Supplementary Information for

3D hole-transporting materials based on coplanar quinolizino acridine for highly efficient perovskite solar cells†

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Syntheses of TTPA-OMeTPA and compound 3:

**Fig. S1.** Synthesis of TTPA-OMeTPA.

**Fig. S2.** Synthetic route of TDT-OMeTPA.
**Materials**

All reagents and solvents were used as received. Methylbenzene, tetrahydrofuran (THF) and N,N’-dimethylformamide (DMF) were distilled with CaH₂. O.O’O’’-amino-trisbenzoic acid-trimethylester (1) was synthesized by a reported method [26]. NMR spectra were measured using Bruker 400 MHz FT-NMR and 500 NMR spectrometers. MALDI-TOF (matrix-assisted laser desorption ionization time-of-flight) analysis was performed on Bruker Daltonics Ultraflex MALDI TOF/TOF Mass Spectrometer, using α-Cyano-4-hydroxycinnamic acid as matrix.

**Synthetic procedures**

4,4,8,8,12,12-hexakis(4-hexylphenyl)-8,12-dihydro-4H-benzo[1,9]quinolizino[3,4,5,6-def-g]acridine (3)

To a solution of p-bromotoluene (3.87 g, 22.6 mmol) in dry diethyl ether (30 ml) was added slowly a 2.45 M n-butyllithium/hexane solution (9.3 ml, 22.8 mmol) at -10 °C (ice-salt bath). The resulting mixture was allowed to stir for 1 h at -10 °C, and then a solution of O.O’O’’-amino-trisbenzoic acid-trimethylester (1) (0.90 g, 2.15 mmol) in 20 ml dry THF was added dropwise. After the addition, the mixture was allowed to warm to room temperature and stirred overnight. Then adding minimum water to the mixture solution to quench the reaction, and excess solvent was evaporated. The crude product was treated with boiling ethanol and filtered after cooling. The residue was washed with water and ethanol, then dried under vacuum. The dried solid was dissolved in boiling acetic acid (30 ml) and concentrated HCl (aq) (3 ml) was added dropwise. After refluxed for 3 hours, the mixture was poured into ice water (200 ml). The sediment was collected and washed twice with ethanol, then purified by column chromatography on silica gel using 10 : 1 petroleum ether/ethyl acetate as the eluent. Recrystallization from ethanol to afford the product as white crystals (yield: 85%). 1H NMR (500 MHz, CDCl₃): δ, [ppm]: 6.97 (t, 3H, J = 7.60 Hz), 6.86 (d, 18H, J = 7.85 Hz), 6.56 (d, 12H, J = 8.05 Hz), 2.31 (s, 18H).

2,6,10-tribromo-4,4,8,8,12,12-hexakis(4-hexylphenyl)-8,12-dihydro-4H-benzo[1,9]quinolizino[3,4,5,6-def-g]acridine (4)

To a solution of 3 (1.0 g, 1.22mmol) in 20 mL of chloroform was added NBS (0.68 g, 3.82 mmol) at 0 °C. The mixture was stirred for 12 h at room temperature and
then filtered. The filtrate was washed with water three times, and the organic layers were dried with anhydrous sodium sulfate. After removal of organic solvent, the resulting solid was recrystallized from ethanol to give a white solid (Yield: 97%). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$, [ppm]: 6.94 (s, 6H), 6.88 (d, 12H, $J = 7.85$ Hz), 6.57 (d, 12H, $J = 8.05$ Hz), 2.33 (s, 18H).

**Measurements**

$^1$H and $^{13}$C NMR spectra were measured using Bruker 400 MHz FT-NMR and 500 NMR spectrometers. Ultraviolet-visible ($UV$-$vis$) spectroscopy was investigated with a Shimadzu UV-3600 in dichloromethane solution using a 10 mm quartz cuvette that dissolves the corresponding HTMs. The cyclic voltammetry (CV) was determined with a CorrTest electrochemical workstation using a three-electrode cell with a glassy carbon disk electrode, a platinum wire, Ag/AgCl were used as the working electrode, auxiliary electrode, and reference electrode, respectively. 0.1 M tetrabutylammonium perchlorate (TBAP) was applied as the electrolyte in DMF solution at a scan rate of 50 mV s$^{-1}$. Ferrocene was added to each sample solution, and the ferrocenium/ferrocene (Fc/Fc$^+$) redox couple was used as a potential internal reference. Fluorescent emission spectra were recorded on an Agilent Cary100 spectrometer. The morphologies of HTM films were investigated using FE-SEM (Tescan Mira 3 LMU FEG) and Agilent 5500 AFM. Differential scanning calorimetry (DSC) of HTMs was recorded with scan rate of 10 °C min$^{-1}$ (DSC, TA Instruments-Waters LLC, USA, Q2000).
**Fig. S3.** HOMO and LUMO of TTPA-OMeTPA.

**Fig. S4.** DFT calculated molecule structure of TTPA-OMeTPA in vertical (a) and parallel (b) directions of the whole 2D molecule.
**Fig. S5.** DFT calculated molecule structure of TDT-OMeTPA in parallel direction of the 2D coplanar triphenylamine.

**Fig. S6.** Photo-luminance emission of TDT-OMeTPA, TTPA-OMeTPA and Spiro-OMeTAD.
Fig. S7. SEM image of Spiro-OMeTAD layer accumulated on perovskite layer.

Fig. S8. Line profiles of AFM amplitude images for three HTM layers.

Fig. S9. DSC curves of TDT-OMeTPA and Spiro-OMeTAD.
Fig. S10. $J-V$ characteristics of space-charge-limited current of TDT-OMeTPA, TTPA-OMeTPA and Spiro-OMeTAD.

Fig. S11. Cyclic voltammetry (CV) curves of TDT-OMeTPA, TTPA-OMeTPA and Spiro-OMeTAD.
**Fig. S12.** Energy level diagram for the corresponding materials and HTMs used in TiO$_2$/mixed-perovskite/HTM/Ag devices. Calculated HOMO and LUMO values are presented as dashed lines, experimental levels as solid lines, respectively.

**Fig. S13.** The $^1$H NMR spectrum of compound 3 in CDCl$_3$. 
**Fig. S14.** The $^1$H NMR spectrum of compound 4 in CDCl$_3$.

**Fig. S15.** The $^1$H NMR spectrum of TDT-OMeTPA in CDCl$_3$. 
Fig. S16. FT-IR spectra of TDT-OMeTPA and TTPA-OMeTPA.
**Fig. S17.** The $^1$H NMR spectrum of TTPA-OMeTPA in CDCl$_3$. 