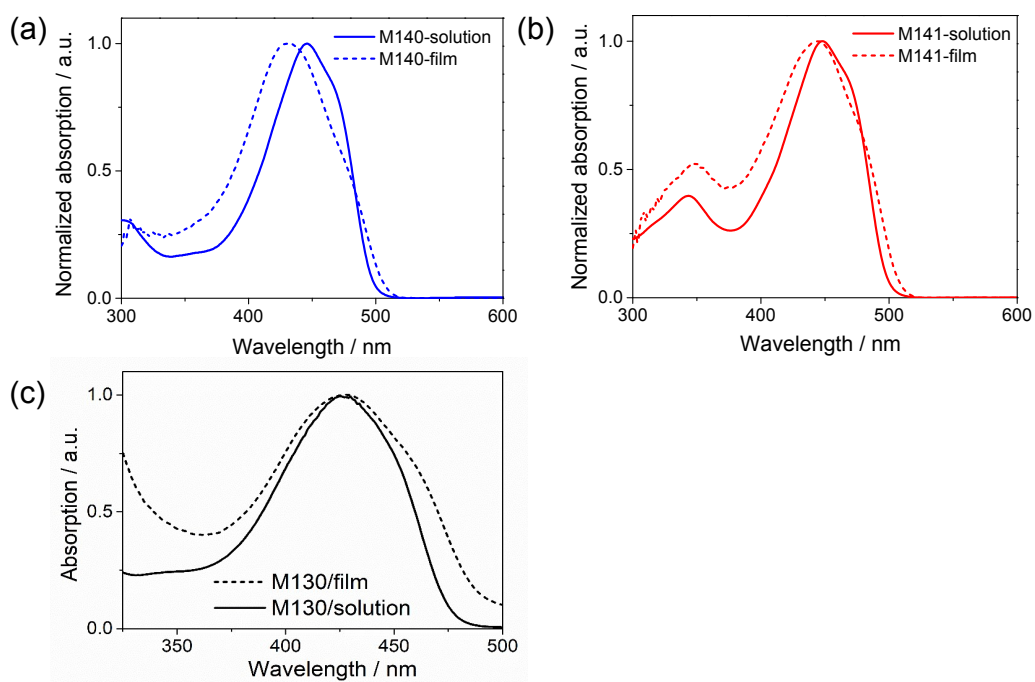


Figure S9. Normalized absorption spectra of film and solution based on M140 (a), M141 (b) and M130 (c).

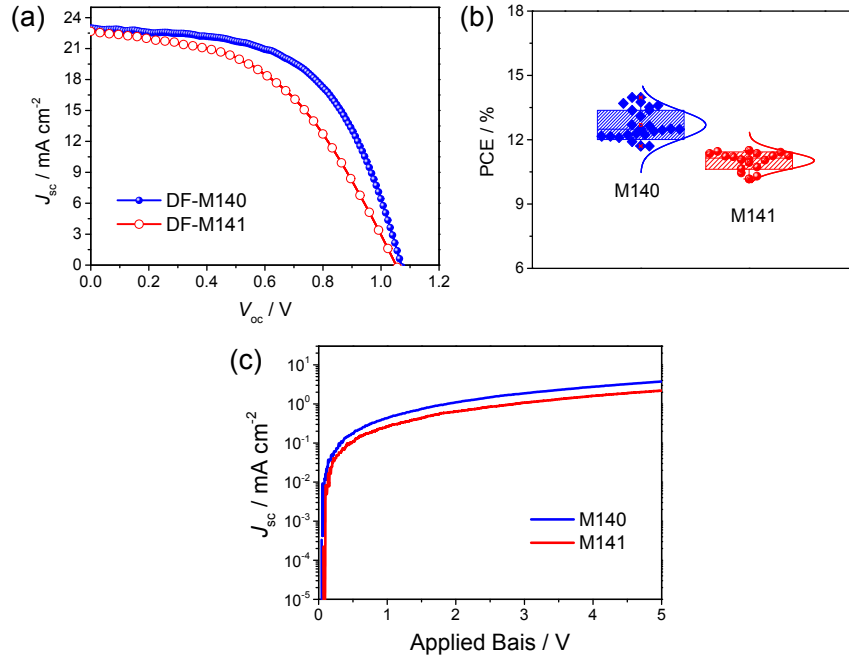


Figure S10. (a) J - V curves of PSCs based on dopant-free M140 and M141. (b) Statistical distribution of PSCs performance with dopant-free M140 and M141. (c) hole mobility of dopant-free M140 and M141.

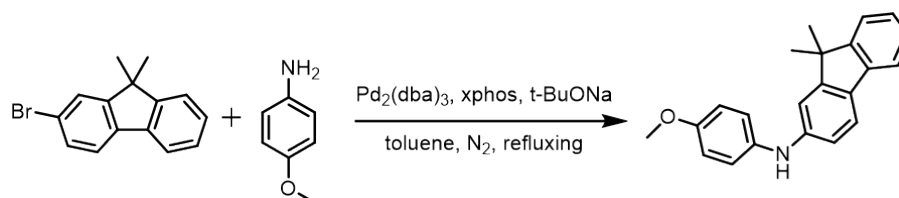
8. Table S1

Table S1. Lifetimes of time-resolved photoluminescence measurement for doped HTMs.

| | PVSK | M130 | M140 | M141 |
|---------------|-------|-------|-------|-------|
| T_1 (ns) | 4.08 | 3.63 | 3.88 | 2.21 |
| T_2 (ns) | 28.55 | 39.84 | 37.02 | 37.28 |
| average T(ns) | 14.69 | 7.06 | 6.21 | 3.29 |

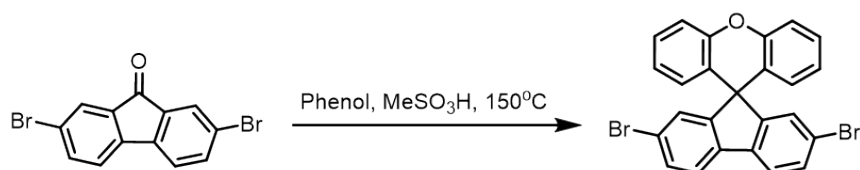
9. The cost analysis of M141's synthesis (The synthesis cost of compound is estimated by using the price of chemical suppliers in China)

Synthetic cost of compound **2**



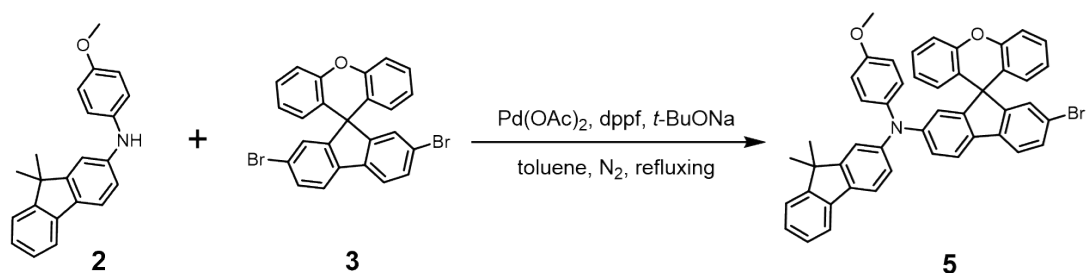
| Reagent | Amount / g | Amount / mL | Price / g or mL | Total price / RMB |
|--|--------------------------|-------------|-----------------|-------------------|
| 7-bromo-9,9-dimethyl-9H-fluoren-2-yl bromide | 1.0 | | 6.5 | 6.5 |
| 4-methoxyaniline | 0.54 | | 0.55 | 0.297 |
| $\text{Pd}_2(\text{dba})_3$ | 0.067 | | 80 | 5.36 |
| Xphos | 0.069 | | 18.4 | 1.26 |
| t-BuONa | 0.56 | | 0.2 | 0.112 |
| Toluene | | 25 | 0.02 | 0.5 |
| Silica gel | 100 | | 0.036 | 3.6 |
| Petroleum ether 60-90 °C | | 500 | 0.022 | 11 |
| Dichloromethane | | 300 | 0.02 | 6 |
| Total cost | 34.62 RMB | | | |
| Amount 2 | 1.1 g | | | |
| COST for 2 | 31.47 RMB/g or 4.85 \$/g | | | |

Synthetic cost of compound **3**



| Reagent | Amount / g | Amount / mL | Price / g or mL | Total price / RMB |
|------------------------------|--------------------------|-------------|-----------------|-------------------|
| 2,7-dibromo-9H-fluoren-9-one | 3.0 | | 7.5 | 22.5 |
| Phenol | 8.34 | | 0.2 | 1.66 |
| MeSO ₃ H | 8.52 | | 0.17 | 1.44 |
| Silica gel | 150 | | 0.036 | 5.4 |
| Petroleum ether 60-90 °C | | 500 | 0.022 | 11 |
| Dichloromethane | | 100 | 0.02 | 2 |
| Total cost | 44 RMB | | | |
| Amount 3 | 4.17 g | | | |
| COST for 3 | 10.55 RMB/g or 1.62 \$/g | | | |

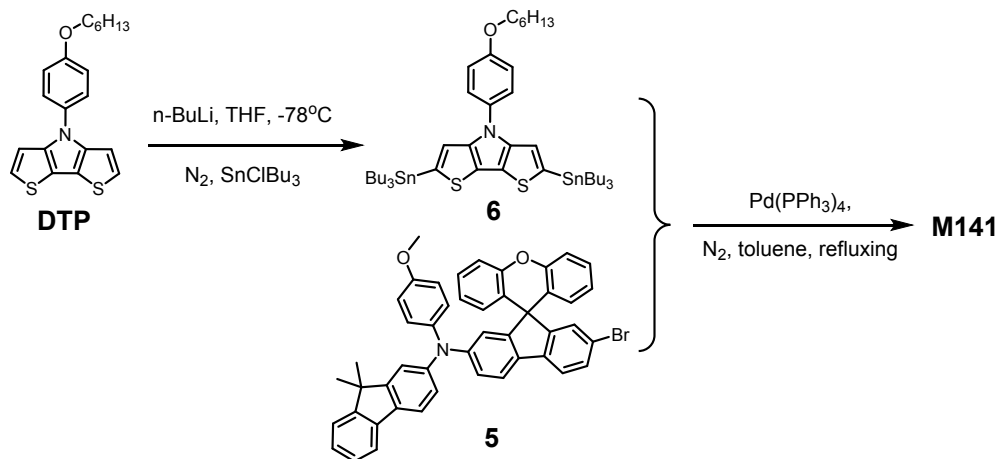
Synthetic cost of compound 5



| Reagent | Amount / g | Amount / mL | Price / g or mL | Total price / RMB |
|--------------------------|------------|-------------|-----------------|-------------------|
| 2 | 0.687 | | 31.47 | 21.61 |
| 3 | 2.138 | | 10.55 | 22.55 |
| Pd(OAc) ₂ | 0.0098 | | 300 | 2.94 |
| dppf | 0.0483 | | 2.98 | 0.143 |
| t-BuONa | 0.335 | | 0.2 | 0.067 |
| Toluene | | 50 | 0.02 | 1 |
| Silica gel | 100 | | 0.036 | 3.6 |
| Petroleum ether 60-90 °C | | 500 | 0.022 | 11 |
| Dichloromethane | | 200 | 0.02 | 4 |
| Total cost | 66.91 RMB | | | |

| | |
|--------------------------|---------------------------|
| Amount 5 | 0.899 g |
| COST for 5 | 74.42 RMB/g or 11.48 \$/g |

Synthetic cost of compound **M141**



| Reagent | Amount / g | Amount / mL | Price / g or mL | Total price / RMB |
|------------------------------|------------|-------------|---------------------------|-------------------|
| DTP | 0.294 | | 117.36 | 34.5 |
| $n\text{-BuLi}$ (2.5mol / L) | | 0.86 | 0.28 | 0.24 |
| SnBu_3Cl | 0.781 | | 1.69 | 1.32 |
| THF | | 10 | 0.2 | 2 |
| 5 | 0.899 | | 74.42 | 66.91 |
| $\text{Pd(PPh}_3)_4$ | 0.057 | | 44 | 2.52 |
| Toluene | | 20 | 0.1 | 2 |
| Silica gel | 200 | | 0.036 | 7.2 |
| Petroleum ether 60-90 °C | | 800 | 0.022 | 17.6 |
| Dichloromethane | | 800 | 0.02 | 16 |
| Total cost | | | 150.29 RMB | |
| Amount M141 | | | 0.57 g | |
| COST for M141 | | | 263.66 RMB/g = 40.68 \$/g | |

10. References

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