

Imidazole core to construct dopant-free asymmetric hole-transporting material for efficient inverted perovskite solar cells

Yang Cheng, Quanping Wu,* Ming Luo, Haolin Wang, Song Xue and Xueping Zong*

Tianjin Key Laboratory of the Design and Intelligent Control of the Advanced Mechanical System,

School of Mechanical Engineering, Tianjin Key Laboratory of Organic Solar Cells and Photoche

mical Conversion, School of Chemistry and Chemical Engineering,

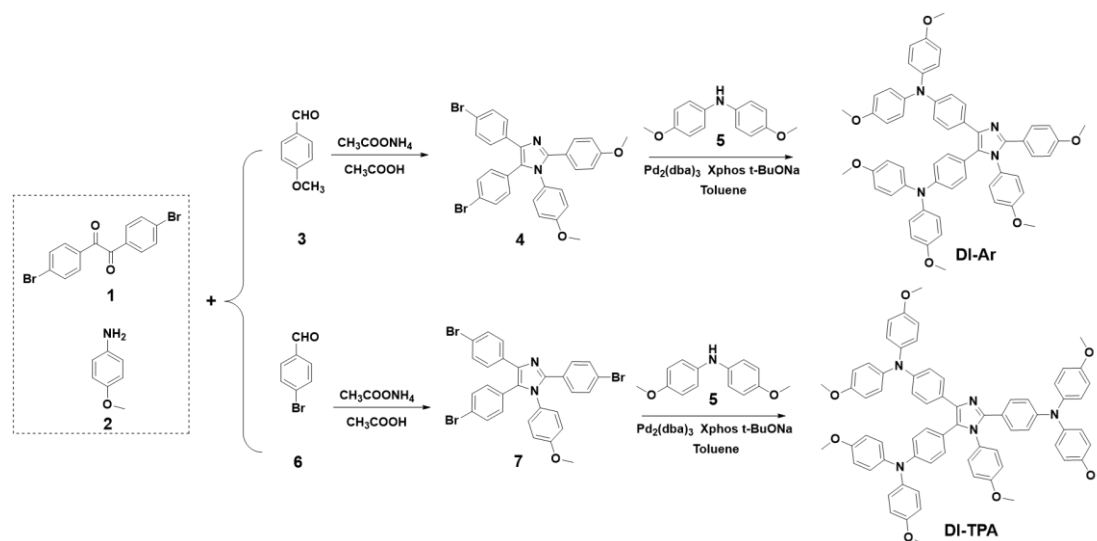
Tianjin University of Technology, Tianjin 300384, P. R. China

Corresponding authors:

E-mail address: wqping@ustc.edu.cn, zongxueping717@163.com.

1. Synthesis

The designed synthetic procedures of DI-Ar and DI-TPA are depicted in **Scheme S1**.



Scheme S1. Synthetic routes to DI-Ar and DI-TPA.

Synthesis of compound 7. In a two-necked flask, a mixture of 1,2-bis(4-bromophenyl)ethane-1,2-dione (**1**) (300 mg, 0.82 mmol), 4-methoxyaniline (**2**) (151 mg, 1.23 mmol), 4-bromobenzaldehyde (**6**) (150 mg, 0.82 mmol) and ammonium acetate (940 mg, 4.10 mmol) in 20 mL acetic acid was heated to 120 °C and stirred overnight under nitrogen atmosphere. The reaction was quenched by 200 mL H₂O and extracted with dichloromethane. The organic solution was dried with anhydrous Na₂SO₄ and removed by vacuum evaporation. The obtained crude product was purified by column chromatography on silica gel using an eluent of petroleum ether (PE) and EtOAc (10:1, v/v) to afford a pale white solid product (438 mg, yield=84%). ¹H NMR (400 MHz, CDCl₃) δ 7.43-7.38 (m, 8 H), 7.32-7.30 (d, *J* = 8.6 Hz, 2 H), 6.99-6.95 (t, *J* = 8.4 Hz, 4 H), 6.84-6.82 (d, *J* = 8.8 Hz, 2 H), 3.83 (s, 3 H).

Synthesis of compound 4. The synthesis route is similar with compound 7. The

reaction affords a white solid with a yield of 87%. ¹H NMR (400 MHz, CDCl₃) δ 7.47-7.44 (d, *J* = 8.4 Hz, 2H), 7.39-7.36 (m, 6 H), 6.99-6.95 (t, *J* = 8 Hz, 4H), 6.82-6.79 (m, 4H), 3.82-3.80 (d, *J* = 7.6 Hz, 6H)

Synthesis of product DI-TPA. A mixture of compound 7 (200 mg, 0.31 mmol) and bis(4-methoxyphenyl)amine (5) (288 mg, 1.26 mmol), Pd₂(dba)₃ (18 mg, 0.0037 mmol), Xphos (18 mg, 0.0037 mmol) and t-BuONa (151 mg, 1.57 mmol) was added into 7 mL toluene solution, and further heated at 90 °C overnight under argon atmosphere. After evaporating the solvent, the crude product was purified by column chromatography using EtOAc: PE (1:3, v/v) as eluent to give compound DI-TPA (299 mg, yield: 88%). ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.37-7.35 (d, *J* = 8.8 Hz, 2 H), 7.14-7.10 (t, *J* = 9.2, 8.8 Hz, 5 H), 7.03-6.96 (m, 14 H), 6.90-6.86 (m, 13 H), 6.69-6.67 (d, *J* = 8.8 Hz, 2 H), 6.58-6.53 (t, *J* = 10.6, 8.5 Hz, 4 H), 3.73-3.72 (d, *J* = 4.0 Hz, 21 H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 156.57, 156.43, 155.91, 148.39, 146.91, 146.03, 140.73, 139.97, 139.84, 136.46, 132.36, 130.35, 130.28, 129.12, 127.75, 127.56, 127.27, 126.75, 122.08, 121.97, 119.95, 118.21, 117.63, 115.46, 115.39, 115.33, 114.59, 55.72, 55.65.

Synthesis of product DI-Ar. The synthesis route of DI-Ar is similar with that of DI-TPA. The reaction affords a brown solid with a yield of 90%. ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.39-7.37 (d, *J* = 8.5 Hz, 2H), 7.28-7.26 (d, *J* = 8.5 Hz, 2H), 7.12-7.10 (d, *J* = 8 Hz, 2H), 7.00-6.98 (d, *J* = 8.3 Hz, 10H), 6.90-6.70 (m, 12H), 6.70-6.68 (d, *J* = 8.4 Hz, 2H), 6.59-6.57 (d, *J* = 8 Hz, 2H), 3.75 – 3.72 (t, *J* = 6.4, 4.4 Hz, 18H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 159.45, 159.18, 156.46, 155.98, 146.98, 146.01, 140.71, 139.98, 132.38, 130.33, 129.91, 127.59, 127.26, 126.84, 119.85, 118.23, 115.41,

115.35, 114.62, 114.03, 55.76, 55.67, 55.55.

2. Characterization

The NMR spectra were recorded with a Bruker AM-400 spectrometer (400 MHz for ^1H and 100 MHz for ^{13}C). The reported chemical shifts were against TMS. Differential scanning calorimetry (DSC) was conducted on a DSC 200 F3 maia (NETZSCH, Germany), and the experiment was carried out from 35 °C to 250 °C at a rate of 10 °C min^{-1} under N_2 atmosphere. Ultraviolet-visible measurements were performed on a SHIMADZU UV-2600 spectrophotometer. A HITACHI F-4500 fluorescence spectrophotometer was used to collect the fluorescence spectra. Cyclic voltammetry (CV) was measured through a CHI660D electrochemical workstation with 0.1 M n-Bu₄NPF₆ in dichloromethane solution as electrolyte. A three-electrode test method was selected with a glassy carbon dish as working electrode, platinum electrode as counter electrode, and Ag/AgCl electrode as reference electrode. Ferrocene was measured as standard. The morphology of perovskite films was characterized by ULTRA plus ZEISS field emission scanning electron microscopy (SEM). Steady-state photoluminescence (PL) measurements were carried out with a HITACHI F-4500 fluorescence Spectrophotometer at the excitation of 500 nm peak.

Hole mobility was measured by space-charge-limited currents (SCLCs) method. The hole only devices were fabricated with a structure of ITO/PEDOT: PSS/HTMs/Ag. Firstly, PEDOT:PSS was spin-coated onto the ITO substrates and then annealed at 120 °C for 30 min. After that, the solution of HTMs with a concentration of 5 mg mL^{-1} was spin-coated on the PEDOT:PSS film at 1000 rpm for 30s, and further annealed at 90°C

for 20 min. Finally, a 150 nm thick Ag back contact was deposited onto the HTMs layer. The thicknesses of the HTMs films were measured using a Dektak profilometer. Current-voltage curve was recorded under dark condition. The SCLC expression is described by the Mott-Gurney law:

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

Here, $\epsilon_r \approx 3$ is the average dielectric constant of the film, ϵ_0 is the vacuum permittivity of the free space (8.85×10^{-12} F/m), μ is the carrier mobility, d is the thickness of HTM film, and V is the applied voltage.

Two-contact electrical conductivity set-up was used for measuring conductivities of HTMs. The HTMs solution were spin-coated on ITO substrates at 1000 rpm for 1 min. Finally, 80 nm thick Ag back contact was deposited by thermal evaporation. The conductivity (σ) was determined by using formula (1).

$$\sigma = L / Rwd \quad (1)$$

in which L is the channel length (0.05 mm), w is the channel width (0.2 μm), d is the thickness of HTM film and R is the resistance.

2. Device Fabrication

2.1 Materials.

Methylammonium iodide (MAI) and lead iodide (PbI_2 , 99.99%) were purchased from Youxuan Tech (China). Phenyl- C_{61} -butyric acid methyl ester (PCBM) and BCP (99.9%) were purchased from Xi'an p-OLED (China). The liquid reagents, including N, N-dimethylformamide (DMF, 99.8%), Dimethyl sulfoxide (DMSO 99.7%), isopropanol (IPA, 99.5%), and chlorobenzene (CB, 99.8%) were purchased from Sigma Aldrich.

2.2 Device Fabrication

The inverted perovskite solar cells (PSCs) were fabricated with a configuration of ITO/HTMs/MAPbI₃/PCBM/BCP/Ag. The etched ITO substrates were cleaned with DI water, acetone, and IPA, sequentially, followed with a treatment by UV-ozone for 30 min. Then, the HTMs solution with a concentration of 5 mg mL⁻¹ in chlorobenzene (CB) were spin-coated on the ITO. Perovskite precursor was prepared by mixing MAI (461 mg) and PbI₂ (159 mg) in a mixture solution of N,N-dimethylformamide (DMF) (600 mg) and dimethyl sulfoxide (78 mg), further stirred for 30 min at 50 °C. The perovskite layers were then fabricated using a two-steps spin-coating procedure. During the second step, 120 μL CB was capped on the substrates, following an annealing at 100 °C for 10 min. Afterwards, PC₆₁BM solution in CB with a concentration of 20 mg mL⁻¹ was deposited at 3000 rpm for 30 s, and annealed at 100 °C for 10 min. Subsequently, BCP (0.5 mg mL⁻¹ in isopropanol) was spin-coated as a buffer-layer at 4500 rpm. Finally, a 120 nm thick Ag contact was deposited on top of BCP film using thermal evaporation. The device of active area is 0.08 cm².

3. Results

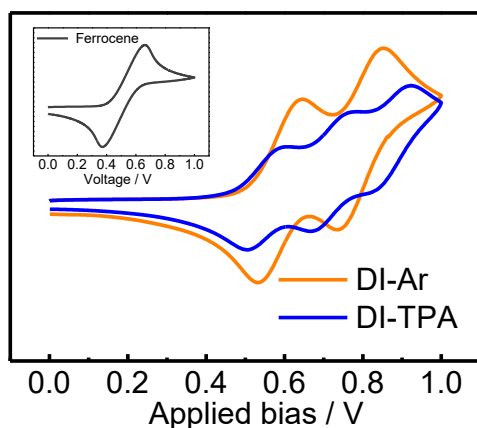


Figure S1 Cyclic voltammograms of DI-Ar and DI-TPA in CH_2Cl_2 . The inserted image is the cyclic voltammetry curve of ferrocene.

Table S1 Hole mobility and conductivity of HTMs.

HTMs	μ_{h}^a [$\text{cm}^2 \text{v}^{-1} \text{s}^{-1}$]	σ_0^b [Scm^{-1}]
DI-Ar	6.32×10^{-6}	4.39×10^{-5}
DI-TPA	2.43×10^{-5}	7.07×10^{-4}

^a μ_{h} is hole mobility of HTMs film

^b σ_0 is conductivity of HTMs film

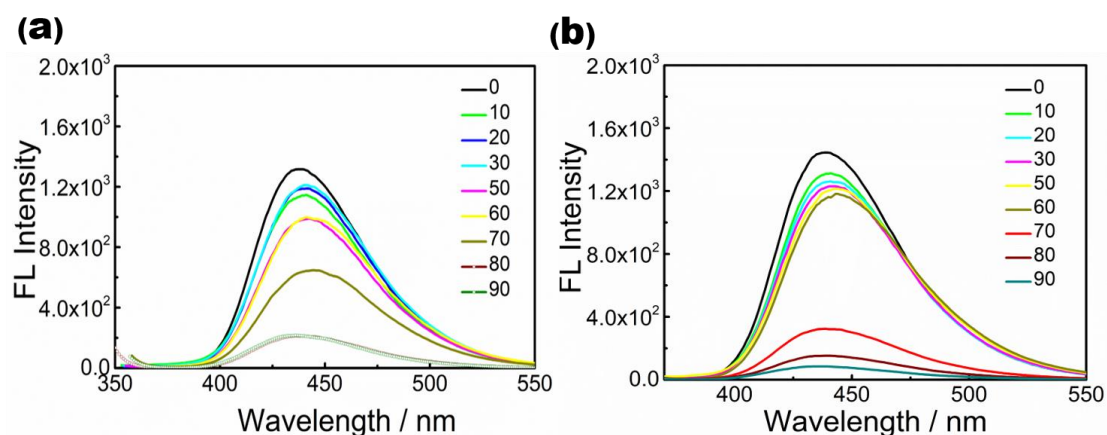


Figure S2 Fluorescence emission spectra of (a) DI-Ar and (b) DI-TPA in THF/water mixtures with different water fractions.

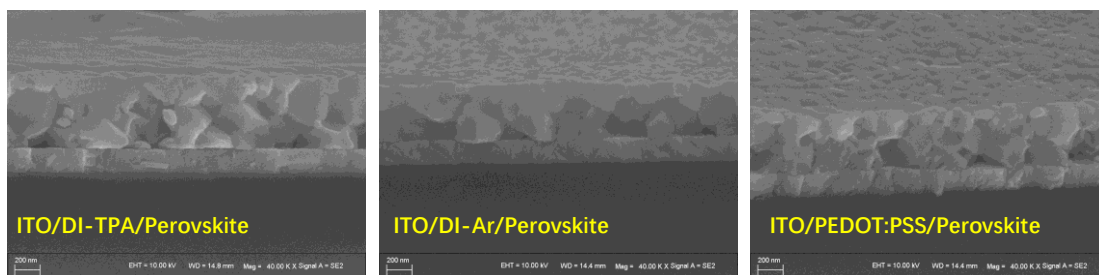


Figure S3 The cross-sectional SEM images of ITO/HTMs/Perovskite.

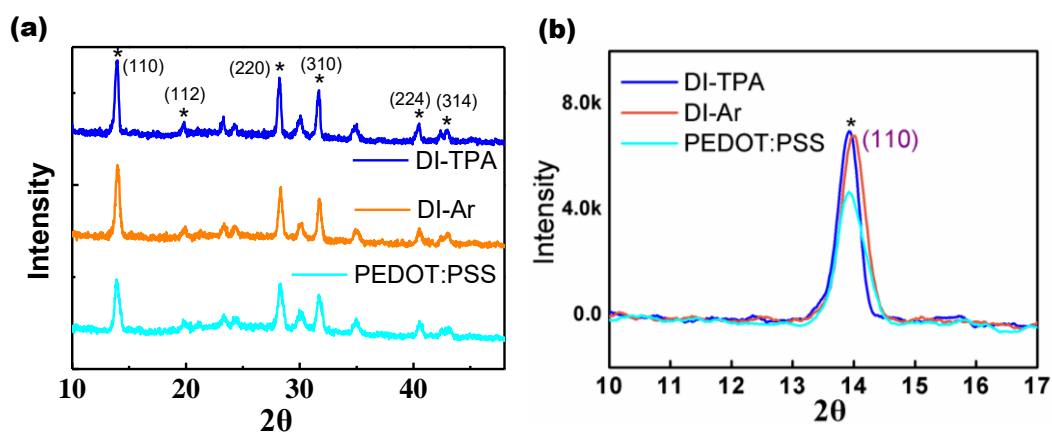


Figure S4 (a) XRD measurements of perovskite films coated on HTMs; (b) The enlarged peak of (110).

Table S2 Fitted parameters of TRPL decay curves of perovskite with/without HTMs.

Sample	τ_1 (ns)	τ_2 (ns)	A ₁ (%)	A ₂ (%)	τ_{ave} (ns)
DI-TPA	10.7	10.7	50	50	10.7
DI-Ar	7.3	37.4	16.4	83.6	36.3
PEDOT:PSS	8.1	53.7	13.1	86.9	52.7
MAPbI ₃	19.7	180.4	93.1	6.9	84.7

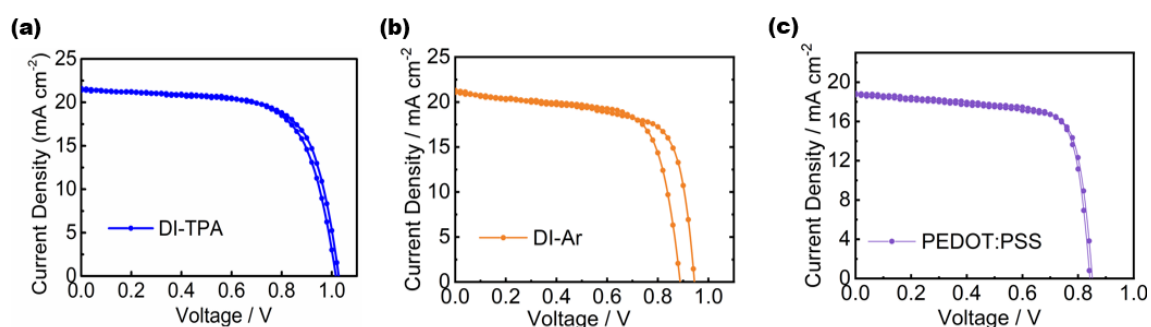


Figure S5 J - V curves of i-PSCs with DI-TPA, DI-Ar and PEDOT:PSS measured by forward and reverse scan at a scan rate of 0.2 mV/s, respectively.

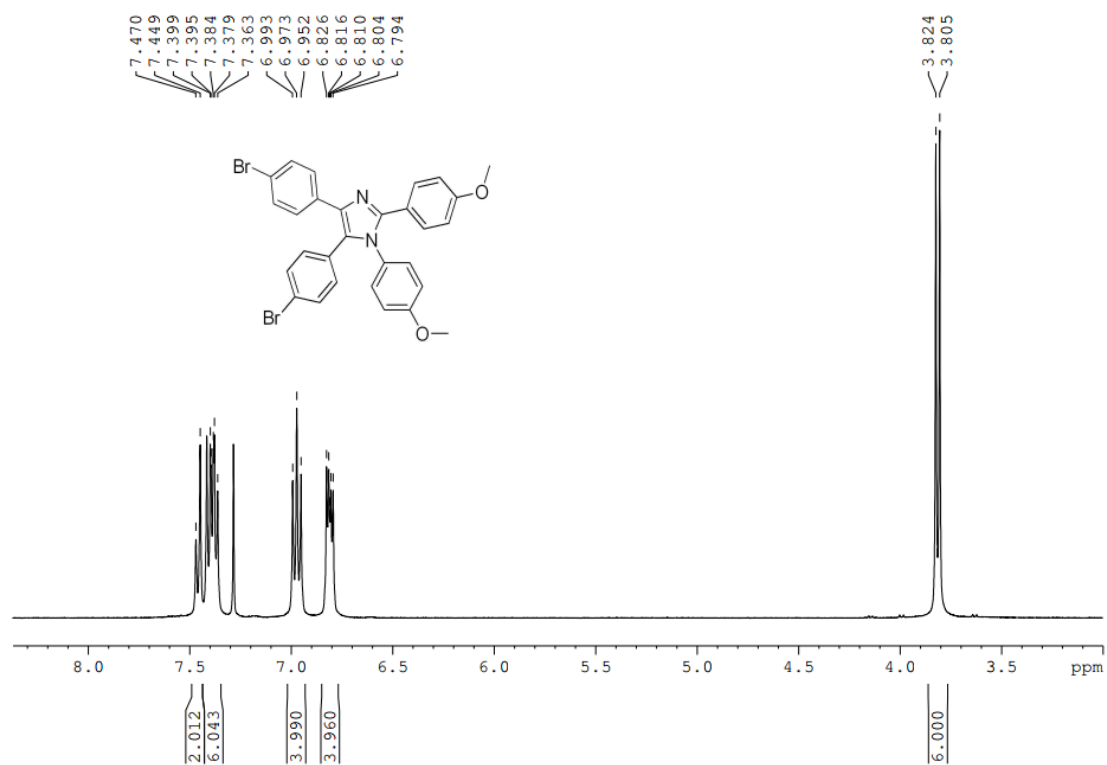


Figure S6. ¹H NMR (CDCl₃) spectrum of compound 4.

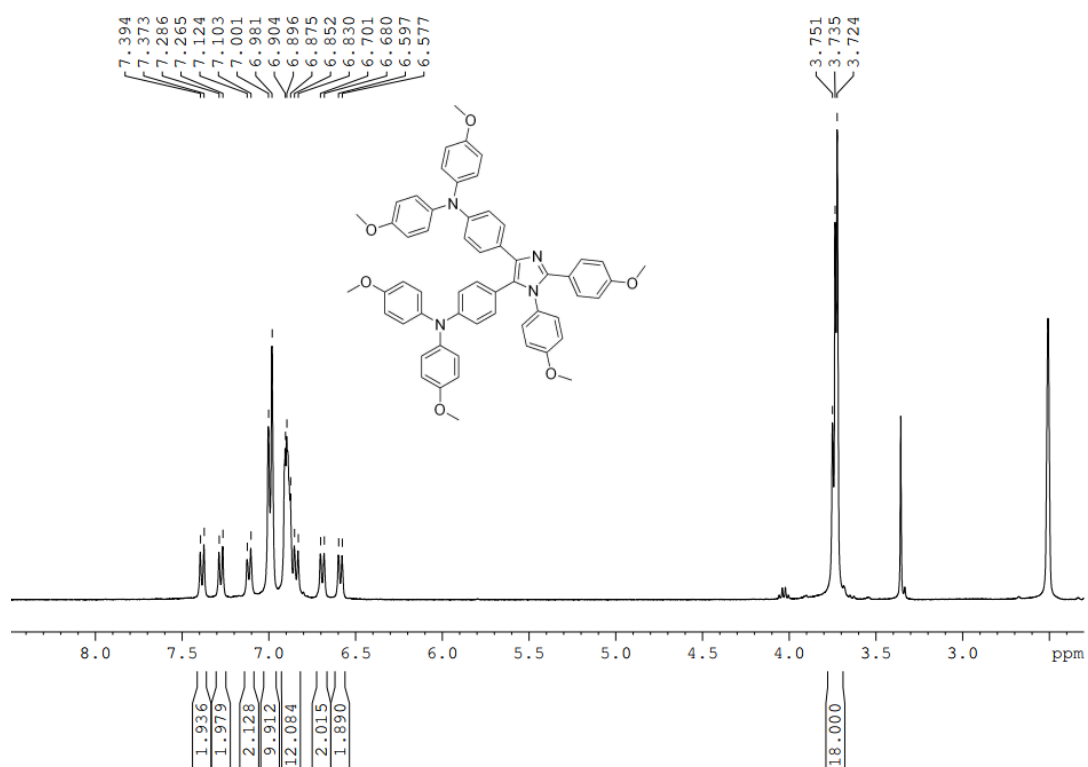


Figure S7. ¹H NMR (DMSO-*d*₆) spectrum of DI-Ar.

