

Effects of the Planarity of Core Building Block and Peripheral Donor Group on the Photovoltaic Performance of Triarylated Amine-Based Hole Transport Materials

Yicheng Wang,^a Chuansu Yang,^{b, c} Jinwei Meng,^{b, c} Cheng Chen,^{b*} Hao Zhuang,^c
Haoxin Wang,^b Ming Zhang,^b Hui Xu,^b Ming Cheng^{b*}

^a Jiangsu Meike Solar Technology INC, Yangzhong 212200, China.

^b Institute for Energy Research, Jiangsu University, Zhenjiang 212013, China.

^c CECEP Solar Energy Technology (ZhenJiang) Co., Ltd., Zhenjiang 212132, China.

* E-mail: chencheng@ujs.edu.cn (C. Chen); mingcheng@ujs.edu.cn (M. Cheng)

1. Materials, Instrument and Methods

1.1 Materials

Lead iodide (PbI₂) was purchased from TCI (Shanghai) Development Co., Ltd. Formamidinium iodide (FAI), 4-tert-butylpyridine (TBP, 96%), Li-TFSI (>99%), FK209 (98%) were purchased from Xi'an Polymer Light Technology Corp. Methylammonium Bromide (MABr), Lead(II) bromide (PbBr₂), 2,2',7,7'-tetrakis[*N,N*-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene (Spiro-OMeTAD) were purchased from Advanced Election Technology Co., Ltd. *N,N*-dimethylformamide (DMF, 99.8%), dimethyl sulfoxide (DMSO, 99%), chlorobenzene (CB, 99.5%) were purchased from Sigma-Aldrich Co., Ltd. Other chemicals were purchased from Energy Chemical Company, Sigma-Aldrich, Alfa and TCI, and used without any further purification.

1.2 Instruments

The SEM images were taken on a JEOL JSM-7800. Steady-state

photoluminescence (PL) and time-resolved PL (TRPL) measurements were measured by using QE65 Pro spectrometer, excited with a picosecond-pulsed diode laser with the wavelength of 475 nm and measured at 770 nm after excitation. Electrochemical impedance spectroscopy (EIS) was performed using a two-electrode system under dark with an electrochemical workstation (Zahner PP211). In it, EIS spectra were recorded in the frequency from 100 mHz to 1 MHz with a bias voltage of 1.20 V. The contact angles of all the HTMs were obtained using the Phoenix 300 Model instrument. The absorption spectra were recorded on an Agilent 8453 spectrophotometer using a 1 cm cuvette. The photovoltaic performance data of fabricated perovskite solar cells were measured with an AM 1.5G solar simulator (Newport). The incident light intensity was $100 \text{ mW}\cdot\text{cm}^{-2}$ calibrated with a standard Si solar cell. The tested solar cells were masked to a working area of 0.09 cm^2 . The $J-V$ 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. The stability test was conducted without encapsulation.

1.3 Characterization Methods

Cyclic voltammetry (CV) was performed in dichloromethane with 0.1 M TBAPF₆ as the supporting electrolyte at room temperature. The Ag/AgNO₃ electrode, platinum wire, and glassy carbon electrode were used as the reference electrode, counter electrode, and working electrode, respectively. The Ag/AgNO₃ reference electrode was calibrated using a ferrocene/ferrocenium (Fc/Fc^+) redox couple as an external standard whose oxidation potential is -5.1 eV with respect to the vacuum level. The HOMO and LUMO energy levels of the HTMs were obtained from the equation:

$$\text{HOMO (eV)} = - (E_{(ox)}^{onset} - E_{(ferrocene)}^{onset} + 5.1)$$

$$\text{LUMO (eV)} = \text{HOMO} + E_g^{opt} \quad (E_g^{opt} = 1240/\lambda_{onset})$$

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 average data. Space-charge-limited current can be described by the equation below:

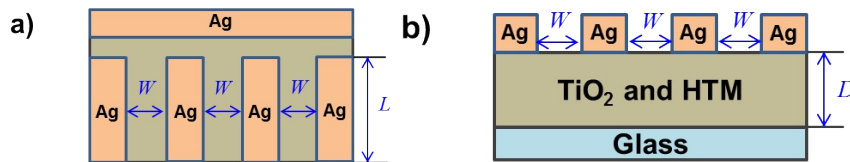
$$J = \frac{9}{8} \mu \epsilon_0 \epsilon_r \frac{V^2}{D^3}$$

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 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:

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

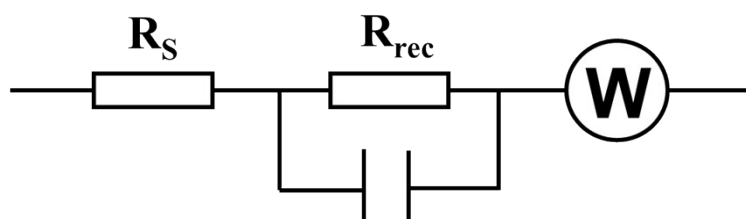
where L is the channel length 10 mm, W is the channel width 2 mm, D is the film thickness of the TiO_2 and HTM, and R is the film resistance calculated from the gradients of the curves.



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

To avoid the excitation of hole transport material, the steady-state photoluminescence (PL) and time-resolved PL (TRPL) measurements were measured the excitation wavelength is fixed to be 475 nm. The laser incidents from the hole transport materials side and the fluorescence peak locating around 770 nm are monitored.

The electrochemical impedance spectroscopy (EIS) was performed using a two-electrode system under the dark condition with an electrochemical workstation (Zahner PP211). The EIS spectra were recorded in the frequency from 100 mHz to 1 MHz with a bias voltage of 1.20 V. Its equivalent circuit model is shown in Scheme S2.



Scheme S2. The equivalent circuit model for the PSCs in EIS

1.4 Preparation of Substrate

The FTO glass substrates (Pilkington, TEC15) were cut (15 mm × 15 mm) and patterned by using Laser ablation (Yuanlu, ET220MIR). The substrates were washed by sonication subsequently in deionized water, acetone and ethanol for 15 minutes each. The electron transporting c-TiO₂ layer was coated by spray-coating technique and annealed at 500 °C for 30 min. The substrates were treated with oxygen plasma for 15 min. The mesoporous TiO₂ (m-TiO₂) layer was deposited over the c-TiO₂ layer via spin coating at 5000 rpm for 30 sec followed by sintering at 110 °C for 10 min and 500 °C for 60 min. Before coating the perovskite layer, the substrate was treated with oxygen plasma for 15 min and transferred immediately to the glove box for further process.

1.5 Preparation of Perovskite Solar Cell

The n-i-p device configuration was adopted in this study (FTO/c-TiO₂/m-

TiO₂/Perovskite/HTM/Au). For 1.28 M (FAPbI₃)_{0.95}(MAPbBr₃)_{0.05} perovskite film deposition, a solution of PbI₂: FAI: PbBr₂: MABr (1.35, 1.28, 0.07, 0.07 in 4:1 DMF: DMSO). The solutions were heated to dissolve the inorganic salts but otherwise kept at room temperature at all times. 30 μ l of the perovskite solution spread onto the TiO₂. The substrate was spin-coated at 1000 rpm for 10 seconds and 5000 rpm for 30 seconds. During the second spin-coating step an antisolvent was injected onto the film after 15 seconds using 180 μ l of chlorobenzene. The perovskite films were then annealed at 100 °C for 30 minutes on a hotplate. Subsequently, the HTMs (Spiro-OMeTAD 80 mg/mL; **TPA-DF**, **CZ-DF** and **CZ-DM** are all 40 mg/mL with additive (30 mM Li-TFSI and 250 mM TBP)) was spin-coated on the perovskite layer at 5000 rpm for 30 s. Finally, the 100 nm Au electrode was thermally evaporated on top of HTMs layer.

2. Synthesis of HTMs

The synthetic routes for **TPA-DF**, **CZ-DF**, and **CZ-DM** are shown in Scheme 1 in main text. All of the solvents and chemicals were used as received unless specially stated. Compound 2, 5 ^[1] and 6 ^[2] were synthesized by referring to the previously reported procedure.

***N'*-(9,9-dimethyl-9H-fluoren-2-yl)-*N,N'*-bis(4-((9,9-dimethyl-9H-fluoren-2-yl)(4-methoxyphenyl)amino)phenyl)-*N'*-(4-methoxyphenyl)benzene-1,4-diamine (TPA-DF):** A suspension of tris(4-bromophenyl)amine (1.21 g, 2.50 mmol), *N*-(*p*-methoxyphenyl)-*N'*-(9,9-dimethylfluoren-2-yl)amine (2.60 g, 8.25 mmol), Pd(OAc)₂ (0.03 g, 0.13 mmol), and tert-butoxide potassium (0.84 g, 7.50mmol) in 120 mL of dry toluene was stirred under nitrogen atmosphere at 120 °C. The system was purged with nitrogen several times. Then P(*t*-Bu)₃ (0.05 g, 0.25 mmol) was placed in mixture solution and reaction was refluxed overnight. After cooling to room temperature, the reaction mixture was concentrated. Organic phase separation by ethyl acetate and

combined organic phases were dried with Na₂SO₄. The residue was purified by chromatography on silica gel (eluting with petroleum ether/CH₂Cl₂, 1.5/1 v/v) afforded a yellow solid to give 2.28 g of **TPA-DF** in 77% yield. ¹H NMR (400 MHz, DMSO) δ 7.65 (dd, *J* = 10.7, 8.0 Hz, 6H), 7.46 (d, *J* = 7.4 Hz, 3H), 7.26 (ddd, *J* = 24.5, 11.0, 6.9 Hz, 6H), 7.07 (d, *J* = 5.9 Hz, 9H), 7.01 – 6.83 (m, 21H), 3.74 (s, 9H), 1.32 (s, 18H).

HR-MS: calculated: C₈₄H₇₂N₄O₃, 1184.5604, found: 1184.5603

***N*³,*N*⁶-bis(9,9-dimethyl-9*H*-fluoren-2-yl)-9-(4-((9,9-dimethyl-9*H*-fluoren-2-yl)(4-methoxyphenyl)amino)phenyl)-*N*³,*N*⁶-bis(4-methoxyphenyl)-9*H*-carbazole-3,6-diamine (CZ-DF):** A suspension of 3,6-dibromo-9-(4-bromophenyl)-9*H*-carbazole (1.44 g, 3.00 mmol), *N*-(4-methoxyphenyl)-9,9-dimethyl-9*H*-fluoren-2-amine (3.12 g, 9.90 mmol), Pd(OAc)₂ (0.03 g, 0.15 mmol), and tert-butoxide potassium (1.01 g, 9.00 mmol) in 120 mL of dry toluene was stirred under nitrogen atmosphere at 120 °C. The system was purged with nitrogen several times. Then P(*t*-Bu)₃ (0.06 g, 0.30 mmol) was placed in mixture solution and reaction was refluxed overnight. After cooling to room temperature, the reaction mixture was concentrated. Organic phase separation by ethyl acetate and combined organic phases were dried with Na₂SO₄. The residue was purified by chromatography on silica gel (eluting with petroleum ether/CH₂Cl₂, 1/2 v/v) afforded a yellow solid to give 2.80 g of **CZ-DF** in 79% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.88 – 7.32 (m, 20H), 7.26 – 6.77 (m, 23H), 3.88 – 3.78 (m, 9H), 1.43 – 1.36 (m, 18H). HR-MS: calculated: C₈₄H₇₀N₄O₃, 1182.5448, found: 1182.5420.

9-(4-(bis(4-methoxyphenyl)amino)phenyl)-*N*³,*N*³,*N*⁶,*N*⁶-tetrakis(4-methoxyphenyl)-9*H*-carbazole-3,6-diamine (CZ-DM): A suspension of 3,6-dibromo-9-(4-bromophenyl)-9*H*-carbazole (1.93 g, 4.00 mmol), 4,4'-dimethyl diphenylamine (3.03g, 13.2 mmol), Pd(OAc)₂ (0.04 g, 0.20 mmol), and tert-butoxide potassium (1.35 g, 12.00 mmol) in 120 mL of dry toluene was stirred under nitrogen atmosphere at 120 °C. The

system was purged with nitrogen several times. Then P(*t*-Bu)₃ (0.08 g, 0.40 mmol) was placed in a mixture solution and the reaction was refluxed overnight. After cooling to room temperature, the reaction mixture was concentrated. Organic phase separation by ethyl acetate and combined organic phases were dried with Na₂SO₄. The residue was purified by chromatography on silica gel (eluting with petroleum ether/CH₂Cl₂, 1/2 v/v) afforded a yellow solid to give 3.03 g of **CZ-DM** in 82% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.68 (s, 2H), 7.60 – 7.51 (m, 1H), 7.42 – 7.35 (m, 1H), 7.28 – 6.65 (m, 30H), 3.79 (ddd, *J* = 9.7, 6.3, 4.8 Hz, 18H). HR-MS: calculated: C₆₀H₅₂N₄O₆, 924.3887, found: 924.3883.

3. The cost analysis of HTMs

Table S1 Synthesis cost of intermediate **TPA-DF**

Reagent	Amount / g	Amount / ml	Price (RMB / g or RMB / ml)	Total price (RMB)
tris(4-bromophenyl)amine	1.210		4.880	5.905
N-(<i>p</i> -methoxyphenyl)-N'-(9,9-dimethylfluoren-2-yl)amine	2.600		42.021	109.255
Pd(OAc) ₂	0.030		369.13	11.074
P(<i>t</i> -Bu) ₃	0.050		5.749	0.287
KO ^t Bu	0.840		0.356	0.299
toluene		120.000	0.046	5.520
Na ₂ SO ₄	35.000		0.024	0.840
ethyl acetate		100.000	0.063	6.300
petroleum ether		150.000	0.119	17.850

Silica gel	100.000		0.292	29.200
Total cost	186.53 RMB			
Amount intermediate TPA-DF	2.28 g			
COST for intermediate TPA-DF	81.81 RMB/g			
Exchange rate	1 \$=6.543RMB			

Table S2 Synthesis cost of intermediate **CZ-DF**

Reagent	Amount / g	Amount / ml	Price (RMB / g or RMB / ml)	Total price (RMB)
3,6-dibromo-9-(4-bromophenyl)-9H-carbazole	1.440		20.942	30.156
N-(p-methoxyphenyl)-N'-(9,9-dimethylfluoren-2-yl)amine	3.120		42.021	131.110
Pd(OAc) ₂	0.030		369.13	11.074
P(t-Bu) ₃	0.060		5.749	0.345
KO ^t Bu	1.010		0.356	0.360
toluene		120.000	0.046	5.520
Na ₂ SO ₄	35.00		0.024	0.840
ethyl acetate		100.000	0.063	6.300

petroleum ether		200.000	0.119	23.800
Silica gel	100		0.292	29.200
Total cost	238.71 RMB			
Amount intermediate CZ-DF	2.80 g			
COST for intermediate CZ-DF	85.25 RMB/g			
Exchange rate	1 \$=6.543RMB			

Table S3 Synthesis cost of intermediate **CZ-DM**

Reagent	Amount / g	Amount / ml	Price (RMB / g or RMB / ml)	Total price (RMB)
3,6-dibromo-9-(4-bromophenyl)-9H-carbazole	1.925		20.942	40.313
4'4-dimethyl diphenylamine	3.030		25.848	78.319
Pd(OAc) ₂	0.040		369.13	14.765
P(t-Bu) ₃	0.080		5.749	0.460
KO ^t Bu	1.345		0.356	0.479
toluene		120.000	0.046	3.680
Na ₂ SO ₄	35.00		0.024	0.840
ethyl acetate		100.000	0.063	6.300
petroleum ether		200.000	0.119	23.800

Silica gel	100		0.292	29.200
Total cost	198.156 RMB			
Amount intermediate CZ-DM	3.03 g			
COST for intermediate CZ-DM	65.40 RMB/g			
Exchange rate	1 \$=6.543RMB			

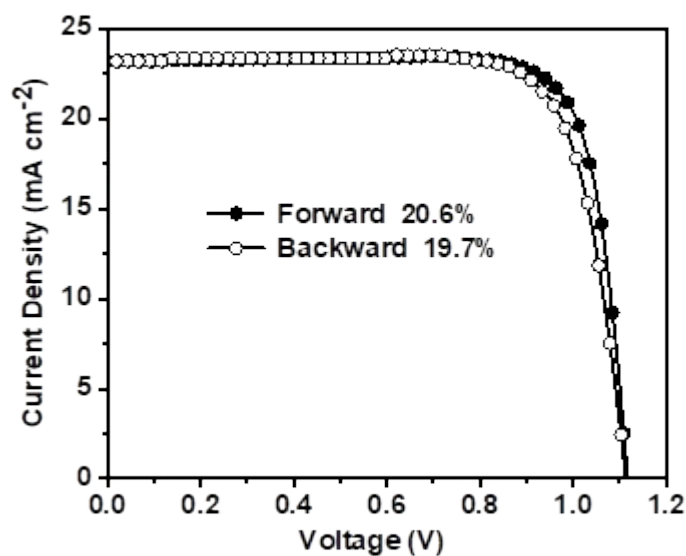


Figure S1 Current-Voltage ($J-V$) curves of PSC device based on HTM Spiro-OMeTAD

Reference

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- [2] Shao JY, Yang N, Guo W, Cui BB, Chen Q, Zhong YW. Introducing fluorene into organic hole transport materials to improve mobility and photovoltage for perovskite solar cells. *Chem Commun.* 2019;55(89):13406-9.