Tetrakis(4-aminophenyl)ethene as Efficient and Robust Hole Transport Material for Methyl Ammonium Lead Iodide Perovskite

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Figure S1. Thermogravimetric Analysis of TAE-1 at scan rate of 10 °C/min

Figure S2. Differential Scanning Calorimetry of TAE-1 with scan rate of 20 °C/min
2. Mobility measurements

**Figure S3:** Hole only TAE-1 (up), Spiro-OMeTAD (down) devices J-V at space charge limited conditions. The red symbols correspond to the measurement under illumination and the blue symbols correspond to the measurement under dark.
3. Experimental Section

**General.** All solvents were dried according to standard procedures. Reagents were used as purchased. All air-sensitive reactions were carried out under argon atmosphere. Flash chromatography was performed using silica gel (Merck, Kieselgel 60, 230-240 mesh or Scharlau 60, 230-240 mesh). Analytical thin layer chromatography (TLC) was performed using aluminum coated Merck Kieselgel 60 F254 plates. NMR spectra were recorded on a Bruker Advance 300 (\(^1\)H: 400 MHz; \(^{13}\)C: 101 MHz) spectrometer at 298 K using partially deuterated solvents as internal standards. Coupling constants (J) are denoted in Hz and chemical shifts (δ) in ppm. Multiplicities are denoted as follows: s = singlet, d = doublet, t = triplet, m = multiplet. FT-IR spectra were recorded on a Bruker Tensor 27 (ATR device) spectrometer. UV-Vis spectra were recorded in a Varian Cary 50 spectrophotometer. Mass spectra Matrix assisted Laser desorption ionization (coupled to a Time-of-Flight analyzer) experiments (MALDI-TOF) were recorded on a MAT 95 thermo spectrometer and a Bruker REFLEX spectrometer respectively. Cyclic voltammetry (CV) experiments were performed on a Windows®-driven Autolab PGSTAT 30 electrochemical analyzer at room temperature with a three-electrode configuration in CH\(_2\)Cl\(_2\) solutions containing the substrate (typically about 1 mmol dm\(^{-3}\)) and the supporting electrolyte. A platinum (\(\varnothing\ 1\) mm) discs served as the working electrode, a platinum wire (\(\varnothing\ 1\) mm) and a commercial Ag/AgNO\(_3\) electrode being the counter and the reference electrodes, respectively. Both the counter and the reference electrodes were directly immersed in the electrolyte solution. Tetrabutylammonium perchlorate (n-Bu\(_4\)NClO\(_4\)) was employed as the supporting electrolyte in 0.1M. Solutions were stirred and deaerated by bubbling argon for a few minutes prior to each voltammetric measurement. The scan rate was 0.05 V s\(^{-1}\) unless otherwise specified. Thermogramiteric analysis (TGA) was performed using a TA Instruments TGAQ500 with a ramp of 10 °C/min under N\(_2\) form 100 to 1000 °C. DSC was run on a Discovery DSC from TA instruments. Three cycles were recorded under nitrogen, heating (until 400 °C) and cooling (50 °C) at 20 °C/min of scanning rate.

**Device Fabrication:** A dense blocking layer of TiO\(_2\) (0.65 ml of Ti (IV) isopropoxide, 0.38 ml of Acetylacetone in 5 ml of Ethanol) was spin coated at 3000rpm for 60s onto the FTO. The substrates were calcined at 500°C for 30min and immersed in a TiCl\(_4\) (40mM) solution at 70°C for 30 min. A solution of TiO\(_2\) paste (18 NR-T Dyesol) in ethanol (2:7 w/w) was spin coated at 5000rpm for 30 seconds. After that, substrates were heated at 325°C for 30 min, 375°C for 5 min, 450°C for 15 min and 500°C for 30 min. CH\(_3\)NH\(_3\)I (MAI) was synthesized as reported previously\(^1\). The MAI synthesized and PbCl\(_2\) were mixed in DMF in 3:1 molar ratio. Perovskite precursor was deposited onto the substrate by spin coating at 2000rpm for 45 sec at controlled humidity of 20%. Substrates were heated at 100°C for 1 hour. A solution of HTM (TAE-1, Spiro-OMeTAD) 0.056M, TBP 0.19M and LiTFSI 0.032M in Chlorobenzene was deposited by spin coating at 2000rpm for 60 seconds. Finally 80nm of Au was deposited by thermal
4. Synthetic details and characterization

[Scheme S1. Reagents and conditions: a) 4-idoanisole, Cu powder, K$_2$CO$_3$, 18-crown-6, nitrobenzene, 188 °C, 63 %; b) Zn dust, TiCl$_3$ 1M, THF/CH$_2$Cl$_2$, reflux, 72 %.

4,4′-Bis(N,N-(4,4′-dimethoxydiphenylamino))benzophenone.

A mixture of 4,4′-Diaminobenzophenone (580 mg, 2.73 mmol), 4-Iodoaniline (10.25 g, 43.79 mmol), Cu powder (1 g, 15.73 mmol), K$_2$CO$_3$ (4.53 g, 32.77 mmol), 18-Crown-6 (57 mg, 0.21 mmol) in nitrobenzene (5 mL) were heated at 188 °C for 72 hours. The reaction mixture was extracted with CHCl$_3$ (3 x 100 ml) and washed with saturated solution of NH$_4$Cl. The combined organic extracts were dried over Na$_2$SO$_4$. After removal the solvents under reduced pressure the crude product was purified by flash column chromatography (silica gel, CH$_2$Cl$_2$) to afford as a yellow solid (1.09 g, 1.71 mmol), yield 63%.

$^1$H NMR (400 MHz, d$_6$-Acetone, 298 K) $\delta$ 7.60 (d, $J$ = 8.9 Hz, 4H), 7.18 (d, $J$ = 9.0 Hz, 8H), 6.97 (d, $J$ = 9.0 Hz, 8H), 6.78 (d, $J$ = 8.9 Hz, 4H), 3.81 (s, 12H); $^{13}$C NMR (101 MHz, CDCl$_3$, 298 K) $\delta$ 193.9, 156.9, 152.1, 139.7, 131.7, 129.2, 127.8, 117.2, 115.0, 55.6; FTIR (neat) $\nu$ 3071, 2972, 2893, 1519, 1479, 1274, 1170, 826 cm$^{-1}$; HRMS calcd for C$_{64}$H$_{46}$N$_4$O$_8$ [M$^+$], 636.3285; found 636.3292.

Tetra{4-[N,N-(4,4′-dimethoxydiphenylamino)]-phenylethene (TAE-1)

Compound 2 (830 mg, 1.30 mmol) in dry THF (10 ml) was added to a slurry of Zn dust (426 mg, 6.51 mmol) and TiCl$_3$ (1M in THF:CH$_2$Cl$_2$ (1:2), 3.25 mL, 3.25 mmol) and heated at reflux for 4 hours under inert atmosphere. The reaction mixture was filtered and concentrated under reduced pressure. The crude product was purified by flash column chromatography (silica gel, CH$_2$Cl$_2$) to afford TAE-1 as a yellow solid, yield 72%. The resulting solid was washed several times with acetone. $^1$H NMR (400 MHz, CDCl$_3$, 298 K) $\delta$ 7.01 (d, $J$ = 8.7 Hz, 16H), 6.87 (d, $J$ = 6.7 Hz, 8H), 6.79 (d, $J$ = 8.7 Hz, 16H), 6.69 (d, $J$ = 8.5 Hz, 8H), 3.77 (s, 24H); $^{13}$C NMR (101 MHz, CDCl$_3$, 298 K) $\delta$ 155.6, 146.6, 141.2, 137.1, 132.3, 126.3, 120.0, 114.7, 55.61; FTIR (neat) $\nu$ 3036, 2932, 2833, 1500, 1238, 1034, 826 cm$^{-1}$; HRMS calcd for C$_{82}$H$_{72}$N$_4$O$_8$ [M$^+$], 1240.5345; found 1240.5334.
5. $^1$H NMR and $^{13}$C NMR for all the compounds

**Figure S4:** $^1$H NMR (400 MHz, d$_6$-Acetone, 298 K) of compound 2.
Figure S5: $^{13}$C NMR (100 MHz, CDCl$_3$, 298 K) of compound 2.

Figure S6: $^1$H NMR (400 MHz, CDCl$_3$, 298 K) of compound TAE-1
**Figure S7:** $^{13}$C NMR (100 MHz, CDCl$_3$, 298 K) of compound **TAE-1**.

6. Device optimization

**Table S1:** J-V parameters (averages)

<table>
<thead>
<tr>
<th>HTM</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (mV)</th>
<th>FF (%)</th>
<th>$\eta$ (%)</th>
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<tbody>
<tr>
<td>TAE-1</td>
<td>17.16 (17.22)</td>
<td>814 (885)</td>
<td>62.9 (72.2)</td>
<td>8.93 (11.02)</td>
</tr>
<tr>
<td>Spiro-OMeTAD</td>
<td>21.00 (21.40)</td>
<td>864 (885)</td>
<td>64.3 (71.4)</td>
<td>11.71 (13.53)</td>
</tr>
</tbody>
</table>

Averages values. (the number of devices was 5 for both HTM). The best PCEs are provided in parentheses.

7. References