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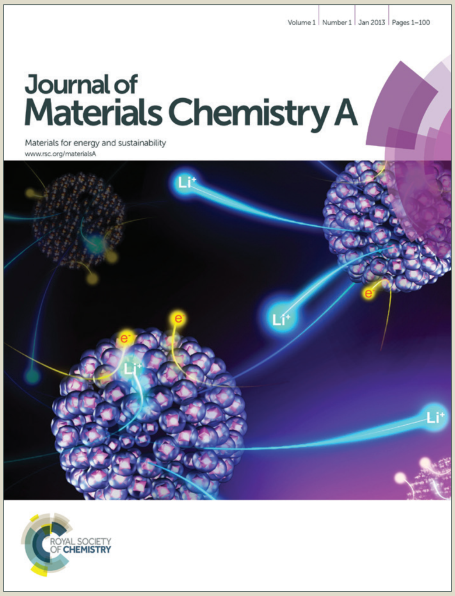

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A low cost azomethine-based hole transporting material for perovskite photovoltaics

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Most hole transporting materials (HTM) prepared for perovskite solar cell applications are synthesized via cross-coupling reactions that require expensive transition metal catalysts, inert reaction conditions and extensive product purification, making large-scale production cost-prohibitive. Here, we describe the synthesis of a simple azomethine-based conjugated small-molecule (EDOT-OMeTPA) which is easily prepared in a cost effective Schiff base condensation reaction, with water being the only by-product. As the hole transporter in planar $NH_3CH_3PbI_3$ perovskite photovoltaics, efficiencies exceeding 11% were reached. This result is comparable to state-of-the-art materials such as Spiro-OMeTAD on a like-to-like comparison, while cost estimations show that the material cost is about one order of magnitude lower for EDOT-OMeTPA, resulting in a negligible cost-per-peak-Watt contribution of 0.004 \$ W^{-1}. In addition, the high synthetic accessibility of EDOT-OMeTPA also reduces the toxic chemical waste and therefore greatly reduces its environmental impact. Our results pave the way towards low-cost, environmentally friendly and efficient HTMs.

The efficiency of methylammonium lead iodide (MAPI) perovskite-based solar cells has increased rapidly in the last five years and is already comparable with current commercial technologies.[1–4] Record efficiencies exceeding 20% have been reported and further improvements are expected.[5] Although the cost of the perovskite material itself is relatively low, most of the state-of-the-art devices incorporate an expensive organic hole transporting material (HTM), termed Spiro-OMeTAD (Figure 1).[6,7] While several other organic HTMs have been reported,[8–12] they generally show a lower performance and/or are expensive to synthesize.

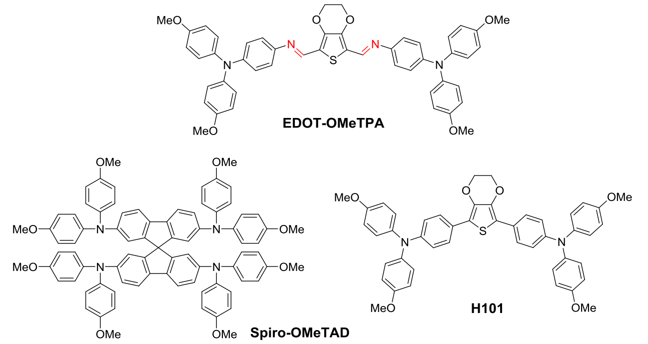

Figure 1: Chemical structures of EDOT-OMeTPA (with the azomethine bond in red), and the reference molecules: Spiro-OMeTAD and H101.[13]

An interesting approach towards the synthesis of low-cost, small-molecule HTM was recently introduced by Li *et al.*[13] They reported a 3,4-ethylenedioxythiophene based HTM with efficiencies up to 13.2%, which is comparable to Spiro-OMeTAD. However, the small-molecule presented by Li *et al.* (H101, Figure 1) and most other novel HTM are synthesized via cross-coupling reactions that require transition metal catalysts, inert reaction conditions and extensive product purification, making large-scale production cost-prohibitive.

Schiff base condensation chemistry offers a less complicated route towards conjugated materials,[14–16] since the reaction can be performed at near ambient conditions and water is the only by-product, making product purification very straightforward.[17–19] The azomethine bond (–CH=N–, also known as Schiff-base) is isoelectronic to the vinyl bond and possesses similar optoelectronic and thermal properties. Azomethine-based conjugated materials have already been successfully applied as donor materials in organic photovoltaics.[20–25]

Here we demonstrate the synthesis and characterisation of a novel azomethine-based small-molecule (EDOT-OMeTPA, Figure 1) based on triphenylamine (TPA) and 3,4-ethylenedioxythiophene (EDOT) moieties. When employed in perovskite solar cells, we show that the obtained performance is comparable to that of state-of-the-art materials such as spiro-OMeTAD in a like-to-like comparison. Our results show a simple route towards obtaining easily up-scalable hole transporters with reduced cost and reduced environmental impact compared to state-of-the-art HTMs.

The small-molecule design was motivated by our previous work on conjugated azomethines.[17] In order to increase the solubility of the small-molecule and to align the energy level with the perovskite material, a cyclic ether and methoxy groups were introduced. In addition, the functionalization makes this small-molecule a direct analogue of its fully aromatic counterpart H101.[13] This gives us the opportunity to study the effect of the azomethine bond on the optoelectronic and thermal properties and device performance.

EDOT-OMeTPA was prepared by condensing 4-amino-4′,4′′-dimethoxytriphenylamine (**1**) with commercially available 2,3-dihydrothieno[3,4-b][1,4]dioxine-5,7-dicarboxaldehyde (**2**) in the presence of a catalytic amount of *para*-toluenesulfonic acid (Figure 2). The product was purified in a simple washing step and obtained in a high yield. During the workup the product was washed with triethylamine to prevent the presence of protonated species which can negatively impact the final device performance.[17] Experimental details and characterization can be found in the SI. As a result of this uncomplicated chemistry this reaction can be performed on a benchtop without the need for advanced equipment (only a beaker and stirrer are required), making the chemistry accessible to a wide range of researchers, rather than confining it to specialized organic chemists.

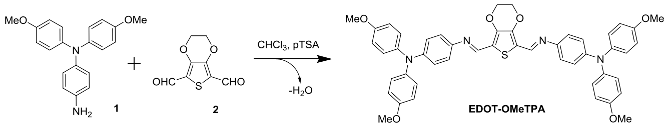

Figure 2: Reaction scheme and molecular structure of the azomethine-based small-molecule EDOT-OMeTPA.

The thermal properties were studied by thermogravic analysis (TGA) and differential scanning calorimetry (DSC) measurements. EDOT-OMeTPA posseses a high thermal stability, with a 5% weight loss at 359 °C (Figure S1), which can be attributed to all-aromatic backbone. On the first heating cycle, DSC measurements show a T_m only at 241 °C and this T_m appears to be solvent induced. After the first heating cycle, the material is fully amorphous. EDOT-OMeTPA shows no T_m but a T_g only at 105 °C. Consecutive heat/cool experiments confirm the amorphous nature of this material. The T_g of EDOT-OMeTPA is well above the general device operating temperature (Figure S2, Table S1),[26] which is considered essential for the stability of the hole transporting layer and the photovoltaic device. Therefore, an increase in T_g of 32 °C of EDOT-OMeTPA over H101 (T_g = 73 °C)[13] should be considered as a very important improvement. In comparison, spiro-OMeTAD exhibits a high T_g, which is well above the operating temperature of photovoltaic devices (125 °C).[27]

UV-Vis absorption spectra of EDOT-OMeTPA (Figure 3, Table S1) show absorption maxima at 495 nm in solution and at 505 nm in the film. The absorption onset was found at 625 nm, resulting in an optical bandgap (E_g) of 2.0 eV. The rather large bathochromic shift of EDOT-OMeTPA compared to H101 can be attributed to the extended conjugation, which is a direct consequence of the electron withdrawing azomethine bond[28] and/or the more planar conformation of the azomethine-based backbone compared to the aromatic backbone.

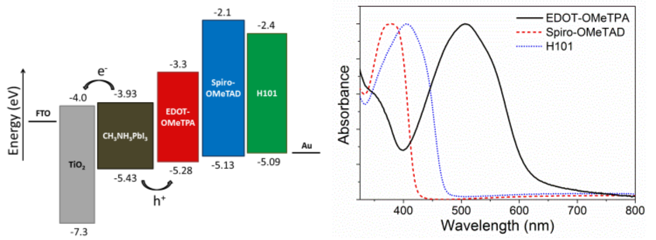

Figure 3: Optoelectronic properties of the different hole transporting materials. Left: Energy level diagram. Right: Normalized UV-vis absorption spectra of the HTMs as film spincoated on glass from chlorobenzene solutions.

A good energy alignment between the hole transporter and the perovskite is essential to maximize the charge transfer processes. In order to study the energy level alignment of EDOT-OMeTPA with state-of-the-art MAPI perovskite, the electronic properties were determined using cyclic voltammetry. The onset of the oxidation potential was found at +0.17 V (vs. Fc^+/Fc), which is approximately 0.15 V higher than Spiro-OMeTAD (Figures 3 and S3 and Table S1). The HOMO energy level was estimated according to literature (assuming that the energy level of Fc^+/Fc is -5.1 eV)[29] to be around 5.28 eV for EDOT-OMeTPA, resulting in an excellent alignment with the MAPI valence band with only a 0.15 eV loss. The energy level of EDOT-OMeTPA is approximately 0.19 eV deeper compared to its analogue H101, which is the result of the electron-withdrawing azomethine bond, and thus higher open circuit voltages can be expected when integrated into solar cells.[28]

Photovoltaic devices were prepared by spincoating the perovskite layer using the solvent engineering process as was described by Jeon *et al.*[30] In our devices, the perovskite layer is approximately 300 nm thick and is known to be relatively smooth with a root mean square roughness of 8.3 nm.[30] On top, the different hole transporting materials were spincoated from a chlorobenzene solution. Due to the limited solubility of the compound, relatively low concentrations (10 mg mL^{-1}) were used for spincoating EDOT-OMeTPA in order to obtain good films. The relatively low concentration results in films with a thickness of approximately 40 nm, which is significantly thinner than generally used for Spiro-OMeTAD (200-400 nm). We note here that spincoating films from low-concentration Spiro-OMeTAD solutions result in poor film quality and severe shunting (details in SI). Photovoltaic devices prepared with EDOT-OMeTPA show efficiencies exceeding 11.0%, which is comparable to optimized Spiro-OMeTAD (11.9%) and H101 (10.9%) (Figure 4). The obtained V_{oc} of EDOT-OMeTPA is comparable to H101 and about 50 mV lower compared to Spiro-OMeTAD, with all materials resulting in similar short circuit currents of approximately 19 mA cm^{-2}. In contrast to H101, doping with the cobalt dopant FK102 did not increase the efficiency for our devices under the tested conditions (see SI).[13] Furthermore, the devices comprising EDOT-OMeTPA as HTM show a good stability over 1000 hours with very little degradation in the PCE (~10%) when stored at ambient conditions *i.e.* room temperature and a relative humidity of 30% (Figure S5).

The efficiencies for EDOT-OMeTPA show a larger spread than Spiro-OMeTAD (Table S2). Here, it is likely that a significant number of pinholes can exist in the thinner EDOT-OMeTPA layers which would result in device shunting paths.[31,32] We believe that optimisation of the chemical structure, for example to increase the solubility which could assist in the formation of thicker films, and the processing conditions would further increase the efficiency and reproducibility; making azomethine-based materials promising alternatives for HTMs that are currently available.

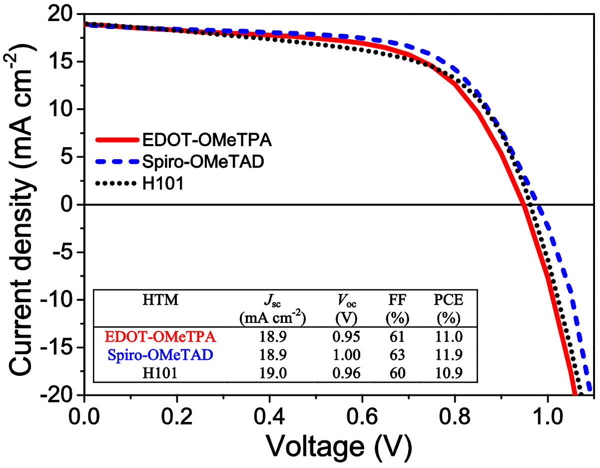

Figure 4: *J-V* curves of solar cells based on the different hole transporting materials. The inset shows the characteristics for the best devices.

Although metal halide perovskite materials show great potential for low-cost solar cells, currently employed state-of-the-art hole transporting materials would add around \$40 per square meter to the photovoltaic devices (see SI for estimation). We have already shown that with EDOT-OMeTPA it is possible to prepare efficient devices with significantly thinner layers, resulting in a first reduction of the cost of almost an order of magnitude.

Furthermore, condensation chemistry offers a simpler and therefore more cost-effective route to conjugated materials compared to (palladium catalysed) cross-coupling reactions. We performed a materials cost estimation for the synthesis of EDOT-OMeTPA and the reference HTMs, Spiro-OMeTAD and H101, following the procedure established by Osedach *et al.* (flow charts and details of the cost estimation can be found in the SI).[33] We estimated that the material cost for EDOT-OMeTPA (~10 $\$\,g^{-1}$) is about an order of magnitude lower compared to the other HTMs (Tables 1 and S4). However, we note here that as a result of the limited amount of reported synthetic protocols towards H101, we believe that the material cost of H101 can be significantly reduced by optimisation of the starting material synthesis. The difference in cost between materials prepared via cross-coupled reactions and condensation reactions mainly originates from the cost for purification; in particular column chromatography has a large impact on the cost (Table S4). Column chromatography is generally necessary to purify products from palladium cross-coupling reactions, since this type of reaction suffers from impurities as a result of homocoupling and halogen-dance, which are difficult to remove via other purification methods.[34] The low cost of EDOT-OMeTPA combined with the thinner layer could reduce the cost of the HTM layer in photovoltaic devices by approximately two orders of magnitude. This results in an estimated cost-per-peak-Watt contribution of 0.004 $\$\,W^{-1}$, which could be considered negligible (details in SI).[33]

As a result of the intensive purification that is required for Spiro-OMeTAD and H101, the amount of chemical waste is significantly higher than for EDOT-OMeTPA, which not only has a large impact on the cost, but also on the environment. Specifically, the quantity of halogenated solvents, known to be highly toxic, used for the synthesis of Spiro-OMeTAD and H101 (1.0 and 2.3 kg per gram of product respectively) is very high compared to the synthesis of EDOT-OMeTPA (0.1 kg/g). This not only makes the azomethine-based hole transporting material a more cost-effective option but also has a reduced environmental impact compared to state-of-the-art materials.

Table 1: Survey of the estimated chemical synthesis cost and waste streams for different HTMs.

HTM	Chemical waste[a] (kg/g)[b]	Material Cost (\$/g)[c]	Commercial price (\$/g)
EDOT-OMeTPA	0.7 (0.1)	10	n/a
Spiro-OMeTAD	3.6 (1.0)	92	170-475
H101	4.0 (2.3)	111	250

[a] Total estimated weight of halogenated solvents is given in parentheses.

[b] Total estimated weight of chemical waste for the synthesis of 1 gram of product.

[c] Total estimated material cost for the synthesis of 1 gram of product.

Conclusions

In conclusion, an azomethine-based hole transporting material, EDOT-OMeTPA, was prepared via a simple condensation reaction. The azomethine-bond in EDOT-OMeTPA increases the glass transition temperature compared to its vinyl analogue (H101) by 32 °C, while it lowers the HOMO energy level (5.28 eV compared to 5.09 eV for H101), which results in a better alignment with the valence band of the perovskite material. Planar ($CH_3NH_3PbI_3$) perovsike-based photovoltaics with EDOT-OMeTPA as the hole transporting layer show power conversion efficiencies exceeding 11%. This efficiency is comparable to state-of-the-art Spiro-OMeTAD on a like-to-like comparison, while significant improvements can be expected after further optimization of the chemical structure and processing conditions. Furthermore, we show that Schiff base condensation chemistry offers a cost-effective and more environmentally friendly route towards up-scalable hole-transporting materials, leading to a reduction of materials costs of approximately two orders of magnitude compared to state-of-the-art materials, resulting in a negligible contribution of 0.004 $\$\,W^{-1}$. Our results demonstrate that Schiff-base condensation chemistry is a viable route to achieving cost-effective hole transporting material, thus bringing perovskite solar cells one step closer to commercial realization.

Notes and references

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Electronic Supplementary Information (ESI) available: Synthesis and characterisation, device preparation, material cost estimation and flow charts. See DOI: 10.1039/c000000x/

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