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

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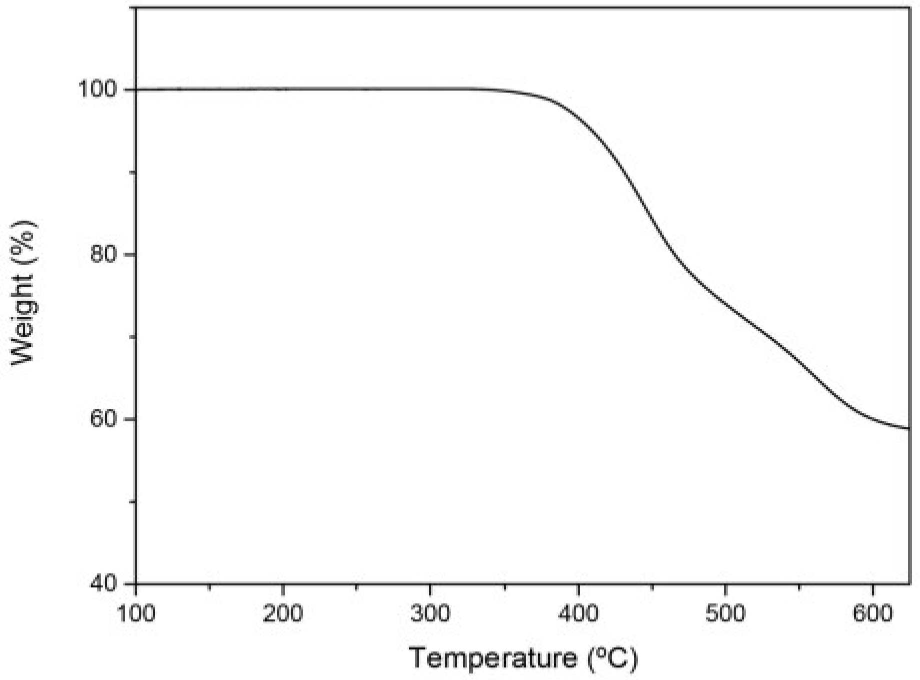


Figure S1. Thermogravimetric Analysis of **TAE-1** at scan rate of 10 ºC/min

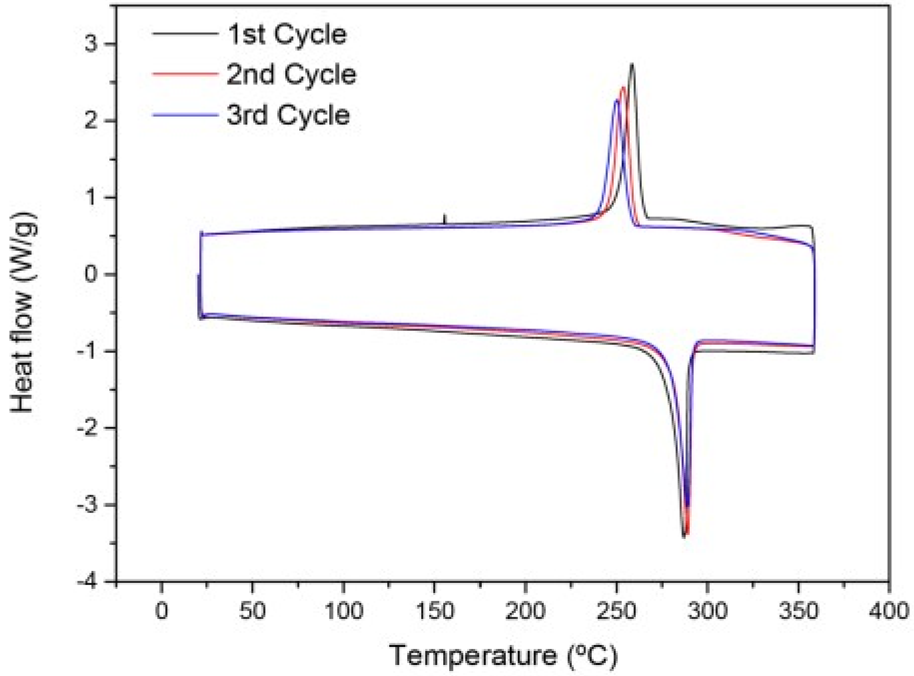


Figure S2. Differential Scanning Calorimetry of **TAE-1** with scan rate of 20 ºC/min

2. Mobility measurements

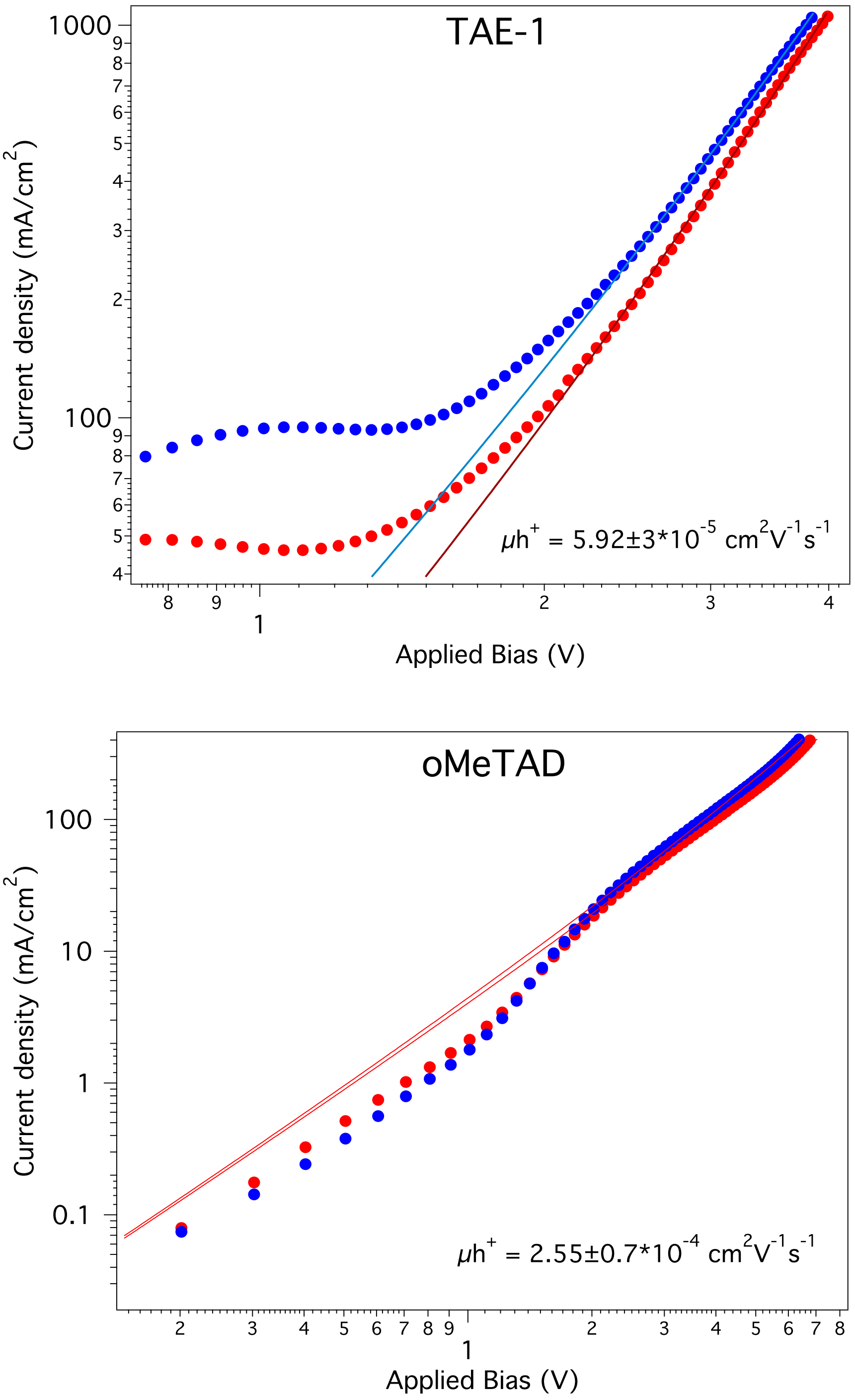


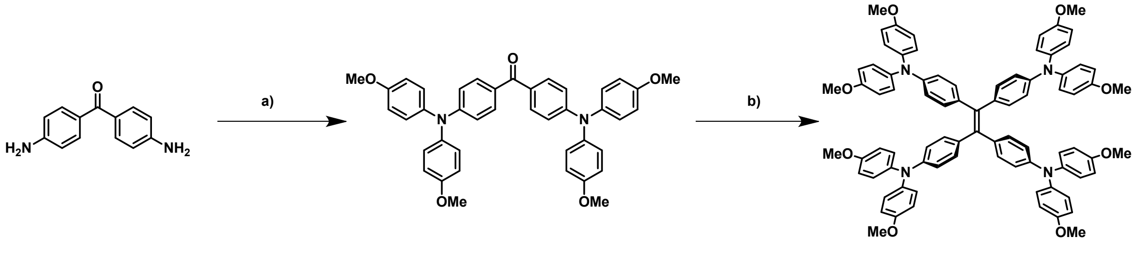
Figure S3: Hole only **TAE-1** (up), Spiro-OMeTAD (down) devices J-V at space charge limited conditions. The red symbols correspond to the measurement under illumination and the blue symbols correspond to the measurement under dark.

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. UVVis 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_2Cl_2 solutions containing the substrate (typically about 1 mmol dm^{-3}) and the supporting electrolyte. A platinum (ø 1 mm) discs served as the working electrode, a platinum wire (ø 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_4NClO_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 ^{o}C/min under N_2 form 100 to 1000 ^{o}C. DSC was run on a Discovery DSC from TA instruments. Three cycles were recorded under nitrogen, heating (unitl 400 ^{o}C) and cooling (50 ^{o}C) at 20 ^{o}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 500ºC for 30min and immersed in a $TiCl_4$ (40mM) solution at 70ºC 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 325ºC for 30 min, 375ºC for 5 min, 450ºC for 15 min and 500ºC for 30 min. CH_3NH_3I (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 100ºC 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 evaporation.

4. Synthetic details and characterization



2

TAE-1

Scheme S1. *Reagents and conditions: a) 4-Iodoanisole, Cu powder, K_2CO_3, 18-crown-6, nitrobenzene, 188 °C, 63 %; b) Zn dust, $TiCl_3$ 1M, THF/CH_2Cl_2, reflux, 72 %.*

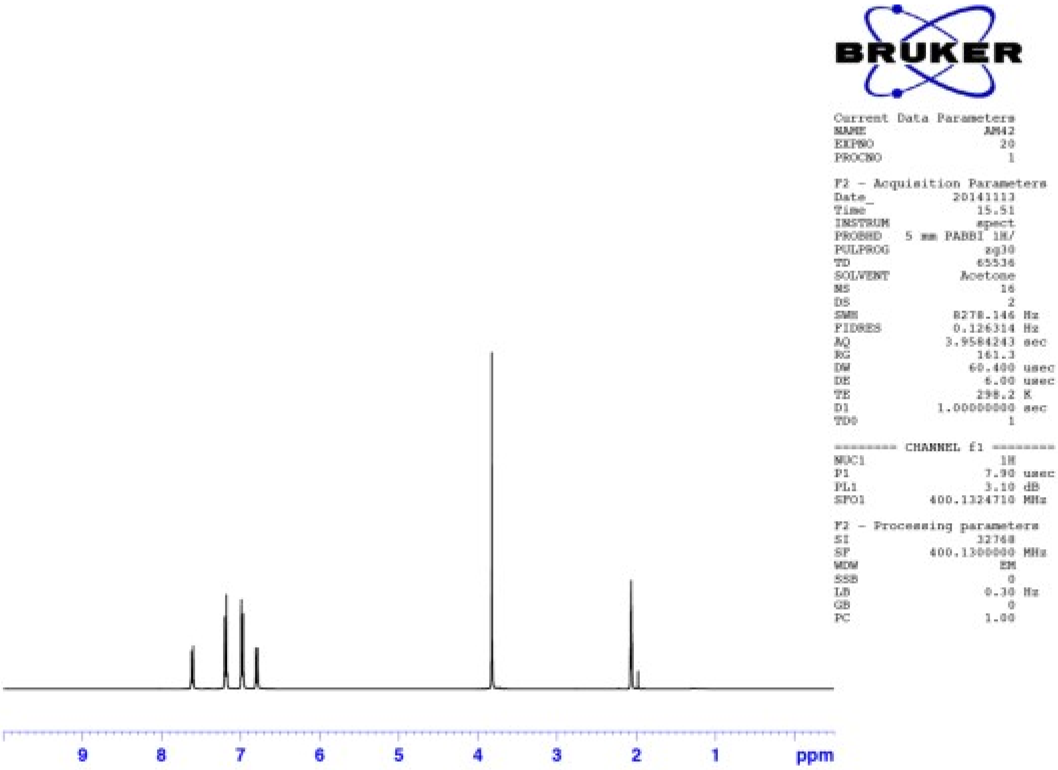
4,4′-Bis(*N*,*N*-(4,4′-dimethoxydiphenylamino))benzophenone.

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_2CO_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_4Cl. The combined organic extracts were dried over Na_2SO_4. After removal the solvents under reduced pressure the crude product was purified by flash column chromatography (silica gel, CH_2Cl_2) to afford **2** as a yellow solid (1.09 g, 1.71 mmol), yield 63%. ^1H NMR (400 MHz, d^6-Acetone, 298 K) δ 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, $CDCl_3$, 298K) δ 193.9, 156.9, 152.1, 139.7, 131.7, 129.2, 127.8, 117.2, 115.0, 55.6; FTIR (neat) ν ⍰⍰⍰⍰⍰⍰⍰⍰⍰⍰, 1635, 1591, 1504, 1311, 1276, 1240, 1170, 828 $cm^{-}1$; MALDI-TOF m/z: 636.3 [M^+].

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_2Cl_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_2Cl_2) to afford **TAE-1** as a yellow solid, yield 72%. The resulting solid was washed several times with acetone. ^1H NMR (400 MHz, $CDCl_3$, 298 K) δ 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) δ 155.6, 146.6, 141.2, 137.1, 132.3, 126.3, 120.0, 114.7, 55.61; FTIR (neat) ν 3036, 2932, 2833, 1500, 1238, 1034, 826 cm^{-1}; HRMS calcd for $C_{82}H_{72}N_4O_8$ [M^+], 1240.5345; found 1240.5334.

5. ^{1}H NMR and ^{13}C NMR for all the compounds



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DS                     2
SWH             8278.146 Hz
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AQ             3.9584243 sec
RG                 161.3
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TE                 298.2 K
D1            1.00000000 sec
TD0                    1

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F2 - Processing parameters
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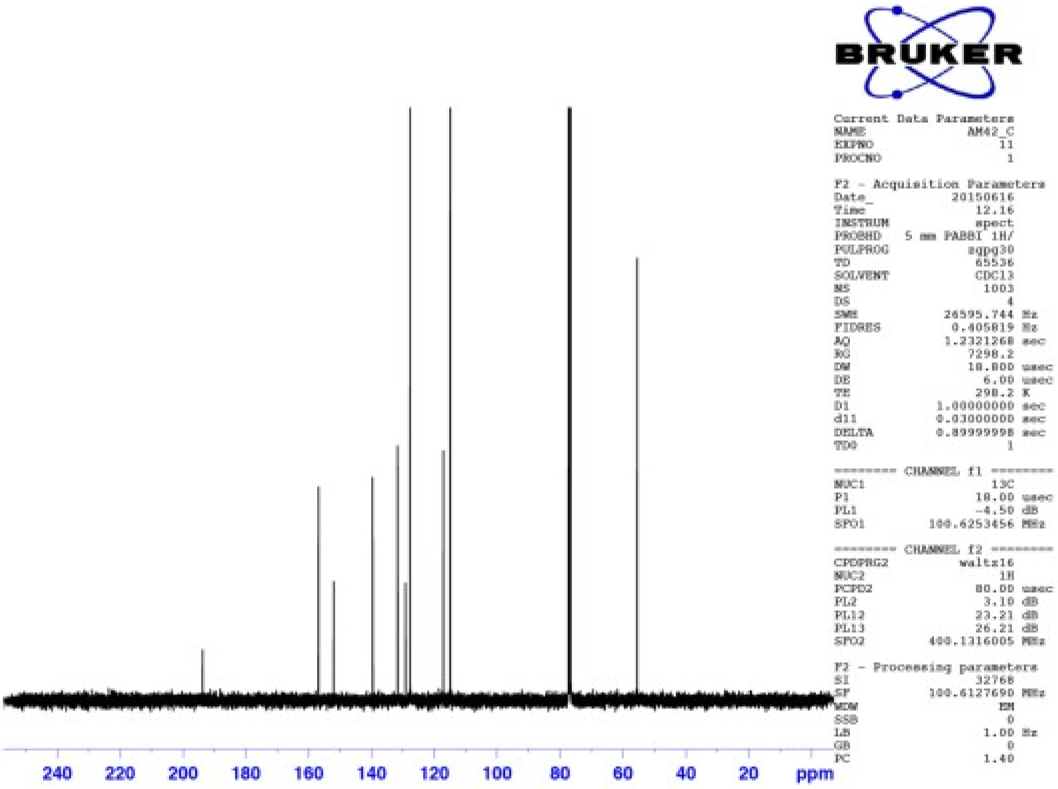
Figure S4: ^{1}H NMR (400 MHz, d^{6}-Acetone, 298 K) of compound **2**.



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DE                  6.00 usec
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TD0                    1

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======== CHANNEL f2 ========
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NUC2                  1H
PCPD2              80.00 usec
PL2                 3.10 dB
PL12               23.21 dB
PL13               26.21 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 32768
SF           100.6127690 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
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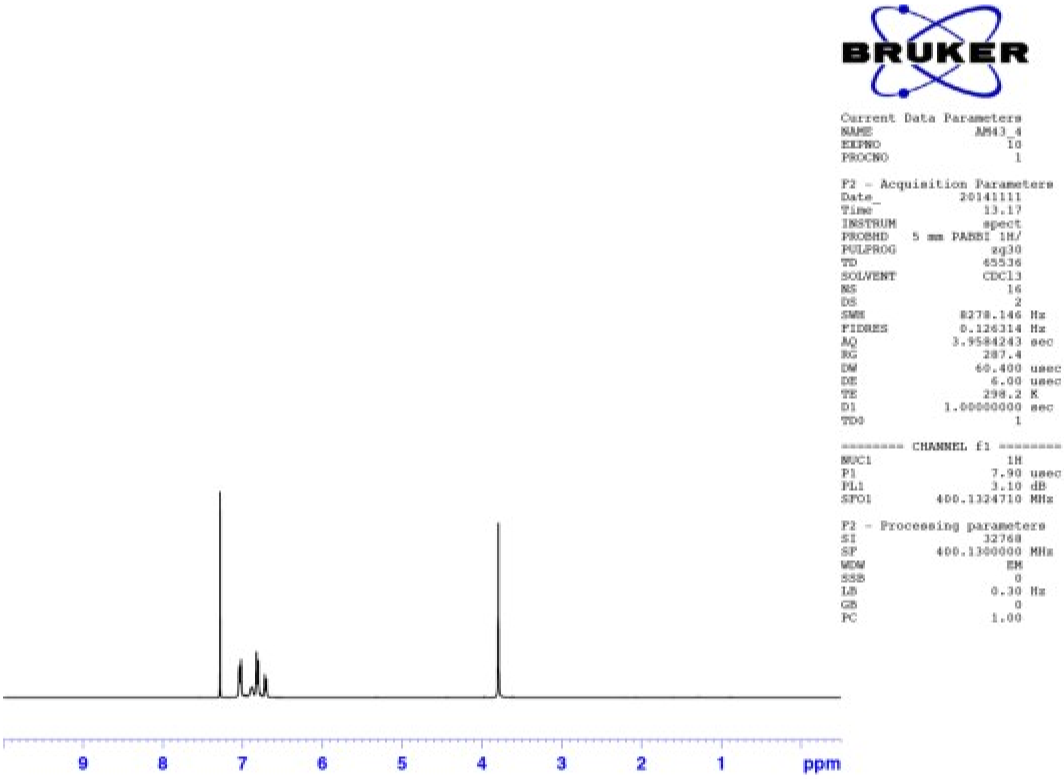
Figure S5: ^{13}C NMR (100 MHz, CDCl$_3$, 298 K) of compound **2**.



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PROCNO                1

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FIDRES         0.126314 Hz
AQ            3.9584243 sec
RG                287.4
DW               60.400 usec
DE                 6.00 usec
TE                298.2 K
D1           1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
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P1                 7.90 usec
PL1                3.10 dB
SFO1        400.1324710 MHz

F2 - Processing parameters
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WDW                  EM
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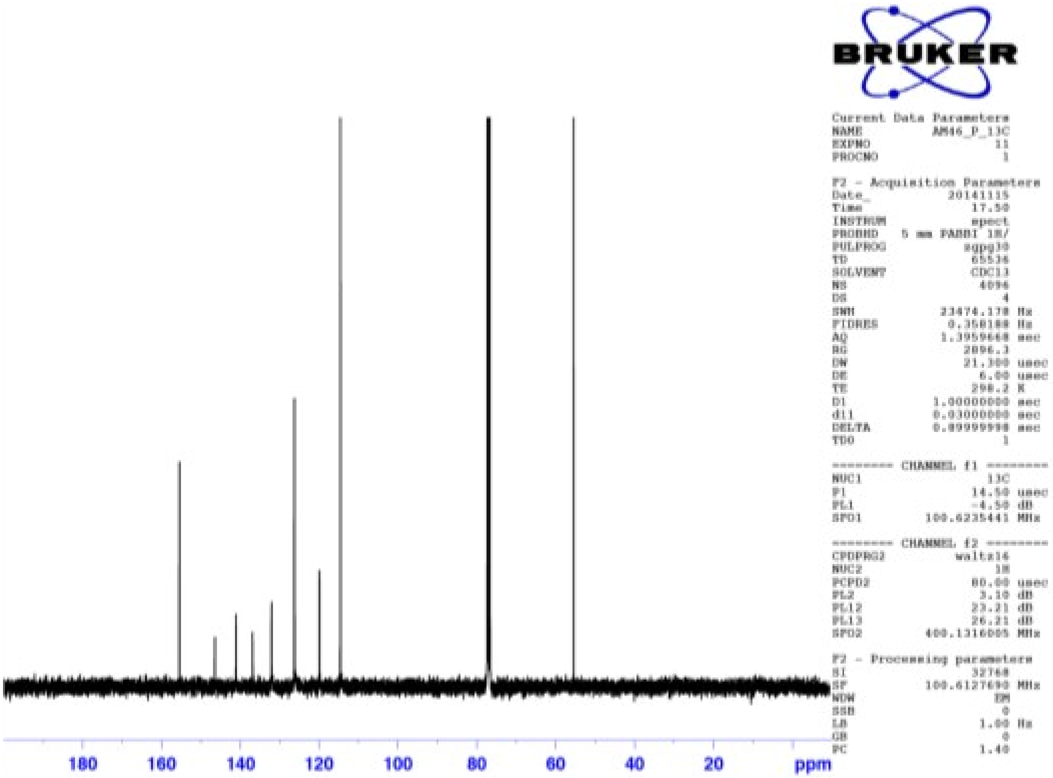
Figure S6: ^{1}H NMR (400 MHz, CDCl$_3$, 298 K) of compound **TAE-1**



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NS                  4096
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SWH            23474.178 Hz
FIDRES          0.358188 Hz
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RG                2896.3
DW                21.300 usec
DE                  6.00 usec
TE                 298.2 K
D1            1.00000000 sec
d11           0.03000000 sec
DELTA         0.89999998 sec
TD0                    1

======== CHANNEL f1 ========
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PL1                -4.50 dB
SFO1         100.6235441 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 3.10 dB
PL12               23.21 dB
PL13               26.21 dB
SFO2         400.1316005 MHz

F2 - Processing parameters
SI                 32768
SP           100.6127690 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
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Figure S7: ^{13}C NMR (100 MHz, $CDCl_3$, 298 K) of compound **TAE-1**.

6. Device optimization

Table S1: J-V parameters (averages)

HTM	J_{sc} (mA/cm^2)	V_{oc} (mV)	FF (%)	η(%)
TAE-1	17.16 (**17.22**)	814 (**885**)	62.9 (**72.2**)	8.93 (**11.02**)
Spiro-OMeTAD	21.00 (**21.40**)	864 (**885**)	64.3 (**71.4**)	11.71 (**13.53**)

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

7. References

1 – J-H. Im, C-R. Lee, J-W. Lee, S-W Park, N-G Park, *Nanoscale*, 2011, **3**, 4088-4093