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Diarylamino-substituted tetraarylethene (TAE) as an efficient and robust hole transport material for 11% methyl ammonium lead iodide perovskite solar cells†

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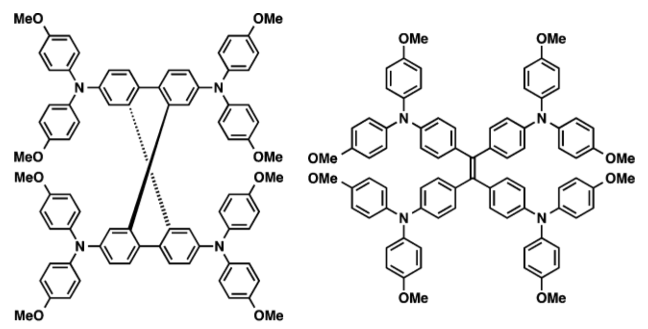
We report the synthesis and characterisation of tetra{4-[N,N-(4,4′-dimethoxydiphenylamino)]phenyl}ethene (TAE-1) as an efficient and robust hole transport material for its application in methyl ammonium lead iodide (MAPI) perovskite solar cells. The solar cells show light-to- energy conversion efficiencies as high as 11.0% under standard measurement conditions without the need of additional dopants.

Organic hole transport materials (HTM) have been the focus of much attention in MAPI perovskite solar cells since the reports on light-to-energy conversion efficiency superior to 10%.[1–3] Although the actual record efficiency[4] does not use the original spiro-OMeTAD molecule (Fig. 1) as HTM and utilises a poly-triarylamine polymer, many efforts are devoted to find an organic HTM substitute for spiro-OMeTAD that ideally can be synthesised in large scale, fewer synthetic steps and increases the stability of the solar cell.[5,6]

Semiconducting polymers, as well as the so called "small organic molecules" have paved the way in organic solar cells (OSC) to notable solar-to-energy conversion efficiencies with values near 10% under standard sun-simulated irradiation (100 mW cm^{-2} 1.5. AMG sun spectra).[7] From decades of research in novel organic semiconductor materials for OSC, the novel topic of MAPI perovskite solar cells feeds to quickly achieve efficiencies over 10%. However, a few examples can be found about the use of well-known semiconductor polymers alike for example P3HT (poly-3-hexylthiophene).[8–11] In contrast, the number of small molecules that are used in MAPI perovskite solar cells as HTM grows much faster.[12–14]

In this communication, we disclose the synthesis of a novel small organic molecule and its application as HTM in MAPI



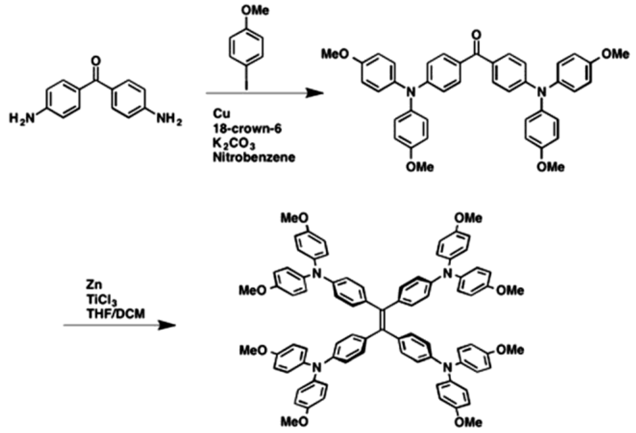
spiro-OMeTAD TAE-1

Fig. 1 Molecular structures of the HTM spiro-OMeTAD and the TAE-1 molecule described in this work.

perovskite solar cells without the need of "dopants" (oxidants) to achieve solar-to-electrical current efficiencies of 11% under 1 sun conditions.

Scheme 1 illustrates the synthetic route for the preparation of the tetra{4-[N,N-(4,4′-dimethoxydiphenylamino)]phenyl}ethene (TAE-1). The synthesis of TAE-1 requires only two synthetic steps from commercially available 4,4′-diaminobenzophenone, which involve a two-fold copper-catalysed Ullmann reaction with 4-iodoanisole, followed by a McMurry reductive coupling of ketones using a low-valent titanium reagent. The final compound was obtained in 72% yield. Detailed synthetic procedures and full chemical characterization are provided in the ESI.† Complete struc- tural characterisation of the tetraarylethene derivative (TAE-1) and the corresponding intermediates was accomplished using standard spectroscopic techniques such as ^{1}H NMR, ^{13}C NMR, FTIR, and UV-Visible (for more details see ESI†). Mass spectrometry (MALDI-TOF) confirmed the presence of TAE-1 with a molecular ion peak $[M]^+$ at 1240.5334 m/z.

The thermal properties were investigated by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC). The new HTM exhibits good thermal stability, up to 350 1C (Fig. S1, ESI†). Furthermore, dfferential scanning calorimetry (DSC) of TAE-1 revealed sharp endothermic peaks at T_m = 288 1C and



Scheme 1 A straightforward synthetic route for TAE-1.

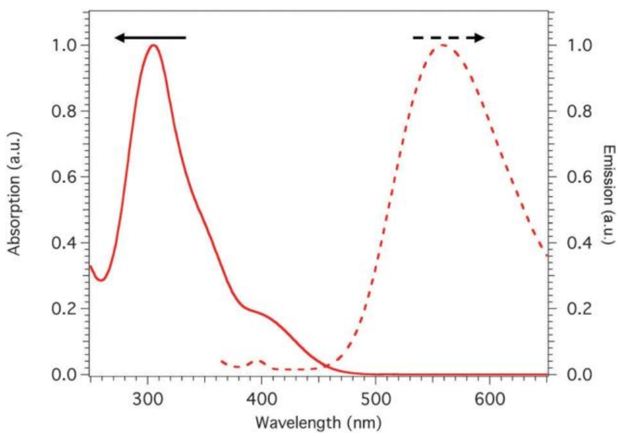


Fig. 2 The UV-Visible (solid line) and fluorescence emission spectra (dashed line) of TAE-1 in THF and THF : water (10 : 90 v/v), respectively. All samples were measured at ambient temperature.

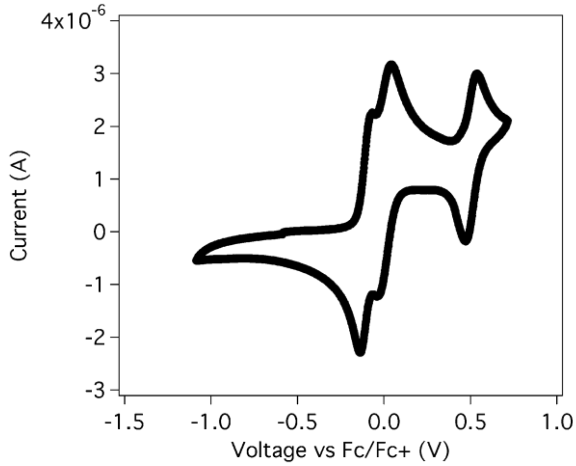


Fig. 3 Cyclic voltammetry of TAE-1 carried out in a 0.1 M solution of tetrabutylammonium hexafluorophosphate in dichloromethane in a three-electrode cell, where the Pt mesh electrode was used as the working electrode and a platinum wire as the counter electrode. The scanning rate was 50 mV s^{-1}.

at T_c = 258 1C, (Fig. S2, ESI†). After consecutive heating/cooling cycles rather small changes in the T_m and T_c were observed, which further confirms the crystalline nature of this material. In contrast, spiro-OMeTAD shows high glass transition tempera- ture (T_g = 125 1C) but no evidence of crystalline behaviour was found.

We first analysed the UV-Visible and luminescence spectra of TAE-1, as shown in Fig. 2. As can be seen, the molecule TAE-1 does not absorb much light in the visible region of the sun spectra with onset absorption at 500 nm. The fluorescence emission spectrum has a maximum centred at 550 nm in a solution of THF and water (10 : 90 v/v, respectively; THF = tetrahydrofuran). From Fig. 2 we can estimate the 0–0 energy, which is defined as the lowest energy transition and has an approximate value of 2.6 eV with λ_{ex} at 350 mn.

Fig. 3 shows the measured cyclic voltammogram for TAE-1 in dichloromethane and using ferrocene as the internal reference.

As can be seen, the oxidation potential value is +0.51 V vs. Fc/Fc^+.

For small molecules, a direct relationship has been shown between the molecule oxidation potential and the HOMO (Highest Occupied Molecular Orbital) energy using the following equation:[15]

$$\mathrm{HOMO} = -(1.4 \pm 0.1) \times (qVoxCV) - (4.6 \pm 0.08)\ \mathrm{eV} \quad (1)$$

where q is the electron charge and VoxCV is the oxidation potential value of the molecule vs. Fc/Fc^+.

We have calculated the HOMO energy value for TAE-1 to be −5.32 eV. The LUMO (Lowest Unoccupied Molecular Orbital) energy value can be calculated using eqn (2).

$$\mathrm{LUMO{-}HOMO} = E_{0-0} \quad (2)$$

We have estimated that the LUMO energy value for TAE-1 is −2.74 eV. The HOMO energy value is above the MAPI perovskite Valence Band (VB) energy (−5.44 eV), which ensures efficient hole transfer from the MAPI perovskite to TAE-1.

For comparison purposes, the cyclic voltammetry of the spiro-OMeTAD HTM was measured under the same conditions. The HOMO energy value for the spiro-OMeTAD was found to be −5.0 eV.

Once the electrochemical properties of TAE-1 were measured we measured the hole mobility properties. We fabricated only hole devices with the following structure: ITO/PEDOT:PSS/HTM/ Au where HTM was either TAE-1 or spiro-OMeTAD. The values obtained were 5.92 $\times$ 10^{-5} cm^2 V^{-1} s^{-1} for TAE-1 and 2.55 $\times$ 10^{-4} cm^2 V^{-1} s^{-1} cm^{-1} for spiro-OMeTAD determined by the SCLC method (Fig. S3, ESI†).

Finally, we fabricated MAPI solar cells with the archetypal structure: FTO/(35 nm) $dTiO_2$/(400 nm) $mpTiO_2$/(250 nm) MAPI/(100 nm) HTM, where the numbers between parentheses correspond to the layer thickness, $dTiO_2$ is the TiO_2 dense layer, mp is the TiO_2 mesoporous layer, and the HTM was either TAE-1 or spiro-OMeTAD.

Fig. 4 shows the measured current vs. voltage curves (IV curves) for a typical MAPI solar cell using TAE-1 and the spiro-OMeTAD as HTM.

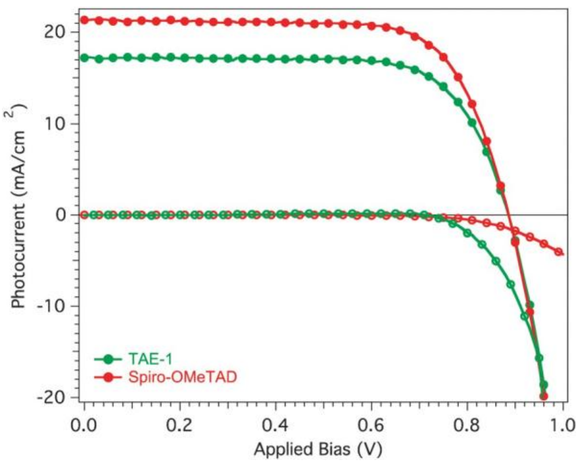


Fig. 4 IV curves measured under 1 Sun conditions (filled symbols) and in the dark (open symbols).

Table 1 Measured performance parameters of the solar cell

	J_{sc} (mA cm^{-2})	V_{oc} (mV)	FF (%)	Z (%)
TAE-1	17.22	885	72.20	11.02
s-OMeTAD	21.40	885	71.40	13.53

As can be seen, the TAE-1 based MAPI perovskite solar cell has an identical open circuit voltage (V_{oc}) to the spiro-OMeTAD and so is the Fill Factor (FF) value (see Table 1). Despite many efforts to optimize the TAE-1 film thickness we were unable to match the current density (J_{sc}) values of the MAPI perovskite solar cell obtained when using spiro-OMeTAD. Nonetheless, it is worthy to notice that in both cases we avoided the use of chemical oxidants that, although several groups have reported higher light-to-electrical conversion efficiency when "doping" the HTM,[16,17] it may lead to greater solar cell instability due to the partial oxidation of the HTM layer.

In conclusion, we have synthesised and characterised a novel hole transport material (TAE-1) that has been used to fabricate efficient MAPI perovskite solar cells. The HOMO energy value was close to the value measured for the spiro-OMeTAD, which is the molecule reference for HTM in MAPI perovskite solar cells. Although the solar cell photocurrent density was unexpectedly lower than that of the reference solar cell using spiro-OMeTAD, we believe that the fact that the AM-1 synthesis only requires two straightforward synthetic steps and has excellent final product yield (72%) makes this molecule, and its possible derivatives, good candidates for top efficiency MAPI solar cells. Moreover, as mentioned above, in contrast to other previously reported small organic molecules, we have avoided the use of chemical oxidants that may lead to lower device stability and yet TAE-1 based MAPI perovskite solar cells overpassed light-to- energy conversion efficiencies well beyond 10%.

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