Electronic Supplementary Material (ESI) for New Journal of Chemistry.
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Supporting Information

Low-cost synthesis of heterocyclic spiro-type hole transporting materials for perovskite solar cell applications

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1. Synthesis of 2,2',7,7'-tetrabromospiro[fluorene-9,9'-xanthene] (SFX-Br4)

Spiro[fluorene-9,9'-xanthene] (SFX) (10 g, 0.03 mol) was dissolved in100 mL of CH_2Cl_2 and a solution of Br_2 in conc. $HBr_{(aq)}$ (12 mL, 0.24 mol) was added drop wise under nitrogen atmosphere. The resulting mixture was stirred 16 hrs under room temperature. After the reaction was complete, the solution was poured into large amount of water containing 3 g sodium thiosulfate. The organic layer was separated (with a separating funnel), dried with magnesium sulfate and the half volume of the solvent was evaporated, and recrystallization with ethanol/chloroform (v/v = 1:1) at low temperature to get white crystalline solid (16 g, yield = 78%). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.68-7.66 (d, 2H), 7.59-7.55 (d, 2H), 7.38-7.34 (d, 2H), 7.23 (s, 2H), 7.15-7.12 (d, 2H), 6.45-6.44 (s, 2H). ^{13}C NMR (300 MHz, $CDCl_3$) δ (ppm): 169.7, 155.4, 149.8, 137.4, 132.0, 130.2, 128.9, 124.6, 122.7, 121.8, 119.0, 116.0, 113.1.

2. Synthesis of 2,2',7,7'-tetrabromospiro[fluorene-9,9'-thioxanthene] (SFT-Br4)

Spiro[fluorene-9,9'-thioxanthene] (SFT) (10 g, 0.028 mol) was dissolved in100 mL of CH_2Cl_2 and a solution of Br_2 in conc. $HBr_{(aq)}$ (12 mL, 0.24 mol) was added drop wise under nitrogen atmosphere. The resulting mixture was stirred for 16 hrs under room temperature. After the reaction was complete, the solution was poured into water containing sodium thiosulfate and the organic layer was separated (with a separating funnel), dried with magnesium sulfate and then half volume of the solvent was evaporated and recrystallization with ethanol/chloroform (v/v= 1:1) at low temperature to get white crystalline solid (13.8 g, yield = 73%). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.83-7.47 (m, 6H), 7.44-7.30 (m, 4H), 6.59-6.56 (d, 2H). ^{13}C NMR (300 MHz, $CDCl_3$) δ (ppm): 154.50, 152.0, 139.1, 138.0, 137.3, 137.0, 132.2, 131.9, 130.7, 129.6, 129.4, 128.5, 128.1, 127.7, 125.8, 122.6, 121.9, 120.6, and 119.9.

3. Synthesis of SFX-TPAM

SFX-Br4 (180 mg, 0.3 mmol) and $Pd(PPh_3)_4$ (17 mg, 0.015 mmol) were dissolved in 10/1 mL anhydrous toluene/DMF and TPAM-$SnMe_3$ (1046 mg, 2.4 mmol) was added into the solution. The mixture was refluxed for 8 hours under argon atmosphere. After the reaction

complete, cooling the mixture to room temperature, filtered it, and the crude solution was extracted by dichloromethane/water (50 mL/200 mL) using a separating funnel, then washed with brine and finally dried with anhydrous magnesium sulfate. The solvent was removed by rotary evaporator and the residue was purified by column chromatography (CH_2Cl_2/hexane = 1:25, v/v) on a silica gel to get a white powder SFX-TPAM (85% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.83-7.80 (d, 2H), 7.61-7.60 (d, 2H), 7.58-7.35 (m, 8H), 7.09-6.91 (m, 46H), 6.88-6.68 (d, 2H), 2.31-2.29 (s, 24H). ^{13}C NMR (300 MHz, $CDCl_3$) δ (ppm): 155.9, 150.5, 147.5, 147.2, 145.2, 140.7, 138.1, 135.9, 132.5, 132.4, 129.8, 127.5, 127.1, 126.4, 125.9, 125.2, 124.5, 123.6, 122.7, 122.6, 120.2, 117.0, 29.7, 20.7. MALDI-HRMS (m/z): calculated 1417.6718; found ($M+H^+$) 1417.6707.

4. Synthesis of SFX-TPA

The SFX-Br4 (180 mg, 0.3 mmol) and $Pd(PPh_3)_4$ (17 mg, 0.015 mmol) were dissolved in 10/1 mL anhydrous toluene/DMF and then TPA-$SnMe_3$ (906 mg, 0.8 mmol) was added into the solution. The mixture was refluxed for 8 hours under argon atmosphere. After the reaction complete, cooling the mixture to room temperature, filtered it and the crude solution was extracted by dichloromethane/water (50 mL/200 mL), then washed with brine and finally dried with anhydrous magnesium sulfate. The solvent was removed by rotary evaporator and the residue solid was purified by column chromatography using CH_2Cl_2/hexane = 1:20, v/v as an eluent on a silica gel to get a white powder SFX-TPA (78% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.64-7.63(d, 2H), 7.617-7.611 (d, 2H), 7.44-7.40 (m, 8H), 7.32-7.19 (m, 25H), 7.14-6.95 (m, 39H), 6.709-6.702 (s, 2H). ^{13}C NMR (300 MHz, $CDCl_3$) δ (ppm): 156.0, 150.6, 147.6, 147.2, 146.7, 140.6, 138.2, 135.8, 134.7, 134.2, 129.2, 129.1, 127.6, 127.3, 126.5, 126.0, 125.1, 124.3, 124.2, 123.88, 123.82, 122.88, 122.80, 120.32, 117.16, 29.7. MALDI-HRMS (m/z): calculated 1305.5466; found ($M+H^+$) 1305.5472

5. Synthesis of SFT-TPAM

SFT-Br4 (180 mg, 0.27 mmol) and $Pd(PPh_3)_4$ (17 mg, 0.015 mmol) were dissolved in 10/1 mL anhydrous toluene/DMF and then TPAM-$SnMe_3$ (945 mg, 2.16 mmol) was added into the solution. The mixture was refluxed for 8 hours under argon atmosphere. After the reaction complete, cooling the mixture to room temperature, filtered it and the crude solution was extracted by dichloromethane/water (50 mL/200 mL), then washed with brine and finally dried with anhydrous magnesium sulfate. The solvent was removed by rotary evaporator and the residue solid was purified by column chromatography (CH_2Cl_2/hexane = 1:20, v/v) on a silica gel column to get a white powder SFT-TPAM (71% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.86 (s, 2H), 7.80-7.77 (d, 2H), 7.62-7.48 (d, 2H), 7.48-7.35 (m, 8H), 7.08-6.99 (m, 32H), 6.95-6.87 (m, 14H), 2.32-2.30 (s, 24H). ^{13}C NMR (300 MHz, $CDCl_3$) δ (ppm): 154.6, 150.1, 147.3, 146.8, 145.6, 140.1, 138.4, 135.2, 132.8, 132.1, 128.2, 127.3, 126.9, 125.8, 125.2, 124.5, 123.6, 122.7, 121.2, 120.8, 117.6, 28.3, 20.1. MALDI-HRMS (m/z): calculated 1433.6489; found ($M+H^+$) 1433.6506.

6. Synthesis of SFT-TPA

SFT-Br4 (180 mg, 0.27 mmol) and $Pd(PPh_3)_4$ (17 mg, 0.015 mmol) were dissolved in 10/1 mL anhydrous toluene/DMF and then TPA-$SnMe_3$ (881 mg, 2.16 mmol) was added into the solution. The mixture was refluxed for 8 hours under argon atmosphere. After the reaction complete, cooling the mixture to room temperature, filtered it and the crude solution was extracted by dichloromethane/water (50 mL/200 mL), then washed with brine and finally dried with anhydrous magnesium sulfate. The solvent was removed by rotary evaporator and the residue solid was purified by column chromatography (CH_2Cl_2/hexane = 1:20, v/v) on a silica gel to get a white powder SFT-TPA (73% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.88 (s, 2H), 7.83-7.81(d, 2H), 7.65-7.62 (d, 2H), 7.50-7.32 (m, 10H), 7.28-7.20 (m, 20H), 7.12-7.94 (m, 40H), 6.89 (s, 2H). ^{13}C NMR (300 MHz, $CDCl_3$) δ (ppm): 155.2, 147.5, 147.2, 147.0, 140.5, 138.4, 138.1, 137.6, 134.7, 133.9, 129.4, 129.2, 128.7, 127.6, 127.1126.6, 126.5, 126.4, 125.4, 124.4, 123.8, 123.7, 123.5, 122.9, 120.4, 60.6. MALDI-HRMS (m/z): calculated 1321.5237; found ($M+H^+$) 1321.5270.

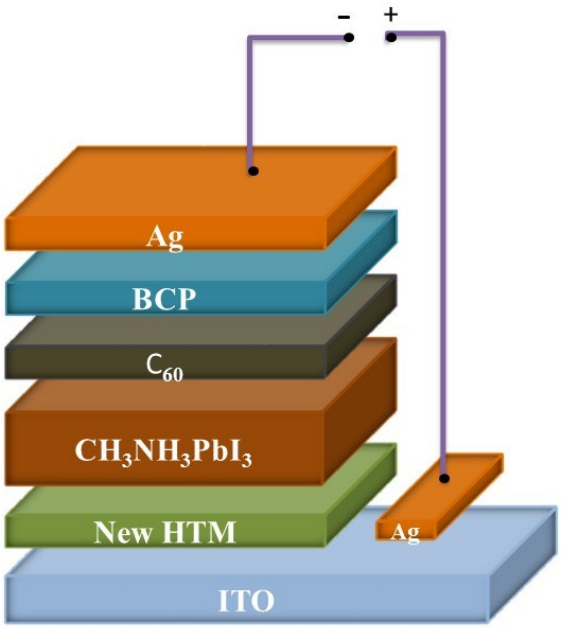

Figure S1: The architecture and components of the inverted perovskite solar cell.

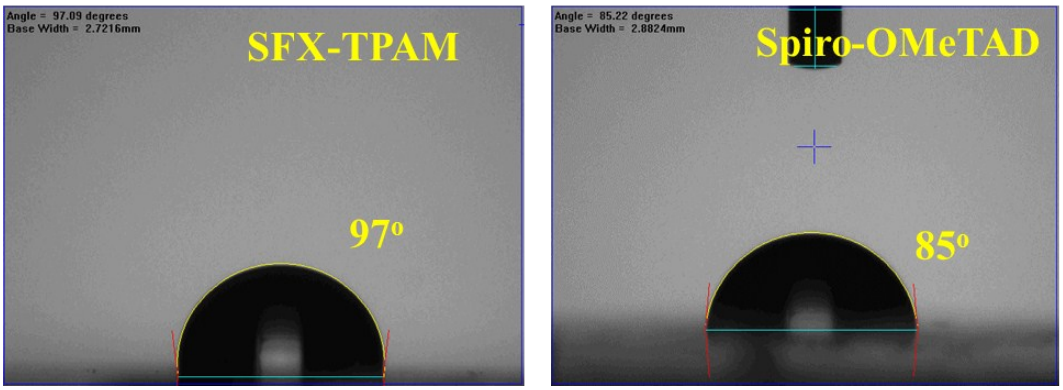

Figure S2: The wetting of H_2O on the surface of SFX-TPAM and spiro-OMeTAD films.

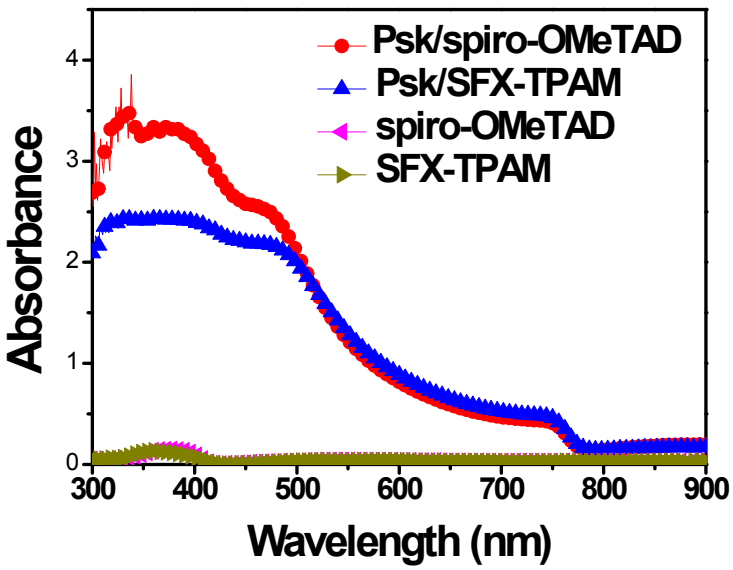

Figure S3: UV/Vis absorption spectra of SFX-TPAM and spiro-OMeTAD films as well as $MAPbI_3$ films deposited on them.

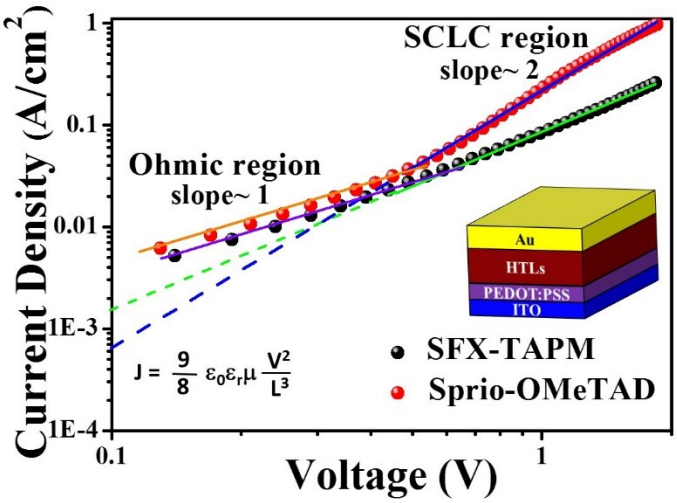

Figure S4: The I-V curves of the hole only devices based on SFX-TPAM and spiro-OMeTAD HTLs (insert: the hole mobility calculated from the curves and the architecture of the hole only device).

The Space-Charge-Limited Current (SCLC) was widely used to estimate the carrier mobility of thin organic semiconductor film. The I-V characteristic of thin semiconductor film between two electrodes may show different behaviors, depends on the applied voltage. In the Ohmic region (in low voltage) where the current is mainly driven by the mobile charge carriers present in the material, so that the charge carrier density need to be known to calculate the mobility. Nevertheless, in the space-charge limited current (SCLC) regime (higher voltage), the current is dominated by charge carriers injected from the contacts and the current-voltage characteristics becomes quadratic (in other words $I \sim V^2$). Therefore in SCLC region the slope of logI vs logV is equal to 2. The mobility of the sample can be calculated using the following equation according to the Mott-Gurney's law. The principle of using SCLC to measure the hole mobility was added in the supporting information of the revised paper.

$$J = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu \frac{V^2}{L^3}$$