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Design Rules for the Preparation of Low-Cost Hole Transporting Materials for Perovskite Solar Cells with Moisture Barrier Properties

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Abstract

The current state-of-the-art hole transporting materials (HTM) for perovskite solar cells are generally synthesized *via* cross-coupling reactions that require expensive catalysts, inert reaction conditions and extensive product purification, resulting in high costs and therefore limiting large-scale commercialisation. Here we describe a series of HTMs prepared *via* simple and clean Schiff-base condensation chemistry with an estimated material cost in the range of 4-54 \$/g. The optoelectronic and thermal properties of the materials are linked to the changes in the chemical structure of the HTMs, which allow us to extract design rules for new materials, supported by density functional theory calculations. Charge transport measurements show hole mobilities in the range of 10^{-5} to 10^{-7} cm² V⁻¹ s⁻¹. Upon addition of LiTFSI the HTMs can be oxidized, resulting in a large increase in the conductivity of the hole transporting layer (HTL). When employed as HTL in perovskite solar cells, power conversion efficiencies close to those of Spiro-OMeTAD are obtained. In particular, devices prepared with Diazo-OMeTPA show a higher open-circuit voltage. Furthermore, we show that azomethine-based HTMs can act as effective moisture barrier, resulting in a significant increase in the stability of the underlying perovskite film. We assign the improved properties to the presence of a dipole in our molecules which assist in a close molecular packing and leading to a high density of the as-formed HTM films, preventing the ingress of water. This work shows that HTMs prepared *via* condensation chemistry are not only a low-cost alternative to Spiro-OMeTAD, but also act as a functional barrier against moisture induced degradation in perovskite solar cells.

Introduction

In the last decades, a large variety of conjugated organic molecules with hole-transporting properties have been synthesized for diverse optoelectronic applications such as organic light emitting diodes (OLED), organic field effect transistors (OFET) and organic, dye-sensitized and

perovskite solar cells (OPV, DSSC and PKSC). Among these, 2,2',7,7'-tetrakis(*N,N*-di-*p*-methoxyphenylamine)-9,9'-spirobifluorene (Spiro-OMeTAD) is one of the most well-known hole-transporting materials (HTM).^[1] This small-molecule was initially developed for solid-state dye-sensitized solar cells, where it was used as a replacement for liquid electrolytes. More recently, Spiro-OMeTAD has been the preferred HTM for perovskite-based solar cells as a result of its good energy level alignment with the valence band of methylammonium lead iodide (CH₃NH₃PbI₃) and related perovskite structures, leading to excellent photovoltaic performance.^[2–4]

However, Spiro-OMeTAD is very expensive to produce as a result of its multistep synthesis, which requires inert reaction conditions, transition metal catalysts and extensive purification.^[5] The high materials cost will in turn result in a significant cost contribution in perovskite solar cells,^[6] making this HTM industrially less interesting. Recently, several research groups have focussed on tuning the structure to reduce the cost,^{[7][8]} without losing the photovoltaic performance in perovskite solar cells.^[2,9–13] The majority of these materials contain methoxy-substituted triphenylamine side groups, which are connected via aryl-aryl bonds to a conjugated core.^[9,10,14] These materials are generally synthesized using transition metal catalysed reactions that require extensive product purification.^[15–20] This is due to the fact that these reactions are prone to produce side-products and leave (metal) catalyst residues that can affect the performance of the resulting devices.^[21] In our previous work, we have shown that condensation chemistry offers an excellent alternative by connecting the core moiety to the triphenylamine *via* an azomethine-bond (–CH=N–, also known as imine or Schiff-base).^[5] More recently, other groups have also shown that condensation chemistry offers an excellent alternative to produce low-cost hole transporting materials.^[22,23] This chemistry has the advantage that it can be performed under ambient conditions without the use of expensive catalysts and with water as the only side-product. The absence of metal catalysts and side reactions results in a simple product workup, if necessary at all.^[24] Although the azomethine bond in aliphatic or semi-aromatic compounds is prone to hydrolysis, studies have shown that in highly conjugated (all-aromatic) compounds the azomethine bond is robust and resists hydrolysis.^[25,26] Furthermore, Koole *et al.* recently showed that the azomethine bond exhibits good electrical conductance, which is expected to be beneficial for charge transport and shows the potential of this chemistry to produce high-quality organic semiconductors.^[27]

In this work we extend our study of azomethine-based HTMs and correlate the effect of the changes to the chemical structure to the material properties. We emphasize that the simple and clean synthesis allows us to prepare a large series of materials, thus enabling the study of a variety of different cores. We find that all these materials can be synthesized in good yields and at low cost. Our computational studies indicate that the energy levels of the small-molecules can be fine-tuned by changing the core, which is in good agreement with our experimental results. In order to investigate the role of the azomethine-linkage, we also synthesized two reference molecules where the azomethine bond was inverted. We observe that the photovoltaic performance is strongly influenced by the core of the HTMs and that the best values are obtained for HTMs that have a strong dipole within the core. The reversed orientation of the azomethine bond slightly lowers the HOMO energy levels, which also influences the energy alignment with the perovskite. Furthermore, we performed *in-situ* X-ray diffraction measurements to study moisture-induced degradation of a perovskite film covered by a thin layer of these HTMs, which shows the superior function of these materials as a barrier against moisture-induced degradation of the perovskite.

Synthesis

Figure 1. Reaction scheme of the Schiff-base condensation reaction to prepare the isomers.

For this study, we designed and synthesized a series of azomethine-based HTMs based on the previously reported EDOT-OMeTPA (Figure 1 and Figure 2). We replaced the EDOT core with different (aromatic) groups in order to study their influence on the optoelectronic and charge transport properties. For example, the core was substituted by a phenyl ring in order to further reduce the cost and simplify the molecular structure (**Ph-OMeTPA**). We also synthesized the thiophene (**Th-OMeTPA**) analogue in order to study the effect of the cyclic ether in EDOT, while the use of furan (**Fu-OMeTPA**) results in a more sustainable alternative, allowing us to study the effect of the hetero atom.^[28] By introducing a triphenylamine (**TPA-OMeTPA**) as the core, an azomethine-based small-molecule analogue of the conductive polymer PTAA (polytriarylamine) was synthesized. All these materials were synthesized in a low-cost condensation reaction between 4-amino-4',4''-dimethoxytriphenylamine and the dialdehyde analogue of the different cores (Figure 1).

Figure 2. Chemical structure of the different azomethine-based small-molecules, including the isolated yields and estimated materials cost.

Furthermore, we inverted the azomethine bond in order to study the influence of the position of the nitrogen in the π -bridged linker moiety. This was done by coupling 1,4-phenylenediamine with 4-formyl-4',4''-dimethoxytriphenylamine to synthesize the analogue of **Ph-OMeTPA**, which was termed **Ph-inv-OMeTPA**. By reacting 4-formyl-4',4''-dimethoxytriphenylamine with hydrazine, a simplified analogue with a reversed bond sequence was synthesized that does not contain any core, but just a double azomethine linkage (**Diazo-OMeTPA**). This material has already been published by Ma *et al.*, where the authors reported a relatively poor photovoltaic performance compared to Spiro-OMeTAD.^[29] The authors attributed this to the relatively low mobility of the material and the resulting high series resistance.

All these materials were synthesized in high yields (>80%) and purified with a simple washing step. **Fu-OMeTPA** has a relatively high solubility and is soluble in isopropanol, it is therefore important to use stoichiometric amount of starting materials, simplifying the purification.

Cost estimation and environmental impact

Since material cost will have a major influence on the commercial viability of these materials as HTMs in perovskite solar cells, a cost estimation was performed following our previously published method.^[5] The cost was calculated by quantifying material costs of their published small-scale synthetic routes. The estimated material costs for the azomethine-based small-molecules are in the

range of 4-54 \$ g⁻¹ (Figure 2). The lowest costs are obtained for the small-molecules prepared from 4-amino-4',4''-dimethoxytriphenylamine, as this starting material can be synthesized at an estimated material cost of only \$2.28 g⁻¹ (Scheme S 2, Table S 4). In contrast, the HTMs with the inverted azomethine-bond prepared from 4-formyl-4',4''-dimethoxytriphenylamine show a significantly higher material cost, which is the result of the less efficient synthetic pathways available for this aldehyde. However, we believe that by optimisation of the synthesis this starting material can also be prepared at a comparable cost.

As expected, the **Ph-OMeTPA** shows the lowest material cost at \$4 g⁻¹ as a result of the very low cost of the core. It is worth noting that all other HTMs described here also show a significantly lower material cost than the state-of-the-art HTM Spiro-OMeTAD (estimated 91 \$ g⁻¹),^[5] which stems from the straightforward chemistry and purification of the azomethine-based materials. Additionally, the high yields and simple purification leads to the use of fewer chemicals, which is also beneficial from an environmental point of view (Table S 2). For a better understanding of the environmental impact of a synthetic route, Sheldon introduced the term E factor, which is defined as kg waste per kg product.^[30] Based on our small-scale synthesis route, our materials with the standard azomethine bond show values of E = 400–700, while the materials with an inverted azomethine bond reach E = 1800–2800. In comparison, Spiro-OMeTAD has an E factor of 3600, which gives a clear indication of the environmental impact of the synthesis and the benefit of using simple condensation chemistry.

As a result of the good film-forming properties of the azomethine-based HTMs, relatively thin layers of the HTM can be used in devices (50 nm compared to 250 nm for Spiro-OMeTAD), which additionally reduces the cost contribution and environmental impact by a factor of five for a typical device. In this way, the material cost of the hole transporter becomes negligible compared to the total device cost.^[6]

Thermal properties

Materials with low melting points or glass transition temperatures are expected to have poor stability when used in photovoltaic devices,^[31,32] which can reach temperatures of 80 °C under operational conditions. The thermal properties of our new HTM materials were studied by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC, Table 1). All materials possess excellent thermal stability with degradation temperatures under dynamic conditions exceeding 325 °C, which is well above photovoltaic operation temperatures. The high degradation temperatures are attributed to the conjugated backbone of all these molecules. The reported degradation temperature for **Diazo-OMeTPA** ($T_d^{10\%} = 320$ °C) is in good agreement with our observations.^[29]

Table 1. Thermal properties of the azomethine-based HTMs obtained from DSC, melting point apparatus and TGA measurements.

Compound	T_g (°C)	T_m (°C)	$T_d^{5\%}$ (°C)
EDOT-OMeTPA	105	241	359
Ph-OMeTPA	90	145	390
Th-OMeTPA	100	117	371
Fu-OMeTPA	70	106	325
TPA-OMeTPA	89	127	397
Ph-inv-OMeTPA	84	106	375
Diazo-OMeTPA	120	208	340

After the synthesis, most materials are in an amorphous state and only for **EDOT-OMeTPA** and **Ph-OMeTPA** a melting transition is observed with DSC. The phenyl core in **Ph-OMeTPA** slightly reduces the glass transition temperature (T_g) and melting point (T_m) compared to **EDOT-OMeTPA**, while inverting the azomethine bond further reduces the T_g and T_m . The lower T_m for furan compared to thiophene is in agreement with literature and results from the smaller heteroatom.^[33–35] Both melting points are significantly lower than that of **EDOT-OMeTPA**, which is ascribed to the large dipole moment in **EDOT-OMeTPA**. **TPA-OMeTPA** also shows a relatively low melting point, which originates from the bulky triphenylamine core. In contrast, **Diazo-OMeTPA** shows a high T_g and T_m which is ascribed to the rigid and planar backbone.^[36] Comparing the thermal properties of these azomethine-based HTMs with the reported thermal data of their fully conjugated analogues, we find that the thermal properties for our materials are superior. More specifically, the T_g of **EDOT-OMeTPA** is 32 °C higher than that of its analogue H101; the T_g and T_d of **Th-OMeTPA** are respectively 32 and 88 °C higher than those of its analogue Th101; and the T_m of **Diazo-OMeTPA** is 28 °C higher than that of its fully conjugated analogue, demonstrating the excellent thermal stability of the azomethine-based HTMs.^[10,37,38]

Optoelectronic properties

We evaluate the absorption and transmittance of the HTMs, as a low absorption in the hole transporting layer is important in order to minimize the optical losses. Light absorption spectra of the different materials were recorded in solution and in the solid state. The samples were dissolved in chlorobenzene at a concentration of 20 mg L⁻¹ and measured in a wavelength range of 350 to 800 nm (*Table S 12*, *Figure 3* and *Figure S 4*). All materials show a clear absorption maximum in the measured range and upon increasing the electron donating properties of the core, a redshift was observed as expected from theory.^[39,40]

Figure 3. Normalized UV-Vis absorption spectra of the azomethine-based HTMs. The materials were dissolved in chlorobenzene at a concentration of 20 mg mL⁻¹.

The absorption spectra of the materials in the solid state showed small bathochromic shifts of 4-10 nm compared to the solution spectra (*Table S 12*), which we assign to molecular packing in the solid state. The band gaps (E_g) of the HTMs were estimated from the onset of the absorption spectrum of each of the films. The prepared HTM films are only around 50 nm thick, increasing the transmittance of the films compared to films of Spiro-OMeTAD, which is generally around 250 nm thick. In the spectral range of 350 to 800 nm, films prepared from our materials show a transmittance of more

than 50% at their absorption maximum, while Spiro-OMeTAD absorbs more than 90% of the light at its absorption maximum (*Figure S 4b*). The high transmittance in the visible range makes these materials interesting, especially for tandem applications,^[41] as it would reduce the parasitic absorption. However, as our materials have a smaller bandgap than Spiro-OMeTAD, their absorption maxima appear at higher wavelengths, and therefore increasing the band gap of our HTMs would be desirable to further reduce optical losses.

Inverting the azomethine bond significantly increases the bandgap of the material, as is clear from the comparison of **Ph-OMeTPA** with **Ph-inv-OMeTPA** (*Figure 3*). Similar observations have been reported by Sek *et al.* and Hindson *et al.*^[40,42] In contrast, the introduction of the heteroatom into the core decreases the bandgap, as is clearly shown for **EDOT-OMeTPA** and **Th-OMeTPA**. The smaller bandgap of these materials is consistent with NMR spectroscopic results, where a down-field shift of the azomethine proton is observed, indicating a higher degree of conjugation (*Table S 1*).^[42] This hypothesis is also supported by FTIR measurements, which show that the azomethine stretching vibrations are shifted to lower wavenumbers (*Table S 1*).^[42] Our results demonstrate that by varying the core and inverting the azomethine bond, the bandgap of the HTM can be easily and substantially tuned.

A good alignment of the HOMO energy level of the HTM with the valance band of the perovskite is essential in order to obtain high open circuit voltages in photovoltaic devices.^[43] In order to study the energy level alignment, the oxidation potentials of the HTMs were measured using cyclic voltammetry. Very comparable oxidation potentials were found for all materials, resulting in a small spread in HOMO energy levels. These energy levels are dominated by the electron-donating part of the molecules, which in this series of HTMs is always the triphenylamine side group, hence explaining the similar HOMO energy levels.^[44] Inverting the azomethine bond slightly lowers the HOMO energy level since the electronegative nitrogen in the azomethine-bond is not directly connected to the triphenylamine moiety. Between the two phenyl-based HTMs (**Ph-OMeTPA** and **Ph-inv-OMeTPA**), we observe a difference of 90 meV as a result of inverting the azomethine-bond. The HOMO energy levels are close to the valance band of CH₃NH₃PbI₃ (5.43 eV), which is expected to minimize the energy losses in photovoltaic devices and should enable high open circuit voltages.

The LUMO energy levels were estimated by adding the optical bandgap to the HOMO energy levels; they mainly depend on the core of the small molecules, resulting in a wide range of energies for these levels.^[44] In all cases, the LUMO levels are higher than the conduction band of CH₃NH₃PbI₃, making them good electron blocking materials.

Figure 4. Electrostatic surface potential, frontier molecular orbital distributions and energies. Kohn-Sham HOMO and LUMO at B3LYP 6-31G(d,p) level and the calculated HOMO energy level following the procedure of Chi *et al.* (red dotted line).^[45] Grey box and black lines indicate the experimentally determined energy levels and bandgap. The blue line indicates the valence and conduction band of $\text{CH}_3\text{NH}_3\text{PbI}_3$.

Computational study

To gain insights into the geometric and electronic structure of the different small molecules, density functional theory (DFT) geometry optimisations (B3LYP/6-31G(d,p) level) were performed in vacuum and in dichloromethane as the solvent, by means of the conductor-like polarizable continuum model (CPCM) as implemented in the Gaussian 09 program package. Except for **TPA-OMeTPA**, the HOMO is distributed over the entire molecule (Figure 4). For **TPA-OMeTPA** we observed that the HOMO is more localized on the terminal triphenylamines, which we ascribe to the disruption of the conjugation of the central triphenylamine.^[46,47] The disturbance of the conjugation in the triphenylamine-based azomethines was experimentally observed by Skene and co-workers in a previous study.^[47]

HOMO energy levels obtained from computational chemistry for single molecules in vacuum generally strongly differ from the experimental results. Chi *et al.* showed that it is possible to get a good estimate of the experimental HOMO energy levels from the HOMO energy levels obtained from DFT calculations (B3LYP/6-31G(d,p) in dichloromethane)^[45] using the following formula:

$$\text{HOMO}_{\text{calc}} = \text{HOMO}_{\text{DFT, DCM}} + 0.624 \text{ eV}$$

In our case, applying this simple correction resulted in calculated HOMO energy levels that are in excellent agreement with the experimental values and shows that this method is a valuable tool for designing novel azomethine-based HTMs (Figure 4).

The calculated electrostatic potential map is depicted in Figure 4. We observe for all small molecules that the most electronegative part is near the nitrogen of the azomethine bond, while the more electropositive part is much more spread out over the molecule, except for **EDOT-OMeTPA**, where the cyclic ether in the core shows to be the most electropositive. This leads to a strong dipole in the core of **EDOT-OMeTPA**. Similarly, we also observe a clear directional dipole in **Th-OMeTPA**, and **Fu-OMeTPA**. The strong dipole in the core could facilitate close molecular packing in the solid, which is expected to enhance the intermolecular charge transport. Despite the anticipated close molecular

packing, thin films prepared *via* spincoating are amorphous according to thin film XRD measurements.

Table 2. HOMO energy levels obtained from DFT calculations and cyclic voltammetry

Compound	HOMO _{cv} (eV) ^a	HOMO _{calc} (eV) ^b	HOMO _{DFT, vacuum} (eV)	HOMO _{DFT, DCM} (eV)
EDOT-OMeTPA	-5.28	-5.24	-4.37	-4.62
Ph-OMeTPA	-5.30	-5.45	-4.51	-4.83
Th-OMeTPA	-5.30	-5.31	-4.47	-4.68
Fu-OMeTPA	-5.30	-5.29	-4.44	-4.66
TPA-OMeTPA	-5.28	-5.28	-4.44	-4.65
Ph-inv-OMeTPA	-5.39	-5.45	-4.59	-4.83
Diazo-OMeTPA	-5.36	-5.36	-4.49	-4.74

^a HOMO energy level experimentally obtained from cyclic voltammetry measurements. DFT HOMO energy levels from B3LYP/6-31G(d,p) level in vacuum and DCM. ^b Calculated following the procedure by Chi *et al.*^[45] where HOMO_{calc} = HOMO_{DFT, DCM} + 0.624 eV

Charge transport properties

Besides good energy level alignment, the charge transport properties of the HTMs are important in order to obtain an efficient hole-transporting layer. We studied the hole mobility by preparing hole-only devices using the pristine materials. The devices were built using a common device architecture: indium-doped tin oxide (ITO)/MoO_x/HTM/MoO_x/Au.^[39,48,49] The HTM layer was prepared by spincoating the small molecules from chlorobenzene at a concentration of 10 mg mL⁻¹. *J*-*V* curves were recorded in the dark, with the current assumed to be space-charge limited at higher voltages. From this, the charge carrier mobility can be estimated using the Mott-Gurney equation (more details in the supporting information).^[50] The two molecules with the inverted azomethine-bond, **Diazo-OMeTPA** and **Ph-inv-OMeTPA** showed a good fit to this equation with the extracted mobility value for **Diazo-OMeTPA** in good agreement with the one reported by Ma *et al.*^[29] The other small molecules exhibited significant field dependence and the mobilities were extracted using a Poole-Frenkel-type field dependence.^[51] The zero-field mobility (μ_0), field coefficient (γ) and the mobility at a field of 5×10^5 V cm⁻¹ (μ (E)) are listed in *Table 3*. We note that the orientation of the azomethine bond seems to have a strong influence in cases where the mobility shows a field dependence. **Fu-OMeTPA** showed relatively low mobilities at the order of 10^{-7} cm² V⁻¹ s⁻¹, which is significantly lower than its thiophene analogue. This is believed to be the result of the enhanced diene character of the furan compared to the more aromatic character of the thiophene, and is in agreement with a systematic study done by Bijleveld *et al.*^[52] The other materials show significantly higher hole mobilities, at the order of 10^{-5} to 10^{-6} cm² V⁻¹ s⁻¹, which are among the highest reported mobilities for azomethine-based small molecules (*Figure S 7* and *Figure S 8*).^[39,53–55] These mobilities are comparable to values extracted from Spiro-OMeTAD.^[56]

Table 3. Hole mobility of the pristine and the conductivity for the pristine and doped HTMs.

Compound	μ_0 (cm ² V ⁻¹ s ⁻¹)	γ (m ^{1/2} V ^{-1/2})	μ (cm ² V ⁻¹ s ⁻¹)	σ_{pristine} (S cm ⁻¹)	σ_{doped} (S cm ⁻¹) ^a
EDOT-OMeTPA	1×10^{-10}	3×10^{-4}	5×10^{-6}	6×10^{-8}	2×10^{-6}
Ph-OMeTPA	5×10^{-11}	4×10^{-4}	4×10^{-6}	1×10^{-8}	5×10^{-6}
Th-OMeTPA	3×10^{-10}	3×10^{-4}	1×10^{-5}	2×10^{-8}	2×10^{-6}
Fu-OMeTPA	3×10^{-12}	5×10^{-4}	5×10^{-7}	2×10^{-8}	1×10^{-6}
TPA-OMeTPA	2×10^{-11}	4×10^{-4}	1×10^{-6}	1×10^{-8}	1×10^{-6}
Ph-inv-OMeTPA	-	-	6×10^{-6}	7×10^{-9}	1×10^{-7}

Diazo-OMeTPA	-	-	1×10^{-6}	2×10^{-8}	3×10^{-6}
Spiro-OMeTAD	-	-	4×10^{-5}	9×10^{-8}	3×10^{-5}

^a HTM solutions were doped with 30 $\mu\text{L mL}^{-1}$ of a 170 mg/mL LiTFSI solution in acetonitrile before spincoating, and the films were allowed to oxidize overnight.

In order to increase the charge transport in the hole-transporting layer, the HTM is generally oxidized using LiTFSI. Abate *et al.* showed the influence of the addition of LiTFSI to spiro-OMeTAD on the conductivity (σ).^[57] In our previous work we showed that the addition of LiTFSI is necessary to obtain good working devices when **EDOT-OMeTPA** is used.^[5] Although there are several studies regarding electro- and chemical oxidation of azomethine-based dyes,^[58–61] the effect of the oxidation by LiTFSI on azomethine-based HTMs and the effect on the conductivity have not been reported.

The oxidation of the small molecules upon addition of LiTFSI was studied by light absorption measurements, showing an additional absorption band for the oxidized species (ca. 550 nm for **Diazo-OMeTPA**). The fraction of the oxidized species increases upon addition of LiTFSI, while we observe bleaching of the signature of the neutral species as expected. The absorbance of the oxidized species also depends on the HTM and especially for **Ph-inv-OMeTPA**, a strong increase of the oxidized species was observed (Figure 5 and Figure S 5).

The impact of the presence of the oxidized species on the conductivity was measured as a function of the amount of added LiTFSI. The pristine materials show a low conductivity on the order of 10^{-8} S cm^{-1} , which is comparable to the conductivity of pristine Spiro-OMeTAD (Figure 5).

Figure 5. The effect of doping with LiTFSI on the optical properties of **Diazo-OMeTPA** (left) and conductivities of the HTMs as a function of LiTFSI addition (right). The solid grey bar was added as a guide to the eye.

An increase of around two orders of magnitude in the conductivity was observed for all materials upon adding 30 $\mu\text{L mL}^{-1}$ of a 170 mg/mL LiTFSI solution in acetonitrile to the HTM casting solutions. This demonstrates that LiTFSI can be used as an efficient oxidizer for azomethine-based HTMs, resulting in conductivities that are among the highest reported for azomethine-based semiconductors.^[62–66] However, in contrast to Spiro-OMeTAD, where a maximum in conductivity was reported for around 20 mol% doping,^[57] the azomethine-based HTMs require significantly higher amounts of LiTFSI to reach comparably high conductivities. Since the azomethine-based HTMs do not show a maximum in conductivity like Spiro-OMeTAD in the range from 0 to 250 mol%, the conductivity can be increased upon addition of LiTFSI and generally exceeds the conductivity of

Spiro-OMeTAD when approximately 100 mol% of LiTFSI is added to the azomethine-based HTMs. The significant difference in oxidation behaviour of the azomethine-based HTMs compared to Spiro-OMeTAD indicates that for new classes of hole transporters, it is crucial to optimize the additives and their concentration in order to obtain a comparable performance to the state-of-the-art materials.

Photovoltaics properties

The photovoltaic performance of perovskite solar cells is strongly influenced by the quality of the perovskite layer. New synthetic routes for the preparation of perovskite films are frequently reported, leading to a wide spread of the power conversion efficiencies (PCE) in the field and making it difficult to compare the influence of different parameters between different publications.^[23] This poses a significant challenge to compare different HTMs with each other, and therefore developing design rules is difficult. Here we present an entire series of small molecules that we apply as HTM in perovskite photovoltaic devices generated using the same preparation method and in the same batch. This allows for the direct comparison of the performance and assists in the extraction of design rules regarding the core of the HTM, and the influence of the orientation of the azomethine bond.

We prepared solar cells employing a common device architecture (fluorine doped tin oxide/TiO₂/perovskite/HTM/Au) with a planar compact TiO₂ hole-blocking layer (Figure S9–S13). Smooth methylammonium lead iodide (CH₃NH₃PbI₃) perovskite films were prepared using our previously published protocol.^[67] The HTMs were spincoated from chlorobenzene at a concentration of 10 mg mL⁻¹ following our previously optimized procedure,^[5] which results in layers with thicknesses in the 50 nm range. The azomethine-based HTMs generally form uniform, pinhole-free films even though the concentrations in the spincoating solutions are relatively low (Figure S 14). In addition to saving material, the thin HTM layer is particularly interesting for tandem solar cell applications, since the parasitic absorption can be reduced. In a direct comparison, we found that preparing Spiro-OMeTAD films with this thickness results in shunting behaviour and very low device reproducibility.^[5]

Power conversion efficiencies (PCEs) in the range of 9.3 to 14.4% were obtained for devices prepared with the different azomethine-based HTMs, marginally lower than those made with Spiro-OMeTAD showing a PCE of 15.1% on a side-to-side comparison. Besides the previously published **EDOT-OMeTPA**, **Diazo-OMeTPA** also shows a good PCE of 14.4%. Both materials exhibit a stabilized power output that is comparable to devices made with Spiro-OMeTAD (Figure S11). More specifically, **Diazo-OMeTPA** shows a high open circuit voltage (V_{oc}) of 1.10 V, which is slightly higher than the voltage we obtained for Spiro-OMeTAD (1.06 V), and higher than the voltages we obtained with all other azomethine-based HTMs. The high V_{oc} can be ascribed to the relatively deep HOMO energy level of the **Diazo-OMeTPA**, resulting in an optimal alignment with the valence band of the perovskite. Additionally, we expect that the interface between the perovskite and **Diazo-OMeTPA** exhibits less significant surface recombination than **EDOT-OMeTPA**, as was recently shown,^[68] which could explain the high voltages. In contrast, further lowering the HOMO energy level, as in **Ph-inv-OMeTPA**, results in an injection barrier and prevents efficient extraction of the charges, hence explaining the very poor photovoltaic performance of this material.

The HTMs with a heterocycle in the core (**EDOT-OMeTPA**, **Th-OMeTPA** and **Fu-OMeTPA**) show significantly better performance than the HTMs without a heterocycle in the core (**Ph-OMeTPA** and **TPA-OMeTPA**). We hypothesize that the high electron density in **EDOT-OMeTPA**, **Th-OMeTPA** and

Fu-OMeTPA likely results in stronger interactions with the perovskite interface and/or enhances the packing of the material, as both azomethine bonds face the same direction, resulting in a directional dipole that potentially enhances the interaction with the perovskite interface. **Diazo-OMeTPA** also shows good photovoltaic performance, which could be the result of the flat structure of the core,^[29] enhancing the packing efficiency. In addition, we note that the best performing materials also have the highest melting points, which might also hint at tight molecular packing in the solid.

Despite the significant differences in the mobility of the different HTMs, we do not observe large differences in the short-circuit current (J_{sc}), or a correlation between the hole mobility and the fill factor, which could be related to the relatively thin HTM layer. However, we do observe that the fill factor for all azomethine-based HTMs is lower than for Spiro-OMeTAD. This could originate from the slightly lower mobility and conductivity, although it is more likely the result of the relatively high surface recombination rates between the perovskite and the HTM, as was shown for the MAPbI₃/EDOT-OMeTPA interface.^[68]

Table 4. Device performance of perovskite solar cells containing different HTMs.

Compound	J_{sc} (mA cm ⁻²)	V_{oc} (V)	FF (%)	PCE (%)
EDOT-OMeTPA	19.2	1.01	73	14.4
Ph-OMeTPA	18.6	0.89	55	9.3
Th-OMeTPA	18.9	0.99	70	13.2
Fu-OMeTPA	17.9	0.98	72	13.0
TPA-OMeTPA	17.4	0.93	59	9.6
Ph-inv-OMeTPA	1.4	0.62	26	0.2
Diazo-OMeTPA	18.9	1.10	69	14.4
Spiro-OMeTAD	18.7	1.06	76	15.1

Moisture-induced degradation

The rather poor stability of CH₃NH₃PbI₃ perovskite, especially towards moisture, is a major drawback for the potential commercialisation of the technology. Various groups have studied the degradation of the perovskite and found several decomposition pathways. Frost *et al.* reported that the presence of water can degrade the perovskite to HI, PbI₂ and CH₃NH₂.^[69] Leguy *et al.* showed that humidity can also degrade the perovskite resulting in the formation of CH₃NH₃PbI₃·H₂O and (CH₃NH₃)₄PbI₆·2H₂O.^[70] The formed degradation products depend on several factors like humidity and exposure time, but also on the chemical composition and precursor excess in the perovskite.^[67,70,71] Organic HTMs are generally hydrophobic and are therefore expected to protect the perovskite against degradation. However, if there is a weak adhesion of the HTM with the perovskite, the interface can still be destabilized, leading to large-scale delamination and therefore device failure.^[72] Recent work by Lee *et al.* showed that the adhesion of the HTM with the perovskite at the interface depends on the HTM.^[73] Moreover, pinholes in the HTM layer can play an important role as well and are known as a starting point for moisture-induced degradation.^[74]

Our azomethine-based HTMs show good film-forming properties and we are able to form relatively thin (~50 nm compared to 250 nm for Spiro-OMeTAD) pinhole-free films of the HTMs, even upon addition of the additives LiTFSI and tBP (Figure S 14). To study the moisture barrier properties of the HTMs, perovskite films covered with a layer of the HTMs (with additives) were stored under a high humidity environment with a controlled relative humidity (R.H.) of 75% in air. The edges of the films were covered with epoxy to slow down moisture-induced degradation initiating from the edge of the substrate (schematic in Figure S 16). Despite the significantly thicker layer of Spiro-OMeTAD, the perovskite covered with the latter starts to degrade within several hours, which is in agreement with

literature.^[73] In contrast, all our azomethine-based HTMs protected the perovskite significantly better, as can be observed in the photos in *Figure 6* and *Figure S 15*, and even after 14 days the perovskite does not appear to degrade as a result of hydration, demonstrating the excellent barrier properties of our HTMs (*Figure S 18*).

The moisture-induced degradation of the perovskite was confirmed by *in-situ* XRD measurements at 90% R.H. for perovskite/HTM bilayers with **EDOT-OMeTPA** and **Diazo-OMeTPA**. We compared the results to pristine perovskite films and perovskite/Spiro-OMeTAD bilayers as reference (*Figure 6*, *Figure S 17*). The XRD patterns show the influence of water through the formation of PbI_2 as a degradation product for the reference devices within hours,^[67] while the perovskites covered with the azomethine-based HTMs show no sign of degradation over a period of 8 hours. Additionally, bilayers that have been exposed for 30 days at 75% RH do not show the formation of degradation products. In contrast, the Spiro-OMeTAD based reference device, which lost its colour, shows diffraction peaks for the monohydrate species of the perovskite and no peak assigned to the perovskite was observed any longer, indicating complete degradation of the perovskite (*Figure S 18*).

Dense and pinhole-free HTM layers are key for a good barrier against the infiltration of moisture.^[74] Microscopy images show that the azomethine-based HTMs show good film-forming properties with few pinholes, but more importantly, these films have a significantly higher density than Spiro-OMeTAD. We determined the density for **EDOT-OMeTPA** and **Diazo-OMeTPA** to be 1.24 and 1.27 g cm^{-3} respectively (details in Supporting Information), which is significantly higher than the density of 1.03 g cm^{-3} for Spiro-OMeTAD.^[75] The spiro-core in Spiro-OMeTAD results in a large molecule with a large free volume and also makes it difficult to form a tight molecular packing, thus explaining the relatively low density. The large free volume could facilitate the diffusion of water molecules through the film and degrade the underlying perovskite. Reducing the free volume in the HTM could therefore be a suitable design route to prepare HTMs with good moisture barrier properties.

Considering an additional point, Lee *et al.* report that the adhesion between the HTM and the perovskite makes a significant contribution to the degradation.^[73] It is possible that azomethine-based HTMs also have an improved adhesion to the perovskite, explaining the improved stability towards moisture. All the azomethine-based HTMs have in common that they contain heteroatoms with an accessible free electron pair that could interact with the perovskite, and thereby passivate the surface. This is in agreement with the work of Saliba *et al.* who reported simulations showing the thiophene-iodine interaction between a thiophene-containing HTM and the perovskite.^[9] Further studies are required to study possible interactions between the azomethine-bond and the perovskite, however, our results clearly demonstrate the superior performance of these azomethine-based HTMs.

Figure 6. (a) Photos of perovskite films covered with a layer of the HTM and stored at 75% RH. (b, c, d) XRD patterns obtained from in-situ hydration measurements of the perovskite:HTM bilayers at 90% RH. The reflection from PbI_2 , which is the degradation product of the perovskite, is indicated with an asterisk. All perovskites were prepared using 5% PbI_2 excess in the precursor solution, explaining the initial small PbI_2 peak observed in all samples.

Conclusions

In conclusion, we have prepared a series of azomethine-based HTMs in which we changed the core and the direction of the azomethine bond to study their influence on the optoelectronic properties and photovoltaic performance of perovskite-based solar cells. We show that our materials can be synthesized at low-cost with strongly reduced environmental impact, while changing the chemical structure allows the fine tuning of the energy levels of the HTMs, resulting in a good energy level alignment with the valence band of $CH_3NH_3PbI_3$. The HTMs can be efficiently doped with LiTFSI, leading to a significant increase in conductivity of up to $10^{-3} \text{ S cm}^{-1}$ when $60 \mu\text{L mL}^{-1}$ of the LiTFSI solution is added, while the materials reach hole mobilities comparable to the state-of-the-art. As hole transporting layer in perovskite solar cells, especially **Diazo-OMeTPA** shows an impressive high V_{oc} of 1.10 V, which outperforms that of Spiro-OMeTAD (1.06 V). The orientation of the azomethine bond influences the optoelectronic and charge transport properties, and with both orientations high PCE can be obtained when combined with the appropriate core as demonstrated for **EDOT-OMeTPA** and **Diazo-OMeTPA**. The best photovoltaic performance was achieved with HTMs having heterocycles in the core, rather than non-heterocyclic aromatic rings, which we relate to the strong

dipole in the core of the HTM and to close molecular packing. In contrast to Spiro-OMeTAD, all the azomethine-based HTMs prove to be excellent barriers against moisture-induced degradation of the underlying perovskite. We attribute the superior moisture barrier properties to the relatively high density of the HTM films, $\sim 1.25 \text{ g cm}^{-3}$, compared to Spiro-OMeTAD (1.03 g cm^{-3}). We propose that dense films with close molecular packing make it difficult for water to diffuse through the HTM layer and thereby protect the underlying perovskite against degradation. Our work demonstrates that HTMs prepared *via* condensation chemistry can not only significantly decrease the fabrication cost, but can also significantly improve the stability of perovskite solar cells.

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Table of Content:

A series of azomethine-based HTMs is synthesized using simple condensation chemistry. Design rules are extracted from their photovoltaic performance and moisture barrier properties.

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Materials for Perovskite Solar Cells with Moisture Barrier Properties

Figure for possible cover image.

Supporting information

Design Rules for the Preparation of Low-Cost Hole Transporting Materials for Perovskite Solar Cells with Moisture Barrier Properties

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1 Materials and Methods

1.1 Synthesis

All chemicals were purchased from commercial sources and used as received unless stated otherwise.

The structures were confirmed by ^1H -NMR (Bruker spectrometer Avance III, 400 MHz or Jeol 400 MHz) and ^{13}C -NMR (Bruker spectrometer Avance III 100 MHz or Jeol 100 MHz). All samples were dissolved in deuterated solvents and the recorded spectra were referenced to the solvent (CDCl_3 : ^1H , 7.26 and ^{13}C 77.0 ppm C_6D_6 : 7.36 ppm) relative to TMS. Infrared spectra were obtained with a PerkinElmer FT-infrared Spectrometer Paragon 1000 and UV-Vis spectra were collected using a PerkinElmer Lambda 1050 spectrometer. LRMS and HRMS measurements were carried out using a JMS GCmate II jeol applying the FAB+ and on a Thermo Finnigan LTQ FT Ultra applying the ESI method.

1.1.1 Synthesis of 4,4'-dimethoxy-4''-nitrotriphenylamine

Copper(I)iodide (3.43 g, 18.0 mmol), potassium carbonate (77.3 g, 560 mmol) and *L*-proline (6.7 g, 58.0 mmol) were dissolved in 100 mL of DMF. 4-Nitroaniline (9.9 g, 72 mmol) and 4-iodoanisole (54 g, 240 mmol) were dissolved in another 100 mL of DMF and slowly added *via* a syringe. The reaction was then heated to 115 °C under vigorous stirring. After five days the reaction mixture was poured in water (1000 mL) and extracted with ethyl acetate. The organic phase was washed with brine (twice 500 mL). After drying over magnesium sulphate the solvent was removed under vacuum. Crystallisation from diethyl ether, resulted in bright orange crystals in a yield of 63% (15.58 g, 45.2 mmol).

Characterization in agreement with literature.^[S1]

^1H -NMR (CDCl_3 , 400MHz) δ = 7.97 (d, J = 9.3 Hz, 2H); 7.13 (d, J = 8.9 Hz, 4H); 6.90 (d, J = 8.9 Hz, 4H); 6.75 (d, J = 9.3 Hz, 2H); 3.81 (s, 6H) ppm;

^{13}C -NMR (CDCl_3 , 100MHz) δ = 157.6; 154.1; 138.9; 138.2; 128.0; 125.4; 115.6; 115.1; 55.4 ppm;

FTIR: $\nu(\text{cm}^{-1})$: 3041, 2841, 1583, 1493, 1236, 1105, 830, 748, 691;

GCMS: m/z (relative intensity): t_R = 20.6 min, 450.0 (100), 335.0 (58), 289.0 (25), 351.0 (21), 336.0 (12), 77.1 (12)

1.1.2 Synthesis of 4,4'-dimethoxy-4''-aminotriphenylamine

6.16 g of compound **1** (17.6 mmol) was dissolved in 80 mL THF. 0.2 g of palladium on carbon was mixed with 2 mL of THF and added slowly to the solution. The mixture was heated to reflux (it is important to heat to reflux before adding the hydrazine) and 6 g hydrazine solution (66% in water) in 20 mL THF was added slowly via a dropping funnel over one hour. After addition, the reaction was refluxed for two more hours. After cooling down to room temperature, the palladium on carbon was removed *via* filtration under nitrogen and the volume was reduced. Upon addition of water the product precipitates, was filtered off as a clear white powder and was dried under vacuum (5.2 g, 16.2 mmol, 92%).

Characterization in agreement with literature.^[S1]

¹H-NMR (CDCl₃, 400MHz) δ : 6.98 (d, J = 8.9 Hz, 4H); 6.90 (d, J = 8.6 Hz, 2H); 6.79 (d, J = 9.0 Hz, 4H); 6.59 (d, J = 8.7 Hz, 2H); 3.78 (s, 6H); 3.58 (s, broad, 2H) ppm;

¹³C-NMR (CDCl₃, 100MHz) δ : 154.4; 142.1; 414.6; 139.9; 125.5; 124.1; 115.9; 114.3; 55.3 ppm;

FTIR: $\nu(\text{cm}^{-1})$: 3457, 3373, 3033, 2836, 1634, 1497, 1232, 1027, 817;

MS m/z (relative intensity): 320.0 (100), 305.0 (63), 321.1 (20), 160.0 (18), 306.0 (13)

1.1.3 General synthesis of hole transporting materials

EDOT-OMeTPA and Diazo-OMeTPA were synthesized according to literature (density 1.24 g cm⁻³).^[S2, S3]

4,4'-dimethoxy-4''-aminotriphenylamine (2.40 eq) and the dialdehyde (1.00 eq) were dissolved in 40 mL dry chloroform. After addition of one drop of trifluoroacetic acid the mixture was refluxed for 4 hours. After cooling down to R.T. the reaction mixture was slowly poured into an isopropanol/hexane solution (250 mL), which also contained 0.5 mL of trimethylamine to neutralize the acid and the azomethine bond. The precipitate was obtained *via* filtration and additionally washed twice with an isopropanol/hexane solution. The products were dried under vacuum at elevated temperature.

1.1.3.1 Ph-OMeTPA

4,4'-dimethoxy-4''-aminotriphenylamine (0.890 g, 2.78 mmol) and isophthalaldehyde (0.160 g, 1.16 mmol), yield = 0.830 g (1.12 mmol, 97%).

Orange powder, R_f = 0.25 (DCM);

$^1\text{H-NMR}$ (400 MHz, CDCl_3) δ = 8.53 (s, 2H), 7.96 (s, 4H), 7.21 – 7.15 (m, 4H), 7.10 – 7.04 (m, 8H), 6.99 – 6.94 (m, 4H), 6.87 – 6.81 (m, 8H), 3.80 (s, 12H) ppm;

$^1\text{H-NMR}$ (400 MHz, C_6D_6) δ = 8.31 (s, 2H), 7.92 (s, 4H), 7.33 – 7.27 (m, 4H), 7.19 – 7.11 (m, 12H), 6.81 – 6.74 (m, 8H), 3.34 (s, 12H) ppm;

$^{13}\text{C-NMR}$ (101 MHz, CDCl_3) δ = 156.4, 155.9, 147.7, 144.7, 141.2, 140.9, 128.8, 126.5, 122.1, 121.2, 114.7, 55.5 ppm;

$^{13}\text{C-NMR}$ (101 MHz, C_6D_6) δ = 156.2, 156.0, 147.8, 144.8, 141., 138.9, 128.8, 126.5, 122.4, 121.6, 114.9, 54.7 ppm;

LRMS (FAB pos): m/z (%) = 739.0 (68), 460.6 (30), 307.5 (100), 289.4 (94), 155.3 (100), 107.2 (91), 65.2 (22);

HRMS (FAB pos): m/z calcd for $\text{C}_{48}\text{H}_{42}\text{N}_4\text{O}_4^+$ $[\text{M}+\text{H}]^+$: 739.3279; found: 739.3298;

FTIR: $\nu(\text{cm}^{-1})$: 3000 (w), 2947 (w), 2832 (w), 1618 (m), 1586 (w), 1502 (s), 1462 (m), 1441 (m), 1315 (m), 1284 (m), 1272 (m), 1235 (s), 1178 (m), 1107 (m), 1032 (s), 830 (s);

1.1.3.2 Th-OMeTPA

4,4'-dimethoxy-4''-aminotriphenylamine (2.00 g, 6.25 mmol) and 2,5-thiophenedicarboxaldehyde (0.365 g, 2.60 mmol), yield = 1.70 g (2.28 mmol, 88%).

Red powder, R_f = 0.53 (DCM);

$^1\text{H-NMR}$ (400 MHz, CDCl_3) δ = 8.57 (s, 2H), 7.41 (s, 2H), 7.16 (m, 4H), 7.09 – 7.03 (m, 8H), 6.97 – 6.91 (m, 4H), 6.86 – 6.80 (m, 8H), 3.80 (s, 12H) ppm;

$^1\text{H-NMR}$ (400 MHz, C_6D_6) δ = 8.26 (s, 2H), 7.23 – 7.04 (m, 12H), 6.97 (s, 4H), 6.80 – 6.69 (m, 2H), 5.41 (s, 8H), 3.31 (s, 12H) ppm;

$^{13}\text{C-NMR}$ (101 MHz, CDCl_3) δ = 155.9, 149.1, 147.8, 143.3, 140.8, 130.9, 126.8, 126.5, 122.2, 121.1, 114.7, 55.5 ppm;

$^{13}\text{C-NMR}$ (101 MHz, C_6D_6) δ = 156.2, 148.9, 147.9, 146.8, 143.9, 141.1, 130.5, 126.5, 122.6, 121.4, 114.8, 54.7 ppm;

LRMS (FAB pos): m/z (%) = 744.9 (82), 460.6 (7), 307.5 (62), 154.3 (100), 136.3 (97);

HRMS (FAB pos): m/z calcd for $\text{C}_{46}\text{H}_{40}\text{N}_4\text{O}_4\text{S}^+$ $[\text{M}+\text{H}]^+$: 745.2843; found: 745.2856;

FTIR: $\nu(\text{cm}^{-1})$: 2930 (w), 2831 (w), 1605 (m), 1500 (s), 1461 (m), 1440 (w), 1317 (w), 1280 (m), 1229 (s), 1178 (m), 1104 (w), 1033 (m), 828 (s);

1.1.3.3 Fu-OMeTPA

4,4'-dimethoxy-4''-aminotriphenylamine (0.50 g, 1.56 mmol) and 2,5-furandicarboxaldehyde (0.097 g, 0.78 mmol) were used in a stoichiometric ratio, yield = 0.46 g (0.63 mmol, 81%);

Red powder, R_f = 0.87 (DCM);

$^1\text{H-NMR}$ (400 MHz, CDCl_3) δ = 8.43 (s, 2H), 7.21 – 7.15 (m, 4H), 7.11 – 7.03 (m, 10H), 6.97 – 6.91 (m, 4H), 6.87 – 6.80 (m, 8H), 3.80 (s, 12H) ppm;

$^1\text{H-NMR}$ (400 MHz, C_6D_6): δ = 8.20 (s, 2H), 7.23 – 7.21 (m, 4H), 7.10 – 7.06 (m, 12H), 6.81 (s, 2H), 6.75 – 6.71 (m, 8H), 3.31 (s, 12H) ppm;

$^{13}\text{C-NMR}$ (101 MHz, CDCl_3) δ = 156.0, 154.5, 148.1, 144.4, 143.1, 140.7, 126.7, 122.2, 120.7, 115.5, 114.8, 55.5 ppm;

$^{13}\text{C-NMR}$ (101 MHz, C_6D_6): δ = 156.3, 155.0, 148.1, 144.1, 144.1, 141.0, 126.6, 122.43, 121.3, 114.8, 114.6, 54.7 ppm;

LRMS (FAB pos): m/z (%) = 728.9 (94), 727.9 (6), 622.0 (3), 460.6 (5), 307.5 (44), 154.3 (100), 136.3 (92);

HRMS (FAB pos): m/z calcd for $\text{C}_{46}\text{H}_{40}\text{N}_4\text{O}_5^+$ $[\text{M}+\text{H}]^+$: 729.3071; found: 729.3068;

FTIR: $\nu(\text{cm}^{-1})$: 2950 (w), 2832 (w), 1615 (m), 1581 (w), 1501 (s), 1462 (m), 1440 (w), 1317 (w), 1280 (m), 1237 (s), 1179 (m), 1160 (w), 1105 (w), 1032 (m), 825 (s).

1.1.3.4 TPA-OMeTPA

4,4'-dimethoxy-4''-aminotriphenylamine (1.00 g, 3.13 mmol) and triphenylamino-4,4'-dicarboxaldehyde (0.392 g, 1.30 mmol), yield = 1.12 g (1.24 mmol, 95%).

Yellow powder, R_f = 0.47 (DCM);

$^1\text{H-NMR}$ (400 MHz, CDCl_3) δ = 8.42 (s, 2H), 7.76 (m, 4H), 7.36 – 7.30 (m, 2H), 7.20 – 7.09 (m, 11H), 7.09 – 7.03 (m, 8H), 6.99 – 6.94 (m, 4H), 6.86 – 6.80 (m, 8H), 3.80 (s, 12H) ppm;

$^1\text{H-NMR}$ (400 MHz, C_6D_6) δ = 8.30 (s, 2H), 7.79 – 7.73 (m, 4H), 7.30 – 7.23 (m, 4H), 7.15 – 7.09 (m, 13H), 7.07 – 7.01 (m, 8H), 6.76 – 6.71 (m, 8H), 3.32 (s, 12H) ppm;

$^{13}\text{C-NMR}$ (101 MHz, CDCl_3) δ = 156.8, 155.7, 149.6, 147.1, 146.5, 144.9, 141.1, 131.3, 129.9, 129.7, 129.7, 126.2, 126.0, 123.4, 121.8, 121.7, 114.7, 55.5 ppm;

¹³C-NMR (101 MHz, C₆D₆) δ = 156.1, 156.0, 149.5, 147.3, 146.8, 145.6, 141.4, 131.9, 129.9, 129.5, 126.3, 125.7, 124.3, 123.4, 122.2, 122.1, 114.8, 54.7 ppm;

LRMS (ESI 70 eV): m/z (%) = 906.4 (94), 822.5 (49), 527.1 (9), 306.1 (47), 267.0 (60), 213.5 (100);

HRMS (ESI): m/z calcd for C₆₀H₅₁N₅O₄⁺ [M+H]⁺: 906.4014; found: 906.4021;

FTIR: ν(cm⁻¹): 3032 (w), 2929 (w), 2830 (w), 1616 (m), 1593 (w), 1504 (s), 1462 (m), 1439 (m), 1314 (m), 1271 (m-br), 1234 (s), 1165 (s), 1103 (m), 1032 (s), 823 (s);

1.1.3.5 *Ph-inv-OMeTPA*

4,4'-dimethoxy-4''-formyltriphenylamine (1.16 g; 3.48 mmol; 2.5 eq) and the benzene-1,4-diamine (0.15 g; 1.40 mmol; 1.00 eq) were dissolved in 20 mL dry chloroform. After addition of one drop of trifluoroacetic acid the mixture was refluxed for 4 hours. After cooling down to R.T. the reaction mixture was slowly poured into isopropanol, which also contained trimethylamine to neutralize the acid and the azomethine bond. The precipitate was obtained *via* filtration and additionally washed with ethanol. The product was dried under vacuum, the title compound was obtained as a dark orange solid (0.85 g; 1.15 mmol; 82%).

¹H-NMR (400 MHz, CDCl₃) δ = 8.35 (s, 2H), 7.66 (d, ³J = 8.1 Hz, 4H), 7.20 (s, 4H), 7.09 (d, ³J = 9.0 Hz, 8H), 6.90 (d, ³J = 8.6 Hz, 4H), 6.85 (d, ³J = 9.0 Hz, 8H), 3.79 (s, 12H)

¹H-NMR (400 MHz, C₆D₆): δ = 8.29 (s, 2H), 7.86 (d, ³J = 8.8 Hz, 4H), 7.29 (s, 4H), 7.09-7.04 (m, 12H), 6.71 (d, ³J = 9.2 Hz, 8H), 3.30 (s, 12H) ppm;

¹³C-NMR (101 MHz, C₆D₆): δ = 158.3, 157.2, 151.8, 150.8, 140.5, 130.5, 129.3, 127.7, 122.4, 119.3, 115.3, 55.1 ppm;

LRMS (FAB pos): m/z (%) = 739.9 (98), 738.9 (91), 408.6 (5), 307.5 (15), 154.3 (46), 136.3 (26);

HRMS (FAB pos): m/z calcd for C₄₈H₄₂N₄O₄⁺ [M+H]⁺: 738.3206; found: 738.3250;

FTIR: ν(cm⁻¹): 2930 (w), 2832 (w), 1592 (s), 1558 (w), 1500 (s), 1462 (w), 1440 (w), 1430 (w), 1319 (w), 1280 (m), 1237 (s), 1187 (w), 1160 (s), 1104 (m), 1031 (s), 824 (s)

1.1.3.6 *Diazo-OMeTPA*

Synthesis is described in literature.^[S14]

¹H-NMR (400 MHz, CDCl₃) δ = 8.54 (s, 2H), 7.59 (d, ³J = 8.8 Hz, 4H), 7.10 (d, ³J = 9.2 Hz, 8H), 6.89 (d, ³J = 8.8 Hz, 4H), 6.86 (d, ³J = 9.2 Hz, 8H), 3.81 (s, 12H)

¹³C-NMR (101 MHz, DMSO-d₆): δ = 160.8, 156.6, 151.2, 139.9, 129.4, 127.4, 125.6, 118.7, 114.8, 55.5 ppm;

FTIR: ν(cm⁻¹): 1610 (m), 1597 (m), 1470 (s), 1240 (s), 1168 (s), 1033 (s)

Density: 1.27 g cm⁻³

1.1.4 NMR and FTIR data interpretation

Table S 1. NMR and FTIR data from the azomethine bond.

Compound	δ (ppm, ^1H NMR)	ν (nm, FTIR $-\text{HC}=\text{N}-$ stretching)
EDOT-OMeTPA	8.60	1603
Ph-OMeTPA	8.53	1618
Th-OMeTPA	8.57	1605
Fu-OMeTPA	8.43	1615
TPA-OMeTPA	8.42	1616
Ph-inv-OMeTPA	8.35	1592
Diazo-OMeTPA	8.54	1610

The NMR chemical shift and vibrational frequency of the azomethine bond. A down-field shift in the NMR signal indicates an increase in the conjugation of the azomethine-bond. Similarly, lower wavenumbers indicate more conjugation through the azomethine-bond.

1.2 Analytics

1.2.1 X-ray diffraction

X-ray diffraction (XRD) analysis of perovskite films was carried out in reflection mode using a Bruker D8 Discover diffractometer with Ni-filtered Cu $K\alpha_1$ -radiation ($\lambda = 1.5406 \text{ \AA}$) and a position-sensitive semiconductor detector (LynxEye).

For the *in-situ* XRD measurements during the hydration process, a custom-made hydration chamber made of X-ray transparent polymers with a total volume of around 250 mL was utilized. The air humidity within the hydration chamber was measured using a hygrometer and was held constant at around 90% RH by employing vials filled with salt solution. All experiments were performed at room temperature ($24 \pm 2 \text{ }^\circ\text{C}$) without illumination.

Figure S 1. Schematic representation of the hydration chamber.^[S4]

1.2.2 Solar cell characterization

J-V curves of solar cells were recorded under ambient conditions with a Keithley 2400 source meter under simulated AM 1.5G sunlight, with an incident power of approximately 100 mW cm^{-2} , which was corrected for the exact light intensity using a Fraunhofer ISE certified silicon cell. The active area of the solar cells was defined with a square metal aperture mask of 0.0831 cm^2 . The reported device characteristics were estimated from the measured *J-V* curves obtained from the reverse scan (from V_{oc} to J_{sc}) which was recorded at a scan rate of 0.2 V s^{-1} after pre-biasing at 1.5 V for 5 s under illumination. All as-prepared devices show a comparable degree of hysteresis between the forward and reverse scan.

1.2.3 Cyclic voltammetry

Cyclic voltammetry (CV) experiments were performed using a Metrohm Potentiostat (PGSTAT302N) with platinum working and counter electrode and an Ag/AgCl reference electrode. Experiments were performed in anhydrous and degassed dichloromethane solutions of the hole transporter with 0.1 M tetrabutylammonium hexafluorophosphate ($t\text{BuNPF}_6$) as electrolyte and a scan rate of 100 mV s^{-1} . HOMO levels were calculated according to literature (the formal potential of the Fc^+/Fc redox couple used is -5.1 eV).^[S2]

1.2.4 Thermal characterization

Thermogravimetric analysis (TGA) was performed using a Netzsch STA 449 C Jupiter under nitrogen atmosphere with a scan rate of $10 \text{ }^\circ\text{C min}^{-1}$. Differential scanning calorimetry (DSC) was performed under nitrogen atmosphere using a Perkin Elmer DSC8000 at a heating rate of $20 \text{ }^\circ\text{C min}^{-1}$. Melting behaviour was confirmed using a melting point apparatus.

1.2.5 Photoluminescence

PL measurements were performed with a Fluotime 300 Spectrofluorometer (Picoquant GmbH). The excitation wavelength was fixed at 510 nm . The emission for time resolved measurements was monitored at the maximum intensity if the steady state photo emission.

1.2.6 External quantum efficiency

External quantum efficiency measurements were performed at short-circuit and referenced to a Si photodiode (Hamamatsu). The device was illuminated using a white bias light (Solar light Co. Inc. Model S16, 150 W xenon lamp $\sim 100 \text{ W m}^{-2}$) and light from a 150 W Xe short arc lamp (LOT Oriel) was used as probe light and modulated with a mechanical chopper (12 Hz) and passed through a monochromator (Horiba MicroHR) to select the wavelength. The response was recorded using a lock-in amplifier (Ametek Signal Recovery SR 7230 DSP) with a low-noise pre-amplifier (Femto DLPCA-200).

1.3 Film preparation for hydration studies

Microscopy glass substrates (2.5 x 2.5 cm) were successively cleaned with a 2% Hellmanex solution and rinsed with de-ionized water, ethanol and acetone. Directly before spin-coating the perovskite film, the substrates were plasma cleaned for 5 min. A precursor solution containing 1.31 M PbI_2 (TCI, >98%) and 1.25 M methylammonium iodide (Dyesol) in a *N,N*-dimethylformamide (DMF) : dimethyl sulfoxide (DMSO) solvent mixture (1:4 vol/vol) was prepared. The solutions were spin-coated dynamically (first at 1000 rpm for 10 s, followed by a second step at 5000 rpm for 30 s) onto the substrate. After 25 s, chlorobenzene was added on top of the spinning substrate and afterwards the substrate was annealed on a hotplate (first at 40 °C for 40 min, followed by a second step at 100 °C for 10 min). The hole transporting material spiro-OMeTAD (Borun Chemicals, 99.5% purity) was applied on the perovskite film using a 75 mg/mL solution in chlorobenzene, while the azomethine-based HTMs were spincoated from a 10 mg/mL solution in chlorobenzene. To all HTM solutions 10 $\mu\text{L/mL}$ 4-*tert*-butylpyridine (tBP) and 30 $\mu\text{L/mL}$ of a 170 mg/mL bis(trifluoromethane)sulfonamide lithium salt (LiTFSI) solution in acetonitrile were added. The HTM solutions were spin-coated dynamically at 1500 rpm for 45 s.

1.3.1 Hydration studies

For hydration studies the edges of the substrates were first covered with epoxy for the samples with the epoxy covered edge. All samples were allowed to oxidize overnight at <30% R.H, before they were placed in an excicator with a R.H. of 75% which was held constant using salt solutions and monitored using a hygrometer. The desiccator was closed with a glass plate that allows taking photos without removing the lid, in order to reduce fluctuations in the humidity. The excicator was stored in the dark to prevent light induced degradation.

1.4 Solar cell preparation

Fluorine-doped tin oxide (FTO) coated glass sheets (7 Ω/sq , Pilkington, USA) were patterned and cleaned. Directly before applying the hole-blocking layer the substrates were plasma cleaned. A compact TiO_2 layer was prepared from a sol-gel precursor solution by spin-coating onto the substrates and calcination at 500 °C for 30 min in air. For the sol-gel solution a 27.2 mM solution of HCl in 2-propanol was added dropwise to a vigorously stirred 0.43 mM solution of titanium isopropoxide (99.999 %, Sigma-Aldrich) in dry 2-propanol. After cooling down, the substrate was transferred to a nitrogen-filled glovebox. The perovskite films and HTM layers were prepared as described above. The devices were stored overnight under air at room temperature and < 30% RH to allow the hole transporting materials to oxidize. The top electrode with a thickness of 40 nm was deposited by thermal evaporation of gold under vacuum (at $\sim 10^{-6}$ mbar).

1.5 Hole only device preparation

ITO-substrates (1.5 x 2.0 cm, VisionTek, 12 Ω/sq to 15 Ω/sq) were etched and cleaned. The substrates were plasma cleaned prior to the thermal deposition of the MoO_x layer (10 nm) under vacuum ($\sim 1 \cdot 10^{-6}$ mbar). The substrates were exposed to air and stored in a nitrogen-filled glovebox. Next, the layers of HTMs were spincoated from chlorobenzene at a concentration of 10 mg mL^{-1} , resulting in a thickness of 40-60 nm. A top electrode of MoO_x (10 nm), followed by a layer of gold

(100 nm) was deposited under vacuum ($1 \cdot 10^{-6}$ mbar). The active area was 16 mm^2 . Current-voltage characteristics were recorded in air in the dark using a Metrohm potentiostat (PGSTAT302N) at a scan rate of 0.1 V s^{-1} . The layer thickness was determined by using atomic force microscopy (AFM) measurements, which were performed in tapping mode using a NanoInk DPN Stage microscope, or with a Veeco Dektak 150.

1.6 Conductivity measurements

Glass substrates with a thin compact layer of Al_2O_3 were used to improve the wetting of the HTMs on the substrate. The HTMs were spincoated at 1000 rpm from a chlorobenzene solution containing the given amount of LiTFSI as oxidant, resulting in a film thickness of 50 nm. The films were stored for 24 h in a desiccator (< 30% R.H.) before 40 nm thick gold electrodes were thermally deposited under vacuum ($\sim 10^{-6}$ mbar). The electrode pattern was designed for two point probe measurements with a channel length of 250, 500 and 1000 μm , a channel width of 0.2, 0.1 and 0.056 m respectively. No significant differences were observed depending on the electrode pattern and the measured values were averaged over at least 8 individual devices. *J-V* curves were recorded under ambient conditions without illumination using a Keithley 2400 source meter at a scan rate of 1 V s^{-1} in the range from -5 to 5 V.

1.7 Density measurements

The density of the HTMs was determined by spincoating films from chlorobenzene onto silicon substrates. Film thickness was measured using a Dektak 150 surface profiler and averaged over at least three different measurements. The bottom and sides of the substrate were carefully cleaned with acetone, to remove any material that ended there during the spincoating. Additionally the edges of the HTM film were removed with a razorblade and cleaned with acetone, in order to remove any edges where increased film thickness is often observed. Afterwards the area of the film was accurately measured, before re-dissolving the film in a known amount of chlorobenzene. With the area and thickness, the volume of the film is calculated. The light absorption of the obtained solution was measured at the absorption maximum of the HTM using an UV-Vis spectrophotometer. A calibration line using known concentrations of the HTM was prepared in order to determine the concentration of the solution containing the dissolved HTM film using Lambert-Beer's law. From the determined concentration, the mass of the HTM film was calculated. With the volume and mass of the film, the density was calculated.

The density of **EDOT-OMeTAD** was determined to be 1.24 g cm^{-3} , **Diazo-OMeTPA** = 1.27 g cm^{-3} and Spiro-OMeTAD 1.03 g cm^{-3} .

2 Cost estimation

The cost estimation was done using our previously published material cost model,^[S2] which was based on the work by Osedach *et al.* The synthetic routes are based on published and peer reviewed synthetic procedures and prices have been taken from Sigma-Aldrich, TCI chemicals and Acros using the largest available package on their websites. The synthetic flow charts and material cost calculations can be found below. The results are summarized in *Table S 2*.

Table S 2. Survey of the estimated material cost and an estimate of the chemicals waste produced.

Compound	Material cost (\$ g ⁻¹)	Estimated chemical waste (kg g ⁻¹)	E Factor (kg waste/kg product)
EDOT-OMeTPA ^[S2]	10	0.7	700
Ph-OMeTPA	4	0.5	500
Th-OMeTPA	7	0.5	500
Fu-OMeTPA	17	0.4	400
TPA-OMeTPA	22	0.5	500
Ph-inv-OMeTPA	32	1.3	1300
Diazo-OMeTPA	54	2.8	2800
Spiro-OMeTAD ^[S2]	92	3.6	3600

2.1 Waste and Environment

The chemical waste for the synthesis was estimated from the synthetic flow charts; the results are summarized in *Table S 2*. We observe that all azomethine-based HTMs require significant less chemicals than Spiro-OMeTAD. Reducing the amount of chemicals is beneficial from a cost point of view as is clear from the material cost, but also regarding the cost involved with chemical waste management. Furthermore, reducing the amount of (toxic) chemicals is beneficial for the environment.

2.2 4-amino-4',4''-dimethoxytriphenylamine

2.2.1 Halogen free synthetic route for 4-amino-4',4''-dimethoxytriphenylamine

Scheme S 1. Flow chart describing the synthesis of 4-amino-4',4''-dimethoxytriphenylamine as reported in this work. This halogen free synthetic route results in a cost of \$4.70 per gram.

Table S 3. Estimated materials cost for the synthesis of 4-amino-4',4''-dimethoxytriphenylamine.

Chemical name	Price of Chemical (\$/kg)	Material cost (\$/g product)
4-nitroaniline	\$222.60	\$0.17
4-iodoanisole	\$474.18	\$1.94
K ₂ CO ₃	\$6.27	\$0.04
Cu powder	\$61.57	\$0.02
L-proline	\$90.63	\$0.05
DMF	\$5.09	\$0.07
Water	\$0.00	\$0.00
EtOAc	\$3.63	\$0.58
MgSO ₄	\$54.24	\$0.07
EtO ₂	\$16.57	\$1.39
Hydrazine	\$33.17	\$0.04
Pd/C 10%	\$4,790.10	\$0.18
THF	\$9.24	\$0.16
water	\$0.00	\$0.00
Total	-	\$4.70

2.2.2 Low cost synthetic route for 4-amino-4',4''-dimethoxytriphenylamine

Scheme S 2. Flow chart describing the synthesis of 4-amino-4',4''-dimethoxytriphenylamine using reported synthetic procedures resulting in a minimum cost. This synthetic route results in a cost of \$2.45 per gram for the triphenylamine. However, halogenated solvents are used in this synthetic procedure.^[S5-S6]

Table S 4. Estimated materials cost for the synthesis of 4-amino-4',4''-dimethoxytriphenylamine.

Chemical name	Price of Chemical (\$/kg)	Material cost (\$/g product)
4-nitroaniline	\$222.60	\$0.14
4-iodoanisole	\$474.18	\$1.19
K ₂ CO ₃	\$6.27	\$0.01
Cu powder	\$61.57	\$0.02
18-crown-6-ether	\$2,333.31	\$0.09
oDCB	\$10.46	\$0.16
ethanol	\$3.24	\$0.30
Hydrazine	\$33.17	\$0.04
Pd/C 10%	\$4,790.10	\$0.18
THF	\$9.24	\$0.16
water	\$0.00	\$0.00
Total	-	\$2.28

2.3 4-formyl-4',4''-dimethoxytriphenylamine

Scheme S 3. Flow chart describing the synthesis of 4-formyl-4',4''-dimethoxytriphenylamine.^[S7-S10]

Table S 5. Estimated materials cost for the synthesis of 4-formyl-4',4''-dimethoxytriphenylamine.^a estimated price.

Chemical name	Price of Chemical (\$/kg)	Material cost (\$/g product)
aniline	\$26.16	0.01
4-bromoanisole	\$109.20	0.20
<i>t</i> BuONa	\$115.74	0.01
Pd cat ^a	\$100,000.00	0.30
DCM	\$11.16	0.56
Silica (short path)	\$66.41	0.90
DMF	\$5.09	0.01
POCl ₃	\$70.35	0.08
1,2-dichloroethane	\$9.96	0.28
NaOH	\$5.38	0.01
water	\$0.00	0.00
DCM	\$11.16	1.56
NaSO ₄	\$12.79	0.02
Silica	\$66.41	24.44
ethyl acetate	\$3.63	0.30
petroleum ether	\$13.95	4.25
Total	-	\$23.31

2.4 Ph-OMeTPA

Scheme S 4. Flow chart describing the synthesis of **Ph-OMeTPA**.

Table S 6. *Materials quantities and cost for the synthesis of Ph-OMeTPA.*

Chemical name	Price of Chemical (\$/kg)	Material cost (\$/g product)
terephthalaldehyde	\$233.42	\$0.04
TPA-NH ₂	\$2,280.00	\$2.44
TFA	\$141.12	\$0.00
CHCl ₃	\$2.42	\$0.15
hexane	\$6.31	\$0.83
isopropanol	\$4.18	\$0.16
isopropanol	\$4.18	\$0.49
triethylamine	\$21.54	\$0.04
Total	-	\$4.16

2.5 Th-OMeTPA

Scheme S 5. Flow chart describing the synthesis of **Th-OMeTPA**.

Table S 7. Materials quantities and cost for the synthesis of **Th-OMeTPA**.

Chemical name	Price of Chemical (\$/kg)	Material cost (\$/g product)
2,5-thiophenedicarboxaldehyde	\$21,907.20	\$2.41
TPA-NH ₂	\$2,280.00	\$2.67
TFA	\$141.12	\$0.00
CHCl ₃	\$2.42	\$0.08
hexane	\$6.31	\$0.83
isopropanol	\$4.18	\$0.16
isopropanol	\$4.18	\$0.49
Total	-	\$6.69

2.6 Fu-OMeTPA

Scheme S 6. Flow chart describing the synthesis of **Fu-OMeTPA**.

Table S 8. Materials quantities and cost for the synthesis of **Fu-OMeTPA**.

Chemical name	Price of Chemical (\$/kg)	Material cost (\$/g product)
2,5-Furandicarboxaldehyde	\$80,535.00	\$13.69
TPA-NH ₂	\$2,280.00	\$1.98
TFA	\$141.12	\$0.00
CHCl ₃	\$2.42	\$0.08
hexane	\$6.31	\$0.83
isopropanol	\$4.18	\$0.16
isopropanol	\$4.18	\$0.49
triethylamine	\$21.54	\$0.04
Total	-	\$17.29

2.8 TPA-OMeTPA

Scheme S 7. Flow chart describing the synthesis of **TPA-OMeTPA**.

Table S 9. Materials quantities and cost for the synthesis of **TPA-OMeTPA**.

Chemical name	Price of Chemical (\$/kg)	Material cost (\$/g product)
4,4'-Diformyltriphenylamine	\$52,689.00	\$18.44
TPA-NH ₂	\$2,280.00	\$2.03
TFA	\$141.12	\$0.00
CHCl ₃	\$2.42	\$0.13
hexane	\$6.31	\$0.83
isopropanol	\$4.18	\$0.16
isopropanol	\$4.18	\$0.49
triethylamine	\$21.54	\$0.04
Total	-	\$22.13

2.9 Ph-inv-OMeTPA

Scheme S 8. Flow chart describing the synthesis of **Ph-inv-OMeTPA**.

Table S 10. Materials quantities and cost for the synthesis of **Ph-inv-OMeTPA**.

Chemical name	Price of Chemical (\$/kg)	Material cost (\$/g product)
TPA-CHO	\$23,310.00	31.47
p -phenylenediamine	\$153.68	\$0.03
CHCl_3	\$2.42	\$0.08
ethanol	\$3.24	\$0.26
isopropanol	\$4.18	\$0.50
triethylamine	\$21.54	\$0.04
Total	-	\$32.38

2.10 Diazo-OMeTPA

Scheme S 9. Flow chart describing the synthesis of **Diazo-OMeTPA**.

Table S 11. Materials quantities and cost for the synthesis of **Diazo-OMeTPA**.

Chemical name	Price of Chemical (\$/kg)	Material cost (\$/g product)
TPA-CHO	\$23,310.00	\$50.58
hydrazine	\$35.70	\$0.12
ethanol	\$3.48	\$0.89
DCM	\$4.48	\$1.94
Water	\$0.00	\$0.00
MgSO ₄	\$54.24	\$0.12
Total	-	\$53.66

3 Thermal properties

Figure S 2. TGA thermograms of the azomethine-based small molecules at a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ under nitrogen.

Figure S 3. DSC curves of the azomethine based small molecules at a heating rate of $20\text{ }^{\circ}\text{C min}^{-1}$ under nitrogen. Measurements obtained from the first heating ramp.

4 Optoelectronic properties

4.1 UV-Vis spectroscopy

Figure S 4. (a) Normalized UV-Vis absorption spectra of the azomethine-based HTMs in the solid state. The materials were spincoated from chlorobenzene at a concentration of 10 mg mL^{-1} on glass substrates coated with a thin compact layer of Al_2O_3 . (b) The transmittance two azomethine-based HTMs and Spiro-OMeTAD ($\sim 250 \text{ nm}$) as a reference.

Table S 12. Optical properties of the HTMs obtained from UV-Vis, the bandgap was obtained from the absorption onset.

Compound	$\lambda_{\text{max, solution}} \text{ (nm)}$	$\lambda_{\text{max, film}} \text{ (nm)}$	$\lambda_{\text{onset, film}} \text{ (nm)}$	$E_g \text{ (eV)}$
EDOT-OMeTPA	501	507	625	1.98
Ph-OMeTPA	457	466	553	2.24
Th-OMeTPA	492	500	605	2.05
Fu-OMeTPA	472	482	583	2.13
TPA-OMeTPA	430	434	507	2.45
Ph-inv-OMeTPA	415	416	490	2.53
Diazo-OMeTPA	419	417	483	2.57

4.1.1 Oxidation with LiTFSI

Figure S 5. UV-Vis spectra of thin HTM films prepared from solutions containing different amounts of LiTFSI (170 mg/mL) as oxidant. All films were stored for 24 h under air (< 30% R.H.) before measuring. An absorption peak attributed to the oxidized species is observed with a redshift compared to the pristine material.

4.2 Cyclic voltammetry

Figure S 6. Cyclic voltammograms of the azomethine-based HTMs measured in a dichloromethane solution containing $t\text{BuNPF}_6$ as electrolyte. Oxidation potential is measured vs. Ag/Ag^+ . Left graph showing HTMs with the standard azomethine bond, right HTMs with the inverted azomethine bond.

Table S 13. Energy levels obtained from cyclic voltammetry

Compound	HOMO _{exp.} (eV)	LUMO _{exp.} (eV) ^a	E_g exp. (eV)
EDOT-OMeTPA	-5.28	-3.3	1.98
Ph-OMeTPA	-5.30	-3.1	2.24
Th-OMeTPA	-5.30	-3.3	2.05
Fu-OMeTPA	-5.30	-3.2	2.13
TPA-OMeTPA	-5.28	-2.8	2.45
Ph-inv-OMeTPA	-5.39	-2.9	2.53
Diazo-OMeTPA	-5.36	-2.8	2.57

^a estimated by adding the optical bandgap to the HOMO energy level

4.3 Computational studies

Table S 14. Energy levels obtained from DFT calculations in vacuum.

Compound	HOMO _{DFT} (eV)	LUMO _{DFT} (eV)	E_g DFT (eV)
EDOT-OMeTPA	-4.37	-1.95	2.42
Ph-OMeTPA	-4.52	-1.91	2.61
Th-OMeTPA	-4.47	-2.04	2.43
Fu-OMeTPA	-4.42	-1.85	2.57
TPA-OMeTPA	-4.45	-1.56	2.89
Ph-inv-OMeTPA	-4.59	-1.46	3.13
Diazo-OMeTPA	-4.49	-1.40	3.09

5 Hole mobility

The high work function of the MoO_x electrodes makes it possible to selectively collect holes. The current-voltage characteristics were recorded in the dark. At higher voltages, assuming ohmic injecting contacts and trap-free transport, the current measured is space-charge limited. The charge carrier mobility can be estimated by using the Mott-Gurney equation.^[S12]

$$J = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu \frac{V^2}{L^3}$$

where J is the current density, ε_r is the dielectric constant of the organic semiconductor blend (assumed to be 3 in our calculations), ε_0 is the permittivity of free space, μ is the charge carrier mobility, L is the thickness of the active layer and V is the voltage drop across the device.

The charge mobility of the HTMs with the azomethine-bond in the standard orientation shows a field dependence which can be described with the Poole-Frenkel effect.^[S11]

$$\mu(E) = \mu_0 \exp(\gamma \sqrt{E}),$$

where μ_0 is the zero-field hole mobility, γ the field coefficient and E the electric field, which was stated as:

$$E = \frac{V}{L}$$

The electric field was considered to be constant along the active layer thickness.

The values of γ and μ_0 were obtained by fitting equations to find a best fit with the experimental data. Details for deriving these equations are published by Murgatroyd.^[S12]

Figure S 7. Linear-logarithmic and logarithmic-logarithmic voltage-current density plots to determine the field-dependent mobility of the azomethine-based HTMs by fitting the equation for the space-charge limited current. The layer thicknesses are added to the legend.

Figure S 8. Linear-logarithmic and logarithmic-logarithmic voltage-current density plots to determine the field-dependent mobility of the azomethine-based HTMs by fitting the equation for the space-charge limited current. Spiro-OMeTAD was added as a reference and the layer thicknesses are added to the legend.

6 Solar cell performance

Figure S 9. Photovoltaic characterization. a) J-V curves of the perovskite solar cells comprising the different HTMs. b) Box-diagram showing the distribution of the performance of 9 individual devices.

Figure S 10. Photovoltaic characterization. Typical hysteresis in these devices. We assign the hysteresis to the perovskite and/or electron transporting layer, rather than the HTM.

Figure S 11. Power conversion efficiency and current density as a function of time under operating conditions of solar cells comprising the two most efficient azomethine-based hole-transporting materials.

Figure S 12. External quantum efficiency spectrum of a device based on MAPbI₃.

Figure S 13. Photoluminescence emission scans for the neat MAPbI₃ and bilayer samples.

7 Moisture barrier properties

Figure S 14. Light microscopy images of pristine HTM films and films prepared with the additives LiTFSI and tBP. All pristine films look smooth and mostly defect and pinhole free. Upon addition of the additives (used at the same amount as used for the preparation of photovoltaic devices), the quality of the Spiro-OMeTAD film is significantly reduced, which is in agreement with literature,^{S13} while the azomethine-based HTMs still show high quality films.

Material	0 h	8 h	24 h	14 days
EDOT-OMeTPA
Ph-OMeTPA
Th-OMeTPA
Fu-OMeTPA
TPA-OMeTPA
Ph-inv-OMeTPA
Diazo-OMeTPA
Spiro-OMeTAD

Figure S 15. Photographs of $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite films covered with a layer of the HTMs stored at 75% RH. The decolouration, which is clearly observed for the sample with Spiro-OMeTAD, is attributed to the degradation of the perovskite. For the azomethine-based films, degradation starts from the epoxy-covered edge of the samples.

Figure S 16. Photographs of $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite films covered with a layer of the HTMs stored at 75% RH, without covering the edges with epoxy. Clearly all samples degrade from the edge inwards, as is depicted in the schematic representation on the right. Nevertheless, here we also observe that the Spiro-OMeTAD sample degrades significantly faster.

Figure S 17. XRD patterns obtained from in-situ hydration measurements of the pristine perovskite at 90% RH. The reflection from PbI_2 , which is the degradation product of the perovskite, is indicated with an asterisk. The perovskite is prepared using 5% PbI_2 excess in the precursor solution, which explains the initial small PbI_2 peak. The pristine sample degrades faster than all bilayer films.

Figure S 18. XRD patterns obtained from HTM-perovskite bilayers after hydration for 30 days at 75% RH (same films as in Figure 6). The edges of the films were covered with epoxy to prevent moisture-induced degradation from the side. The perovskite was prepared using 5% Pbl₂ excess in the precursor solution, however, a small increase in the Pbl₂ peak is observed for the **Diazo-OMeTPA** sample, while the bilayer with **EDOT-OMeTPA** does not show any degradation. This is in strong contrast with the bilayers containing Spiro-OMeTAD, where the perovskite is complete degraded, and only the monohydrated species and a small Pbl₂ peak are observed, confirming the origin of the colour loss of the film.

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