



## Non-Planar and Flexible Hole Transporting Materials from Bis-Xanthene and Bis-Thioxanthene units for Perovskite Solar Cells

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#### Abstract

Two new hole-transporting materials (HTMs), BX-OMeTAD and BTX-OMeTAD, based on xanthene and thioxanthene units, respectively, and bearing pmethoxydiphenylamine peripheral groups are presented for their use in perovskite solar cells (PSCs). The novelty of the newly designed molecules relies on the use of a single carbon-carbon bond "C-C" as a linker between the two functionalized heterocycles, which increases the flexibility of the molecule compared with the more rigid structure of the widely used HTM spiro-OMeTAD. The new HTMs display a limited absorbance in the visible region, due to the lack of conjugation between the two halves, and the chemical design used has a remarkable impact on the thermal properties when compared to spiro-OMeTAD. **BX-OMeTAD** and **BTX-OMeTAD** have been tested in ([(FAPbI<sub>3</sub>)<sub>0.87</sub>(MAPbBr<sub>3</sub>)<sub>0.13</sub>]<sub>0.92</sub>[CsPbI<sub>3</sub>]<sub>0.08</sub>)-based PSC devices exhibiting power conversion efficiencies of 14.19 % and 16.55 %, respectively. The efficiencies reached, although lower than those measured for spiro-OMeTAD (19.63%), are good enough to consider the chemical strategy used as an interesting via to design HTMs for PSCs.

### Introduction

Photovoltaic technologies have raised as one of the most promising alternatives for harvesting energy in the search of a society based on non-fossil fuels. In this context, organic–inorganic hybrid perovskite solar cells (PSCs), in which the perovskite has the general formula  $ABX_3$  (A = cation, such as methylammonium (MA<sup>+</sup>), formamidinium

(FA<sup>+</sup>) or cesium (Cs<sup>+</sup>); B = Pb<sup>2+</sup>; X = halide), have stepped into the spotlight of photovoltaic devices since the groundbreaking discovery of Miyasaka and co-workers.<sup>[1]</sup> In just a few years, efficiencies of PSCs have been boosted from the initial 3.8 % to 23.7 % certified<sup>[2]</sup> due to the outstanding properties of the perovskite,<sup>[3]</sup> such as long chargecarriers diffusion lengths,<sup>[4-5]</sup> panchromatic light absorption with tunable band gap,<sup>[6-7]</sup> high charge-carrier mobilities<sup>[8-9]</sup> and solution-processed fabrication. All these attractive properties can be easily tuned by precisely engineering of the cations and/or halides in the composition of the perovskite.<sup>[10-12]</sup> Taking advantage of its singular ambipolar behavior, organic-inorganic perovskites can be sandwiched between *n*-type and/or *p*-type semiconducting layers in planar or mesoporous architectures.<sup>[13]</sup> Generally, the best performing devices incorporate small organic molecules<sup>[14-15]</sup> as hole-transporting materials (HTMs) for an efficient extraction of the photogenerated holes, improving their transport to the counter-electrode and acting as an energetic barrier to block the electron migration to the cathode. Inorganic salts<sup>[16-18]</sup> or classical polymeric structures<sup>[19-21]</sup> can also be used as HTMs although they present certain drawbacks such as batch-to-batch reproducibility, difficult purification, and broad molar mass distribution. In this sense, small organic molecules offer potential advantages such as well-defined molecular weight, easy purification, and less batch-to-batch variations.

An extensive assortment of organic molecules have been reported with the ultimate goal of outperforming the commonly used benchmark HTM 2.2',7,7'-tetrakis (N,N-di-pmethoxyphenylamine)-9,9'-spirobifluorene, namely spiro-OMeTAD. Unfortunately, the preparation of the spirobifluorene central scaffold present in spiro-OMeTAD requires a complicated synthetic protocol, which significantly limits its practical compatibility for low-cost and large-scale photovoltaic applications.<sup>[22]</sup> Small organic molecules have attracted special attention as HTMs because of their simple deposition processes (from solution or vapor) and their molecular structure tunability. The design and synthesis of HTMs have provided a wide variety of molecular structures helping to fine-tune their properties; in particular, the optical and electrochemical properties. Despite this versatility, a clear relationship between the molecular structure of the HTM and the photovoltaic efficiency when used in PSCs has not been yet established. For this reason, a wide variety of strategies have been described for the preparation of HTMs "a la carte". Among these strategies, the combination of large  $\pi$ -conjugated structures and electronrich fused heterocycles has resulted to be one of the most effective, favoring the intermolecular  $\pi - \pi$  stacking and, therefore, improving the hole-carrier mobility.<sup>[23-30]</sup> Conversely, spiro-like structures have also been extensively studied as organic scaffolds

for mimicking the outstanding properties of spiro-OMeTAD, reaching values of up to 22.6 %,<sup>[15]</sup> due to the balance of their electronic and morphological properties and solution processing.<sup>[31-33]</sup>



Figure 1. Chemical structures of BX-OMeTAD, BTX-OMeTAD and spiro-OMeTAD.

Following the aforementioned well-established strategies, herein we present the photovoltaic performance of two new HTMs, in which the twisted spiranic carbon atom between the two halves is replaced by a covalent "C–C" bond. **BX-OMeTAD** and **BTX-OMeTAD** consist of two xanthene or thioxanthene units connected through sp<sup>3</sup>-hybridized carbon atoms, rendering a more flexible conformation than those of spiro-like structures (*Figure 1*). In addition to the detailed optical, electrochemical and thermal properties of the new HTMs, rationalized with the help of density functional theory (DFT) calculations, mesoporous PSCs were prepared in combination with the state-of-the-art perovskite [(FAPbI<sub>3</sub>)<sub>0.87</sub>(MAPbBr<sub>3</sub>)<sub>0.13</sub>]<sub>0.92</sub>[CsPbI<sub>3</sub>]<sub>0.08</sub>. Power conversion efficiencies of up to 16.55% are derived from mesoscopic PSCs using the new HTMs, which, although lower than those obtained for the benchmark spiro-OMeTAD, are good enough for practical applications.



Scheme 1. Synthesis of **BX-OMeTAD** and **BTX-OMeTAD**. Reagents and conditions: a)  $Br_2$ , AcOH, 120 °C, 1a: 69%, 1b: 74%; b)  $BH_3$ 'SMe<sub>2</sub>, THF, 66 °C, 2a: 75%, 2b: 92%; c) bis(4-methoxyphenyl)amine,  $Pd_2(dba)_3$ , XPhos, Na<sup>t</sup>BuO, toluene, 100 °C; d) *n*-BuLi, Fe(acac)<sub>3</sub>, THF, -78 °C to r.t, **BX-OMeTAD**: 52%, **BTX-OMeTAD**: 52%;

# **Results and discussion**

The preparation of the symmetric BX-OMeTAD and BTX-OMeTAD HTMs was carried out by stepwise synthesis following well-established protocols under an inert atmosphere (Scheme 1). The synthetic methodology along with the experimental details are given in the Supplementary Information. Starting from xanthone or thioxanthone, a bromination reaction provided the corresponding dibrominated intermediate in excellent yields. The required xanthene and thioxanthene units were readily prepared upon reduction of the carbonyl groups in the presence of borane dimethyl sulfide complex (BH<sub>3</sub>·SMe<sub>2</sub>), followed by the Buchwald–Hartwig reaction with the *p*-methoxydiphenylamine. Finally, homocoupling of the two halves was achieved by treating **3a** and **3b** with *n*-BuLi in the presence of Fe(acac)<sub>3</sub> in moderate yields. The structures of **BX-OMeTAD** and **BTX-OMeTAD** and the corresponding intermediates were fully characterized by means of standard spectroscopic techniques such as <sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance (NMR), Fourier transform infrared (FTIR), and high-resolution MALDI-TOF (HR-MS) techniques (see the Supporting Information for further details). As representative spectroscopic features, both HTMs showed the corresponding aliphatic and aromatic signals. The chemical structures of both **3a** and **3b** were ascertained by HR-MS.

The structural and electronic properties of the **BX-OMeTAD** and **BTX-OMeTAD** HTMs were initially studied by performing density functional theory (DFT) calculations at the B3LYP/6-31G\*\* level in the presence of CH<sub>2</sub>Cl<sub>2</sub> as solvent. The BX and BTX cores, the pendant diphenylamine DPA moiety, and the reference spiro-OMeTAD compound were also computed for comparison purposes (see the Supporting Information for full computational details). Figure 2 displays the minimum-energy B3LYP/6-31G\*\*optimized structures calculated for the BX and BTX cores. Similar structures are computed for the **BX-OMeTAD** and **BTX-OMeTAD** HTMs (*Figure S1*), and *Figure S2* shows the most representative bond lengths computed for both systems. The molecular structure is determined by the xanthene and thioxanthene units, which are folded along the middle axis of the central heterocyclic ring and point in different directions (up and down) within the same molecule to minimize the steric interactions (Figure 2). The deviation from planarity of the xanthene and thioxanthene moieties is characterized by the folding angle  $\alpha$  that defines the tilting of the lateral benzene rings, which preserve their planarity, with respect to the average molecular plane. Angle  $\alpha$  is calculated to have a smaller value for the xanthene unit in the BX core (34°) than for the thioxanthene moiety

in the BTX core (44°). The incorporation of the four DPA arms to the central cores increases the folding of the xanthene and thioxanthene units and, compared to the pristine cores, slightly higher values are computed for angle  $\alpha$  (38° and 47° for **BX-OMeTAD** and **BTX-OMeTAD**, respectively, *Figure S1*).



**Figure 2.** Top (left) and side (right) views of the B3LYP/6-31G\*\*-optimized geometries calculated in CH<sub>2</sub>Cl<sub>2</sub> solution for the BX (a) and BTX (b) cores. The value of angle  $\alpha$  characterizing the folding of the xanthene and thioxanthene units is quoted.

The benzene rings condensed to the central heterocyclic ring both in the xanthene and in thioxanthene units preserve their characteristic delocalized structural pattern with similar carbon–carbon (CC) lengths in the 1.394–1.401 Å range (*Figure S2*). For both the BX and BTX cores, the  $C(sp^3)$ – $C(sp^3)$  bond linking the xanthene and thioxanthene halves is calculated to have a long length of ~1.600 Å. The main difference in terms of bond lengths between the BX and BTX cores is the lengthening of all bonds forming the central heterocyclic ring as a consequence of the substitution of oxygen in BX by sulfur in BTX, the largest difference being found for the carbon–sulfur bonds. For **BX-OMeTAD** and **BTX-OMeTAD**, the insertion of the four DPA units hardly causes any significant change in the structural shape and in the bond distances of the spiro-like cores. Regarding the latter, a lengthening of the CC bonds to which the DPA groups are anchored is obtained (*Figure S2*).



**Figure 3.** Energy diagram displaying the frontier molecular orbitals computed at the B3LYP/6-31G\*\* level in CH<sub>2</sub>Cl<sub>2</sub> for the DPA unit, the BX and BTX cores, the **BX-OMeTAD** and **BTX-OMeTAD** HTMs and the spiro-OMeTAD reference compound.

Figure 3 displays the frontier molecular orbitals calculated for the DPA unit, the BX and BTX cores, the BX-OMeTAD and BTX-OMeTAD HTMs and the spiro-OMeTAD reference compound. The highest-occupied molecular orbital (HOMO) of the BX core, computed at -5.84 eV, is noticeably lower in energy than the HOMO of DPA (-4.72 eV) indicating a weaker electron-donor character. The substitution of oxygen by sulfur in BTX causes a slight but non-negligible destabilization of the HOMO level (-5.69 eV). For the four-armed BX-OMeTAD and BTX-OMeTAD HTMs, the insertion of the DPA moieties results in a significant destabilization of the HOMO level, which is now computed at -4.60 and -4.65 eV, respectively, thus approaching the HOMO level calculated for spiro-OMeTAD (-4.44 eV). The HOMO of both BX-OMeTAD and BTX-OMeTAD spreads primarily over the central covalent carbon-carbon linkage cores with contributions from the DPA moieties (mostly from the nitrogen atoms). It should be noted that an important charge transfer occurs from the central cores, which hold a total net charge of 0.81e and 0.73e for BX-OMeTAD and BTX-OMeTAD, respectively, to the peripheral DPA groups. The electronic structure of the BX-OMeTAD and BTX-**OMeTAD** HTMs is therefore predicted to be significantly polarized.



**Figure 4.** a) Differential pulse voltammetry recorded in  $CH_2Cl_2$  containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) at a scan rate of 100 mV s<sup>-1</sup>. b) UV-vis absorption spectra (solid line) and fluorescence emission spectra (dashed line) of spiro-OMeTAD, **BX-OMeTAD** and **BTX-OMeTAD** in  $CH_2Cl_2.c$ ) Thermogravimetric analysis curves recorded under nitrogen at 10 °C min<sup>-1</sup> of heating rate. d) Differential scanning calorimetry curves under nitrogen at a heating rate of 20 °C min<sup>-1</sup> (second cycle).

The electrochemical properties of the novel HTMs and spiro-OMeTAD were analyzed by differential pulse voltammetry (DPV) (*Figure 4a*) in TBAPF<sub>6</sub>/CH<sub>2</sub>Cl<sub>2</sub> at a scan rate of 100 mV s<sup>-1</sup>. The recorded oxidation potentials and the derived HOMO energies are gathered in *Table 1*. **BX-OMeTAD** exhibits three oxidation waves centered at 0.83, 1.25 and 1.34 V versus normal hydrogen electrode (NHE). The change of the oxygen atom in the central core by sulfur, resulted in a slightly increase of the donor ability (0.79, 1.21 and 1.30 V versus NHE). Spiro-OMeTAD also shows three oxidation waves centered at 0.70, 0.82 and 1.03 V, in which the first oxidation potential is cathodically shifted by 0.09 and 0.13 V in comparison with that of **BTX-OMeTAD** and **BX-OMeTAD**, respectively. The estimated HOMO energies inferred from the first oxidation potential for **BX-OMeTAD**, **BTX-OMeTAD** and spiro-OMeTAD are -5.27, -5.23 and -5.14 eV, respectively. Therefore, the novel HTMs feature an excellent band alignment with the

10.1002/hlca.201900056

valence band edge of the triple cation [(FAPbI<sub>3</sub>)<sub>0.87</sub>(MAPbBr<sub>3</sub>)<sub>0.13</sub>]<sub>0.92</sub>[CsPbI<sub>3</sub>]<sub>0.08</sub> perovskite (*ca.* -5.7 eV).

HTM	$E^{\text{ox}}_{1/2}  [V]^{[a]}$	$E_{\rm HOMO}  [{\rm eV}]^{[{\rm b}]}$	λ <sub>max, abs</sub> [nm] <sup>[c]</sup>	λ <sub>max, em</sub> [nm] <sup>[c]</sup>	$E^{0-0} [{ m eV}]^{[{ m d}]}$	$E_{\text{LUMO}} [eV]^{[e]}$
BX-OMeTAD	0.83	-5.27	309	414	3.24	-2.03
BTX-OMeTAD	0.79	-5.23	310	403	3.32	-1.91
spiro-OMeTAD	0.70	-5.14	386	419	3.05	-2.11

Table 1. Electrochemical and optical properties of BX-OMeTAD, BTX-OMeTAD and spiro-OMeTAD.

[a] Determined from DPV measurements vs. normal hydrogen electrode (NHE). [b]  $E_{\text{HOMO}}$  is estimated in eV by  $E_{\text{HOMO}} = -4.44 \text{ eV} - E^{\text{ox}_{1/2}}$ . [c]  $\lambda_{\text{max}}$  of absorption and emission measured in CH<sub>2</sub>Cl<sub>2</sub> solutions. [d]  $E^{0.0}$  was determined at the intersection of normalized absorption and emission spectra. [e]  $E_{\text{LUMO}}$  was estimated by  $E_{\text{LUMO}} = E_{\text{HOMO}} + E^{0.0}$ .

To gain insight into the oxidation processes, the oxidized species (up to the tetracation) of **BX-OMeTAD** and **BTX-OMeTAD** were calculated at the B3LYP/6-31G\*\* level in CH<sub>2</sub>Cl<sub>2</sub>. *Table S2* gathers the charges accumulated by the constituting fragments (central core and DPA units) as oxidation occurs. For **BX-OMeTAD**<sup>++</sup>, the charge for the radical cation species are drawn from the core (*ca.* 0.36e) and the DPA units (0.16e from each unit). A slightly larger charge removal from the core (*ca.* 0.40e) is calculated for **BTX-OMeTAD**<sup>++</sup>. Upon further oxidation (dication, trication and tetracations), the charge is gradually extracted from both the core and the four DPA units. For the tetracations, the excess of positive charge is still more concentrated in the core (*ca.* +1.70e) than in the DPA units (*ca.* +0.57e, Table S2). This indicates that the xanthene and thioxanthene cores are directly involved in the oxidation processes.

To evaluate the capability of the **BX-OMeTAD** and **BTX-OMeTAD** systems as HTMs, hole reorganization energies ( $\lambda$ ) were estimated at the B3LYP/6-31G\*\* level in gas phase (see the *Supporting Information* for full computational details). The  $\lambda$  values calculated for **BX-OMeTAD** and **BTX-OMeTAD** are 0.120 and 0.124 eV, which are notably smaller than the values obtained for its constituting fragments (0,192 and 0.198 eV for the BX and BTX cores, respectively, and 0.274 eV for the DPA units). The decrease in  $\lambda$  results from to the fact that charge extraction involves both the core and the peripheral DPA moieties. **BX-OMeTAD** and **BTX-OMeTAD** therefore exhibit low reorganization energies similar to that computed for spiro-OMeTAD (0.139 eV).<sup>[25]</sup> The small  $\lambda$  values together with the adequate energy level alignment with the valence band edge of the perovskite indicate the potential of this family as HTMs for PSC devices.

The optical properties of **BX-OMeTAD** and **BTX-OMeTAD** were investigated in solution as depicted in *Figure 4b* and compared with spiro-OMeTAD. Maximum

absorption and emission wavelengths are listed in *Table 1*. The derived optical bandgaps  $(E^{0-0})$  were estimated from the intersection of the absorption and emission bands. **BX-OMeTAD** and **BTX-OMeTAD** show similar absorption patterns in dichloromethane with an intense absorption band below 350 nm, which is broader for the latter. An asset of these kind of systems as HTMs for PSCs is their lack of conjugation, which keeps the visible range of the spectrum transparent, in contrast to the spiro-OMeTAD. The lack of absorption in the visible region determines that the new HTMs exhibit relatively high energies for the lowest energy 0–0 transition ( $E^{0-0}$ ), which ensures a good electron-blocking capability. The emission spectra show broad bands with maximum emission peaks centred at 414 and 403 nm for **BX-OMeTAD** and **BTX-OMeTAD**, respectively. The optical absorption and fluorescence of spiro-OMeTAD are shifted towards higher wavelengths compared to **BX-OMeTAD** and **BTX-OMeTAD** owing to the enhanced  $\pi$ -conjugation of the spirocyclic central scaffold in spiro-OMeTAD.

The absorption spectra of **BX-OMeTAD** and **BTX-OMeTAD** was theoretically simulated from the B3LYP/6-31G\*\* time-dependent DFT (TDDFT) calculation of the lowest-energy 80 singlet excited electronic states (S<sub>n</sub>) in the presence of CH<sub>2</sub>Cl<sub>2</sub> (*Figure* S3) The theoretical spectra correctly reproduce the shape of the experimental spectra with an intense band approximately centred at 310 and 314 nm for **BX-OMeTAD** and **BTX-OMeTAD**, respectively, in perfect agreement with the experimental bands peaking at 309 and 310 nm, respectively. The simulated absorption bands come from a plethora of electronic transitions close in energy and a simple assignment is not easy. Nevertheless, a dominant electronic transition is predicted for both **BX-OMeTAD** (S<sub>0</sub>  $\rightarrow$  S<sub>10</sub>) and **BTX-OMeTAD** (S<sub>0</sub>  $\rightarrow$  S<sub>7</sub>) (see Figure S3 and Table S1). These electronic transitions are of  $\pi \rightarrow \pi^*$  nature, and imply excitations with a partial charge transfer from the central BX and BTX moieties to the peripheral DPA units (Table S1 and Figure S4).

To elucidate the thermal stability of the pristine HTMs, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed (*Figure 4c* and *4d*) and compared with spiro-OMeTAD. Detailed thermal features are listed in *Table 2*. From TGA, both HTMs possess relatively high decomposition temperatures ( $T_{dec}$ ) of 334 and 360 °C (at a weigh loss of 1 %) for **BX-OMeTAD** and **BTX-OMeTAD**, respectively, but significantly lower than that measured for spiro-OMeTAD (449 °C). The difference in  $T_{dec}$  is due to the relatively more rigid structure of spiro-OMeTAD.<sup>[34]</sup> The morphological study of the new compounds was conducted using DSC analysis. As show

in *Figure 4d*, **BX-OMeTAD** shows a similar morphological behavior to that of spiro-OMeTAD. During the first heating scan, both molecules exhibit a discernible glass transition ( $T_g$ ) and melting temperature ( $T_m$ ) along with an additional crystallization process ( $T_c$ ) which is not observed upon cooling. After consecutive heating/cooling cycles only rather small changes in the  $T_g$  are detected (*Figures S21*). On the other hand, **BTX-OMeTAD**, displays a three-step thermal behavior with a crystallization process ( $T_c = 267$ °C) and a sharp endothermic peak corresponding to a melting temperature of 313 °C. No crystallization process was observed upon cooling and only a glass transition ( $T_g = 119$ °C) was detected during the second heating scan.

Table 2. Thermal properties of BX-OMeTAD and BTX-OMeTAD in comparison with spiro-OMeTAD.

HTM	$T_{\rm dec}  (^{\rm o}{\rm C})^{[a]}$	$T_{\rm m}  (^{\rm o}{\rm C})^{[\rm b]}$	$T_{\rm c} (^{\circ}{\rm C})^{[b]}$	$T_{g} (^{\circ}C)^{[c]}$
<b>BX-OMeTAD</b>	334	280	190	132
BTX-OMeTAD	360	313	267	-
spiro-OMeTAD	449	247	174	131

<sup>[a]</sup> Decomposition temperature determined from TGA (1 % weight loss). <sup>[b]</sup> Melting temperature ( $T_m$ ) and crystallization temperature ( $T_c$ ) determined from the first cycle of the DSC. <sup>[c]</sup> Glass transition temperature ( $T_g$ ) determined from the first cycle. All experiments were performed under N<sub>2</sub> atmosphere.

The performance of the new HTMs, BX-OMeTAD and BTX-OMeTAD, was evaluated in perovskite-based solar cells (PSCs) using the state-of-the-art triple cation perovskite [(FAPbI<sub>3</sub>)<sub>0.87</sub>(MAPbBr<sub>3</sub>)<sub>0.13</sub>]<sub>0.92</sub>[CsPbI<sub>3</sub>]<sub>0.08</sub> (*Table 3*). The relative position of the frontier energy levels of the HTM materials with respect to those of the perovskite and the TiO<sub>2</sub> and Au electrodes is illustrated in *Figure 5a*. Devices were fabricated from a stack of thin films deposited onto a fluorine-doped tin oxide (FTO) conductive glass that serves as support (see the Supporting Information for details). The layers forming the PSC device were deposited as follows. First, as anode, a 30 nm blocking layer is applied by spray pyrolysis onto the FTO followed by 250 nm mesoporous titania. Second, the perovskite layer was spin-coated in a single-step by spinning the perovskite precursor solution at 2000 rpm for 12 s and at 5000 rpm for 30 s. After 15 s of the second step, 100 mL of chlorobenzene was poured onto a rotating substrate to obtain a smooth perovskite layer after annealing for 1 h at 100 °C. The composition of the perovskite layer is [(FAPbI<sub>3</sub>)<sub>0.87</sub>(MAPbBr<sub>3</sub>)<sub>0.13</sub>]<sub>0.92</sub>[CsPbI<sub>3</sub>]<sub>0.08</sub>. Third, the HTM layer was deposited by spincoating a 20 mM solution of the BX-OMeTAD and BTX-OMeTAD derivatives in chlorobenzene using tert-butylpyridine, Li-TFSI and FK-209 as dopants. The thickness

of the HTM layer was optimized to be around 100 nm for both molecules. Finally, the gold electrodes were thermally evaporated using a shadow mask. The individual forminglayers of the PSC architecture can be seen from the cross-sectional scanning electron microscopy (SEM) images as shown in *Figure 5b* and *5c*. As a general trend, the presented chemical structures seem to favor the formation of homogeneous thin films with a good morphology. The current density-voltage (J-V) curves of the bestperforming conventional PSCs (reverse bias) using **BX-OMeTAD** and **BTX-OMeTAD** as HTMs, under 1 sun AM 1.5G (100 mW cm<sup>-2</sup>) simulated sunlight, are shown in *Figure 5d* and their related photovoltaic parameters are collected in *Table 3*. Both HTMs were compared with the reference spiro-OMeTAD. **BTX-OMeTAD**-based PSCs exhibit the highest power conversion efficiency (PCE) up to 16.55 %, mainly arising from an enhanced fill factor (FF) of 69.8% and a short-circuit current ( $J_{sc}$ ) of 23.35 mA cm<sup>-2</sup>. On the other hand, devices incorporating **BX-OMeTAD** yield a significantly lower PCE of 14.19 % with a  $J_{sc}$  of 22.93 mA cm<sup>-2</sup>, a FF of 61.3% and a  $V_{oc}$  of 1.01 V with pronounced hysteresis (see *Figure S7* and *S8*).



**Figure 5.** a) Schematic energy levels diagram for the different layers of PSC including the new HTMs and spiro-OMeTAD. b) Cross-section scanning electron microscopy (SEM) image of a PSC device using **BX-OMeTAD** as HTM. c) Cross-section scanning electron microscopy (SEM) image of a PSC device using **BTX-OMeTAD** as HTM. d) Current density–voltage (J-V) curves of **BX-OMeTAD**, **BTX-OMeTAD** and spiro-OMeTAD in combination with [(FAPbI<sub>3</sub>)<sub>0.87</sub>(MAPbBr<sub>3</sub>)<sub>0.13</sub>]<sub>0.92</sub>[CsPbI<sub>3</sub>]<sub>0.08</sub>-based devices. e) External quantum efficiency (EQE) plots of **BX-OMeTAD**, **BTX-OMeTAD** and spiro-OMeTAD with corresponding integrated current. f) Conductivity of **BX-OMeTAD**, **BTX-OMeTAD** and spiro-OMeTAD measured on substrates with interdigitated gold electrodes with a channel length of 2.5 µm.

The performance of PSCs incorporating spiro-OMeTAD as HTM exhibited a PCE up to 19.63 %. The photovoltaic behavior of the doped spiro-OMeTAD-based PSCs were in good accordance with state-of-the-art results reported in the literature.<sup>[12]</sup>

The electrical conductivity of the HTMs thin films was measured in a lateral configuration between 2.5 mm spaced gold contacts. Thin films of the new HTMs were deposited onto substrates having interdigitated gold electrodes by using the same procedure as for best device preparation, adding 6 mol% and 20 mol% of FK209 as a dopant in **BX-OMeTAD** and **BTX-OMeTAD**, respectively. As it can be seen in *Figure 5f*, **BX-OMeTAD** and **BTX-OMeTAD** exhibit low conductivity values of  $2.2 \times 10^{-8}$  and  $1.0 \times 10^{-7}$  S cm<sup>-1</sup>, respectively, which remarkable lower than that of spiro-OMeTAD. The low conductivity arising from these HTMs is most likely the reason of the low *FF* obtained for their devices, resulting in high series resistance.

The short circuit currents experimentally found by J-V measurements match well with the ones calculated from the integrated external quantum efficiency (EQE) measurements shown in *Figure 5e* (± 5% mismatch).

Table 3. Device performance of PSC devices incorporating BX-OMeTAD and BTX-OMeTAD as HTMs
and the [(FAPbI3)0.87(MAPbBr3)0.13]0.92 [CsPbI3]0.08 perovskite. The figures of merit are compared with
those obtained for the reference spiro-OMeTAD.

HTM	$V_{\rm oc}({ m mV})$	$J_{\rm sc}~({ m mA~cm^{-2}})$	FF (%)	PCE (%)
BX-OMeTAD	1010	22.93	61.3	14.19
BTX-OMeTAD	1015	23.35	69.8	16.55
spiro-OMeTAD	1061	23.57	78.5	19.63

#### Conclusions

In summary, we have successfully designed and synthetized two new flexible, spiro-OMeTAD analogues, as hole-transporting materials (HTMs) for perovskite solar cells (PSCs). The new HTMs (**BX-OMeTAD** and **BTX-OMeTAD**) incorporate a covalently linked bis-xanthene(BX) or bis-thioxanthene (BTX) core decorated with four peripheral p-methoxydiphenylamine (PDA) units. The synthetic route toward their preparation requires an easy and attainable four-step synthesis. Both HTMs exhibit a negligible absorbance in the visible, owing to their lack of conjugation, and therefore useful for tandem solar cells. They exhibit slightly deeper HOMO levels (~0.1 eV) compared to spiro-OMeTAD, and can be used for an efficient hole-charrier extraction from the Helvetica Chimica Acta

perovskite. The flexibility of their central core has a relevant impact on the thermal properties when compared to the more rigid structure of spiro-OMeTAD. The novel derivatives possess high thermal stability (up to 330 °C), good solubility and high LUMO energy to block electrons and suitable HOMO level to extract holes from perovskite. The new compounds were employed in state-of-the-art [(FAPbI<sub>3</sub>)<sub>0.87</sub>(MAPbBr<sub>3</sub>)<sub>0.13</sub>]<sub>0.92</sub>[CsPbI<sub>3</sub>]<sub>0.08</sub> perovskite solar cells and reached relatively moderate performances, lower than those obtained for spiro-OMeTAD (19.63 %). Lightto-energy conversion of up to 16.55 % and 14.19 % were obtained for BTX-OMeTAD and **BX-OMeTAD**, respectively, with noticeable hysteresis in line with the poor conductivity values. This work clearly reveals the importance of the molecular design in HTMs for addressing the efficiency of the PSC. Interestingly, the presence of a more flexible single C-C bond connecting the two halves of the HTM core has a strong impact on the geometrical and electronic properties and, thereby, on the efficiency of the fabricated PSC devices.

#### **Conflicts of interest**

There are no conflicts to declare.

### Acknowledgments

We thank the Swiss National Funds for Scientific Research contract number 200020L\_172929/1, Project "Tailored Design and in-depth understanding of perovskite solar materials using in-house developed 3D/4D nanoscale ion-beam analysis". Borun New Material Technology generously supplied the high-quality spiro-OMeTAD. The authors also thank the European Research Council (ERC-320441-Chirallcarbon), the Spanish Ministry of Economy and Competitiveness MINECO (projects CTQ2017-83531-R, CTQ2015-71154-P, CTQ2016-81911-REDT and Centro de Excelencia Severo Ochoa SEV-2016-0686, CAM (FOTOCARBON project S2013/MIT-2841), the Generalitat Valenciana (PROMETEO/2016/135 and SEJI/2018/035) and European Feder funds (CTQ2015-71154-P). J.A. is grateful to MINECO for a "Ramon-y-Cajal" fellowship (RyC-2017-23500). I.G.B and G.G. acknowledge the Swiss National Science Foundation (SNSF) funding through the Ambizione Energy project Hyper (Grand number PZENP2 173641).

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