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## Diaryl-amino-substituted Tetraarylethene (TAE) as Efficient and Robust Hole Transport Material for 11% Methyl Ammonium Lead Iodide Perovskite Solar Cells.

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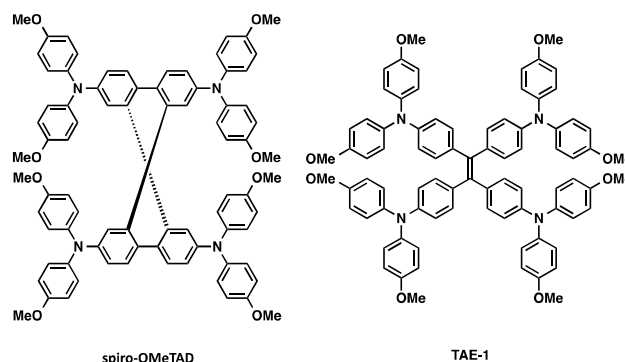
We report the synthesis and characterisation of tetra{4-[N,N-(4,4'-dimethoxydiphenylamino)]phenyl}ethene (**TAE-1**) as efficient and robust hole transport material for its application in methyl ammonium lead iodide (MAPI) perovskite solar cells. The solar cells show light-to-energy conversion efficiencies 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%.<sup>2, 3</sup> Although the actual record efficiency<sup>4</sup> do not use the original spiro-OMeTAD molecule (Figure 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<sup>5, 6</sup>.

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 (100mW/cm<sup>2</sup> 1.5.AMG sun spectra).<sup>7</sup> From these 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).<sup>8-11</sup> In contrast, the number of small molecules that are used in MAPI perovskite solar cells as HTM grows much faster.<sup>12-14</sup>

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

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



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

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 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 structural characterisation of tetraarylethene derivative (**TAE-1**) and the corresponding intermediates was accomplished using standard spectroscopic techniques such as <sup>1</sup>H NMR, <sup>13</sup>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]<sup>+</sup> 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 °C (figure S1). Furthermore, differential scanning calorimetry (DSC) of **TAE-1**

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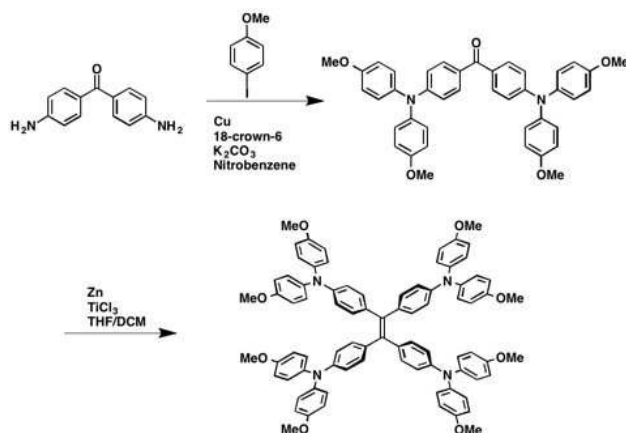
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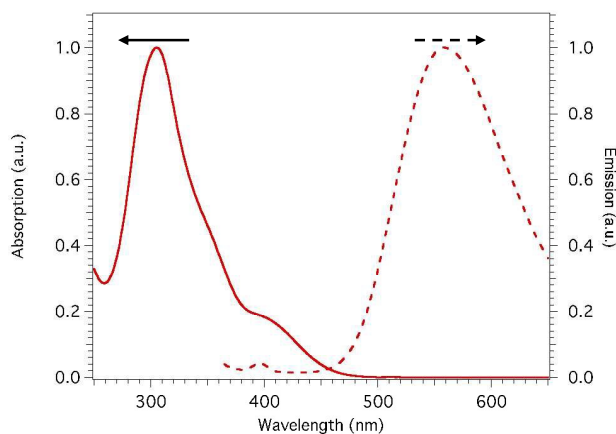
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revealed sharp endothermic peaks at  $T_m = 288$  °C and at  $T_c = 258$  °C, (figure S2). After consecutive heat/cool cycles rather small changes in the  $T_m$  and  $T_c$  were observed, which further confirms the crystalline nature of this material. In contrast, spiro-OMeTAD shows high glass transition temperature ( $T_g = 125$  °C) but no evidence of crystalline behaviour was found.



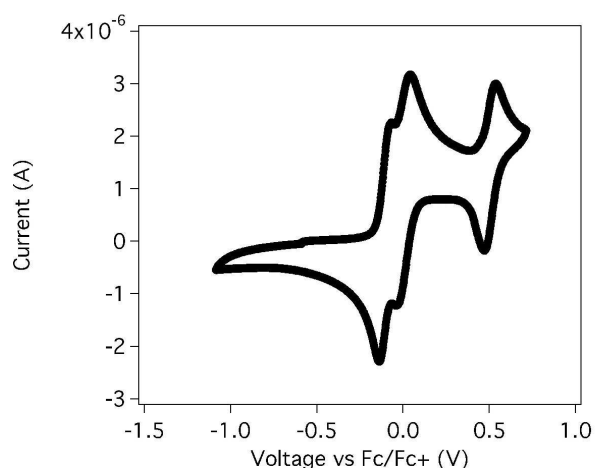
**Scheme 1.** Straightforward synthetic route for **TAE-1**.

We analysed first the UV-Visible and luminescence spectra of **TAE-1**, as shown in Figure 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 spectra has a maximum centred at 550 nm in a solution of THF and water (10:90 v/v, respectively; THF = tetrahydrofuran). From Figure 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  $\lambda_{ex}$  at 350nm.



**Figure 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.

Figure 3 shows the measured cyclic voltamogram for **TAE-1** in dichloromethane and using ferrocene as internal reference. As can be seen, the oxidation potential value is +0.51V vs Fc/Fc+.



**Figure 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 working electrode and a platinum wire as counter electrode. The scanning rate was 50 mV/s.

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:<sup>15</sup>

$$\text{Eq(1)} \quad \text{HOMO} = -(1.4 \pm 0.1) \times (qV_{oxCV}) - (4.6 \pm 0.08) \text{ eV}$$

where  $q$  is the electron charge and  $V_{oxCV}$  is the oxidation potential value of the molecule vs Fc/Fc+.

We have calculated that the HOMO energy value for **TAE-1** is -5.32 eV. The LUMO (Lowest Unoccupied Molecular Orbital) energy value can be calculated using equation 2.

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

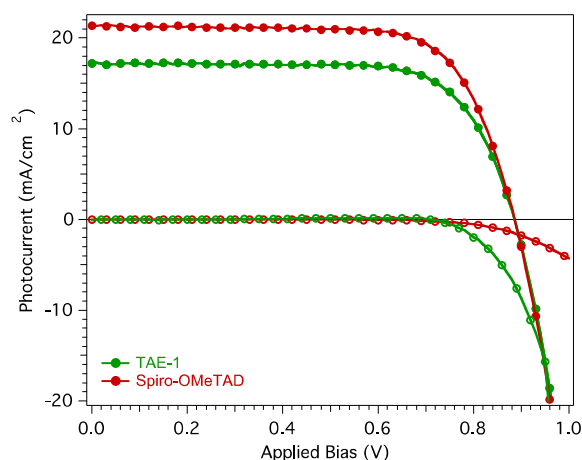
We have estimated that the LUMO energy value for **TAE-1** is -2.74 eV. The HOMO energy value is above the MAPI perovskite Valence Band (VB) energy (-5.44 eV), which ensures efficient hole transfer from the MAPI perovskite to **TAE-1**.

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 AM-1 were measured we turned into the measurement of 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  $5.92e-5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  for **TAE-1** and  $2.55e-4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  for spiro-OMeTAD determined by SCLC method (figure S3).

Finally, we fabricated MAPI solar cells with the archetypal structure: FTO/(35 nm)dTiO<sub>2</sub>/ (400 nm) mpTiO<sub>2</sub>/(250 nm) MAPI/(100 nm) HTM, where the numbers between parentheses correspond to the layer thickness, dTiO<sub>2</sub> is the TiO<sub>2</sub> dense layer, mp is the TiO<sub>2</sub> mesoporous layer, and the HTM was either **TAE-1** or spiro-OMeTAD.

Figure 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.

As can be seen, the **TAE-1** based MAPI perovskite solar cell has identical open circuit voltage ( $V_{oc}$ ) than 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 MAPI perovskite solar cell current density ( $J_{sc}$ ) values 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,<sup>16, 17</sup> it may lead to grater solar cell instability due to the partial oxidation of the HTM layer.



**Figure 4.** IV curves measured under 1 sun conditions (filled symbols) and in dark (open symbols).

**Table 1.** Solar cell measured performance parameters.

|          | $J_{sc}$<br>( $\text{mA}/\text{cm}^2$ ) | $V_{oc}$<br>(mV) | FF<br>(%) | $\eta$<br>(%) |
|----------|---|------------------|-----------|---------------|
| TAE-1    | 17.22                                   | 885              | 72.20     | 11.02         |
| s-OMeTAD | 21.40                                   | 885              | 71.40     | 13.53         |

## Conclusions

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 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%.

## Acknowledgements

EP, AVF and NM thanks MINECO (projects CTQ2013-47183, CTQ2014-52045-R and CTQ2011-24652), respectively, as well as the Severo Ochoa Excellence Accreditation 2014-2018 (SEV-2013-0319). NM thanks the European Research Council ERC-2012-ADG\_20120216 (Chirallcarbon), and the CAM (FOTOCARBON project S2013/ MIT-2841). NM also thanks Alexander von Humboldt Foundation. EP and AV are also grateful to ICIQ and ICREA for economical support.

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