

Electronic Supporting Information

Energy level tuning of TPB-based hole-transporting material for high efficient perovskite solar cells

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1. Chemicals and materials

Starting materials were all commercially available and used as received without further purification if not specially mentioned. N,N'-di(p-tolyl)-N,N'-diphenyl-1,1'-biphenyl-4,4'-diamine were purchased from Tianjin Zhongmin Technology Co. LTD (Tianjin, China), and recrystallized from methylbenzene before use. Potassium t-butoxide (t-BuOK) were purchased from Aladdin Institute (USA). PbI₂ was purchased from Sigma-Aldrich (USA). N,N-dimethylformamide (DMF) and chlorobenzene were purchased from Alfa Aesar (USA). Hydroiodic acid (AR, 45 wt% in water) and methylamine (AR, 27% in methanol) were supplied by Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). Spiro-OMeTAD was obtained from Luminescence Technology Corp.(Taiwan, China). CH₃NH₃I was synthesized according to literatures.^{1,2} Other reagents were purchased from Tianjin Guangfu Fine Chemical Research Institute (Tianjin, China) which were analytical grade. Tetrahydrofuran (THF), N,N-dimethylformamide (DMF) and phosphorus oxychloride (POCl₃) were freshly distilled before use.

2. Instruments and measurement conditions

¹H NMR spectra were recorded with an INOVA 500MHz spectrometer (Fällanden, Switzerland). High resolution mass spectra (HRMS) were measured with a Bruker Micro TOF QII APCI-quadrupole-oe-TOF tandem mass spectrometer (Bruker, Germany). Elemental analysis was performed on a Vario MICRO CHNOS elemental analyzer (Elementar Analysen systeme, Hanau, Germany). UV spectra of the HTMs in dichloromethane solutions (1×10⁻⁵M) were recorded with Thermo Evolution 300 UV-vis spectrometer (Thermo Electron, USA). Thermogravimetical analyses (TGA) were performed on TA Q500 thermo gravimetric apparatus(TA-Instruments, USA) at a heating rate of 10°C/min under nitrogen atmosphere. Differential scanning calorimetry (DSC) was conducted on TA Q20 Instrument (TA-Instruments, USA) at a heating rate of 10 °C /min under nitrogen atmosphere.

The cyclic voltammetry measurements were performed on a Zahner Elektrik IM6e electrochemistry workstation (Zahner, Germany) with a three-electrode system in dry dichloromethane in the presence of tetrabutylammonium hexafluorophosphate

(n-Bu₄NPF₆, 0.1M) as supporting electrolyte with a scanning rate of 30mV/s at room temperature. The glassy carbon electrode was used as the working electrode. Platinum wire and Ag/AgNO₃ were used as auxiliary and reference electrode respectively. The ferrocene/ferrocenium redox couple was applied as an external standard.

The time-of-flight (TOF) measurements were conducted on TOF401 (Sumitomo Heavy Industries. Ltd., Japan). Samples were prepared through spin coating using a structure ITO/HTM (about 1μm)/Al (150nm) having an active area of 3 mm×10 mm.

Surface morphology of the TiO₂/CH₃NH₃PbI₃/HTM/Au film was obtained by using a scanning electron microscope (SEM, XL30S-FEG, FEI, USA). The film thickness was determined by a surface profiler (P-6, KLA-Tencor, USA). Electrochemical impedance spectra (EIS) of the perovskite solar cells were performed on a ZAHNER IM6e electrochemical workstation (Zahner, Germany) in the dark in the frequency ranging from 0.1 to 10⁵ Hz with a perturbation amplitude of 10 mV. The obtained impedance spectra were fitted with *Zview* software based on an appropriate equivalent circuit. The cells were illuminated under 100 mW·cm⁻² (AM 1.5G) by an Oriel solar simulator 91192 (Newport, USA), and the *J-V* characteristics of the cells were recorded on Model 263A (Princeton Applied Research, USA). For *J-V* characteristics, a mask with a window of 0.08 cm² was clipped on the TiO₂ side to define the active area of the cell. Photoluminescence spectra were obtained on a PL Spectrometer (Edinburgh Instruments, FLS 900), excited with a picosecond pulsed diode laser (EPL-445).

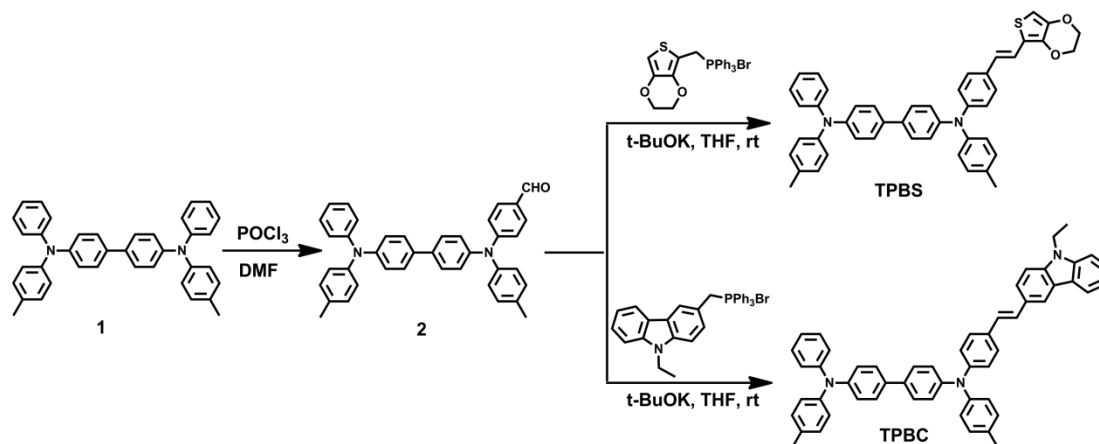
3. Solar cell fabrication

Substrates are fluorine-doped tin oxide conducting glass (FTO, Pilkington, thickness: 2.2 mm, sheet resistance 14 Ω/square). Before use, FTO glass was first washed with mild detergent, rinsed with distilled water for several times and subsequently with ethanol in an ultrasonic bath, finally dried under air stream. For fabricating the device, 50nm-thickness TiO₂ compact layer and 400nm-thickness mesoporous TiO₂anatase compact layer were deposited on FTO glass in sequence according to the literature.³ CH₃NH₃PbI₃ was subsequently deposited on the mesoporous TiO₂ film by using a sequential method as reported.⁴ HTMs with proper

concentrations were spin-coated on the mesoporous $\text{TiO}_2/\text{CH}_3\text{NH}_3\text{PbI}_3$ film at 3000 rpm for 20s, and an 80nm-thickness Au layer was finally deposited on the top of the HTM layer by thermal evaporation.

4. Synthesis

The synthetic route for the HTMs is shown in Scheme 1.



Scheme 1 Synthetic route for TPBS and TPBC

N-phenyl-N'-(4-(2-(3,4-ethylenedioxy)vinyl)phenyl)-N,N'-di-p-tolyl-[1,1'-biphenyl]-4,4'-diamine (TPBS)

Compound **2** was synthesized according to our previous work.⁵ A mixture of 3,4-ethylenedioxy-2-thienylmethyl-triphenylphosphonium bromide (2.48g, 5.00 mmol) and compound **2** (1.63g, 3.00mmol) was dispersed in anhydrous THF (50 mL) and stirred at ambient temperature under nitrogen atmosphere for 15 min. A solution of t-BuOK (1.68 g, 15.00 mmol) in anhydrous THF (20mL) was added dropwise, and then the mixture was stirred overnight. After that, the reaction was quenched by water followed with filtration. The filter residue which contains E and Z isomers was dissolved in THF (60 mL) and refluxed in the presence of I_2 (catalysis amount) for 12h. Then the I_2 was removed with diluted solution of sodium hydroxide (2.5 M). The products were extracted with CH_2Cl_2 . Organic layer was dried with anhydrous sodium sulfate, then purified by silica-gel column chromatography with petroleum ether/ethyl acetate ($V_{\text{PE}}/V_{\text{EA}} = 15/1$) as eluent, to afford pure **TPBS** as yellow solid(1.10 g, 54%), mp 118-119°C; $^1\text{H NMR}$ (500MHz, CDCl_3): δ (ppm) 2.33(s, 3H), 2.34(s, 3H),

4.25(m, 4H), 7.00(m, 2H), 7.05(m, 7H), 7.11(m, 11H), 7.24(d, 2H, $J=10.0\text{Hz}$), 7.32(d, 2H, $J=10.0\text{Hz}$), 7.44(dd, 4H). HRMS (APCI, m/z): 683.2727 (calculated) and 683.2723 (found) for $[M+H]^+$. Elemental analysis: calculated for $C_{46}H_{38}N_2O_2S$: C, 80.91%; H, 5.61%; N, 4.10%; S, 4.70, determined: C, 80.86%; H, 5.62%; N, 4.11; S, 4.71.

N-(4-(2-(9-ethyl-9H-carbazol-3-yl)vinyl)phenyl)-N'-phenyl-N,N'-di-p-tolyl-[1,1'-biphenyl]-4,4'-diamine (TPBC)

The synthesis procedure of compound **TPBC** was same with **TPBS** just replacing 3,4-ethylenedioxy-2-thienylmethyl-triphenylphosphonium bromide with [(9-ethylcarbazol-3-yl)methyl]-triphenylphosphonium bromide. **TPBC** (yellow solid, yield: 72%), mp 122-123°C; $^1\text{H-NMR}$ (500MHz, CDCl_3): δ (ppm) 8.21 (s, 1H), 8.12 (d, $J = 7.7$ Hz, 1H), 7.66 (d, $J = 8.5$ Hz, 1H), 7.49 – 7.35 (m, 9H), 7.24 (d, $J = 6.0$ Hz, 4H), 7.15 – 7.02 (m, 17H), 6.99 (t, $J = 7.3$ Hz, 1H), 4.37 (q, $J = 7.1$ Hz, 2H), 2.34 (s, 3H), 2.33 (s, 3H), 1.43 (t, $J = 7.9$ Hz, 3H). HRMS (APCI, m/z): 736.3686 (calculated) and 736.3682 (found) for $[M+H]^+$. Elemental analysis: calculated for $C_{54}H_{45}N_3$: C, 88.13%; H, 6.16%; N, 5.71%, determined: C, 88.27%; H, 6.15%; N, 5.70%.

Figures and tables

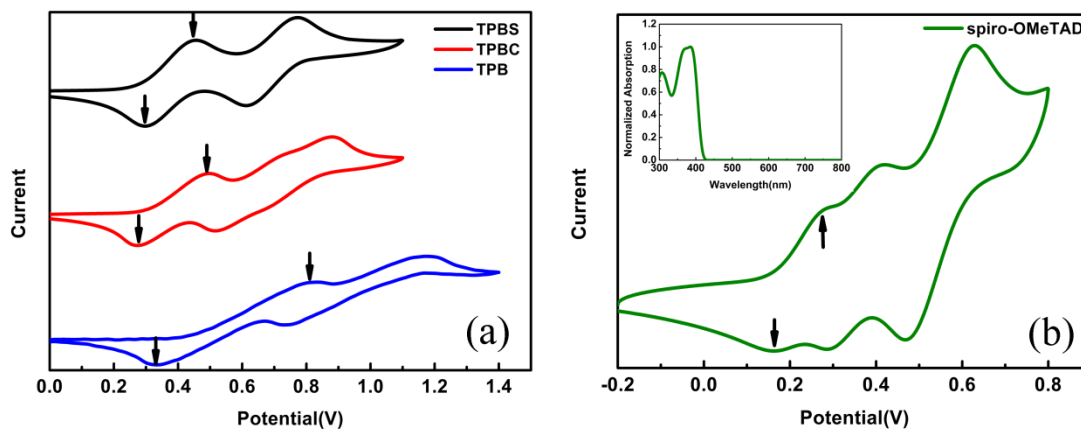


Figure S1 (a) CV curves of TPBS, TPBC and TPB; (b) CV curve and normalized absorption spectrum of spiro-OMeTAD.

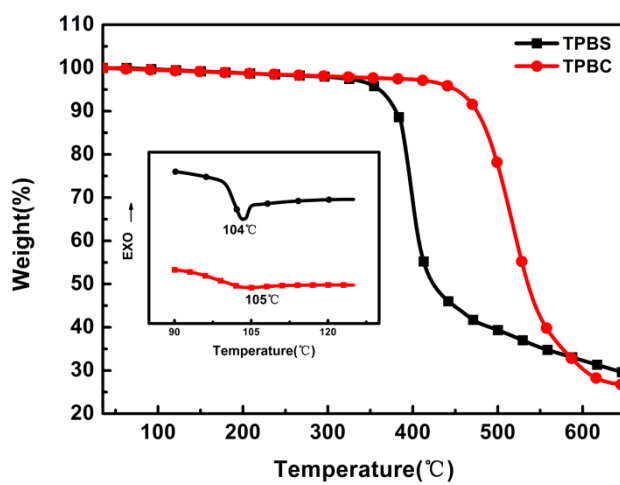


Figure S2 DSC and TGA thermograms of TPBS and TPBC.

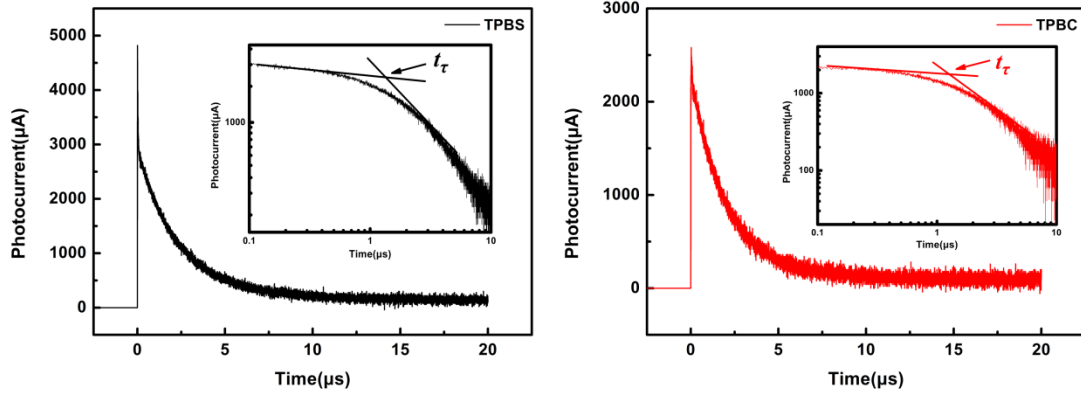


Figure S3 Representative TOF transients for TPBS and TPBC at room temperature.

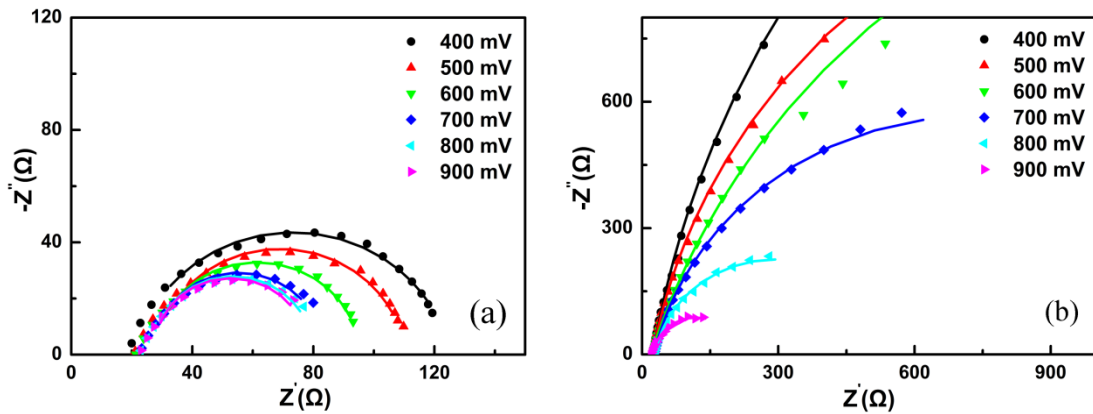


Figure S4 Nyquist plots of the device based on p-type doped TPBS (a) and TPBC (b) in the dark over different forward biases.

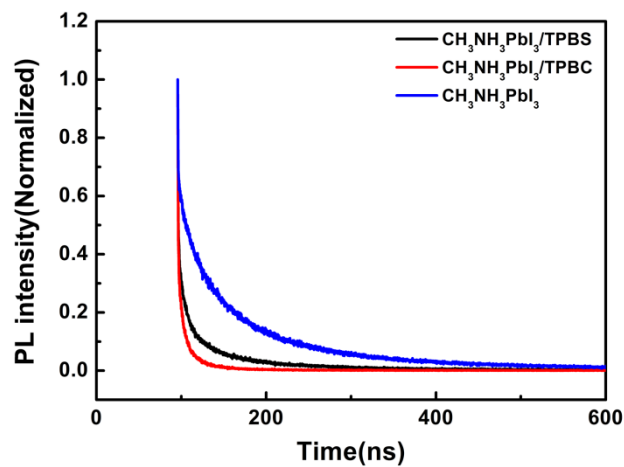


Figure S5 Photoluminescence spectra in the absence and presence of TPBS and TPBC, monitored at 775nm during the transformation, excitation at 445nm.

Table S1 Photovoltaic parameters of perovskite solar cells based on different **TPBC** concentration

concentration/mg·mL ⁻¹	$J_{sc}/\text{mA}\cdot\text{cm}^{-2}$	V_{oc}/mV	FF	$\eta/\%$
5	10.58	816	0.61	5.29
20	19.32	942	0.72	13.10
60	15.44	858	0.53	7.04
100	11.94	837	0.31	3.08

Table S2 Photovoltaic parameters from ten cells with **TPBS** and **TPBC**

HTM	Cell	$J_{sc}/\text{mA}\cdot\text{cm}^{-2}$	V_{oc}/mV	FF	$\eta/\%$
TPBS	1	15.75	932	0.70	10.28
	2	15.95	921	0.70	10.28
	3	15.72	942	0.69	10.22
	4	15.58	932	0.70	10.16
	5	15.63	921	0.68	9.79
	6	15.56	921	0.69	9.89
	7	15.24	921	0.69	9.68
	8	16.35	921	0.64	9.64
	9	15.09	900	0.69	9.37
	10	15.21	921	0.66	9.25
Average		15.61	923	0.68	9.86
TPBC	1	19.32	942	0.72	13.10
	2	19.41	932	0.72	13.02
	3	19.35	932	0.70	12.62
	4	19.21	932	0.70	12.53
	5	19.29	911	0.71	12.48
	6	19.56	911	0.70	12.47
	7	19.24	911	0.71	12.44
	8	19.22	911	0.71	12.43
	9	19.01	890	0.73	12.35
	10	19.44	900	0.70	12.25
Average		19.31	917	0.71	12.57

References

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