Benzotri thiophene-Based Hole-Transporting Materials for 18.2% Perovskite Solar Cells

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Abstract: New star-shaped benzotri thiophene (BTT)-based hole-transporting materials (HTM) BTT-I, BTT-2 and BTT-3 have been obtained through a facile synthetic route by crosslinking triarylamine-based donor groups with a benzotri thiophene (BTT) core. The BTT HTMs were tested on solution-processed lead trihalide perovskite-based solar cells. Power conversion efficiencies in the range of 16% to 18.2% were achieved under AM 1.5 sun with the three derivatives. These values are comparable to those obtained with today’s most commonly used HTM spiro-OMeTAD, which point them out as promising candidates to be used as readily available and cost-effective alternatives in perovskite solar cells (PSCs).

Since its first use as light absorber in a sensitized solar cell by Miyasaka and co-workers,[1] organic–inorganic methylammonium (MA) lead halide MAPbX₃ (X = I, Br) perovskites have experienced a scientific research blast for photovoltaic applications. Organometal trihalide perovskites exhibit exceptional intrinsic properties such as light absorption from visible to near-infrared range, high extinction coefficient, long electron–hole diffusion lengths, a direct band gap as well as high performance and cost. In our case, the BTT series absorbs below 420 nm, where the perovskite strongly absorbs and, therefore, it has no influence on the solar cell efficiency. Nevertheless, there are also fewer examples of HTMs absorbing in the visible and near-infrared region, these materials can act as hole-transporters without interfering the spectral response of the photoactive material.

Hitherto, the most studied HTM in PSC has been the low band-gap Spiro–OMeTAD. Perovskite solar cells employing this semiconductor have achieved PCEs values over 15%. The low band-gap HTM layer enhances light absorption in the device, and exhibits beneficial effects. Actually, it has been previously reported that photons absorbed by low band-gap HTM results in a noticeable improvement of photocurrent.[34] In our case, the BTT series absorbs below 420 nm, where the perovskite strongly absorbs and, therefore, it has no influence on the solar cell efficiency.

Supporting information for this article (detailed synthesis procedure, device preparation, additional SEM images, hysteresis curves, device statistics, detailed characterization including XRD, CV, DSC, TG, NMR, MS) can be found under:
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via the generation of a Lewis base adduct.\[34\] Unfortunately, the preparation of the spirobifluorene central core present in this material requires a complicated synthetic protocol which makes it a relatively expensive material. Besides, sublimation-grade of the Spiro-OMeTAD is an essential requirement in order to achieve high PCEs devices.\[23\]

In this work, we report a new family of ease to prepare HTMs based on a benzo[1,2-b:3,4-b':5,6-b'']trithiophene (BTT) as a central core endowed with \( p \)-methoxydiphenylamine (BTT-1), \( p \)-methoxyphenylamine-substituted carbazole (BTT-2) and \( p \)-methoxytriphenylamine (BTT-3). These compounds exhibit remarkable PCEs values when used in organometal trihalide perovskite solar cells (Figure 1). BTT core exhibits a \( C_{3h} \) symmetry with three thiophene rings fused to a benzene central ring. The planarized star-shaped structure of the BTT is foreseen to promote an effective \( \pi-\pi \) intermolecular interaction, which could eventually lead to efficient hole-transporting properties.

The synthetic pathways and the experimental details for the preparation of the new family of HTMs are given in the Supporting Information (SI). The BTT central core was synthesized by a stepwise approach to obtain the tribromo-derivative BTT-1 and BTT-2. On the other hand, \( p \)-methoxytriphenylamine units were covalently linked to the BTT core by a Suzuki cross-coupling reaction, affording BTT-3. The new compounds were obtained as stable solids in a good overall yield (see Supporting Information).

As previously mentioned, the new HTM molecules BTT-1, BTT-2 and BTT-3 together with spiro-OMeTAD as a reference were tested on perovskite-based solar cells. The energy levels of the HTM materials are shown in Figure 2. As can be observed in the Figure, the HOMO levels of the BTT-1 and BTT-2 molecules are very similar to the one for spiro-OMeTAD whereas the BTT-3 exhibits slightly lower HOMO level, which closely matches the energy level of the valence band edge of the MAPbI$_3$ perovskite. The cell architecture used in this study is shown among the high resolution scanning electron microscopy (SEM) cross-section images displayed in Figure 2. At the anode, a compact and mesoporous layer of TiO$_2$ was deposited on top of a fluorine-doped tin oxide (FTO) coated glass and used as the electron collector, while the cathode consists of a gold electrode thermally evaporated onto the HTM layer. The photoactive material MAPbI$_3$ is sandwiched in between these layers, as well as the modified perovskite (FAPbI$_3$)$_{0.85}$(MAPbBr$_3$)$_{0.15}$ recently introduced by Seok,[\textsuperscript{13}] which was also tested for comparison. Both perovskite layers were fabricated by using a single step spin coating procedure similar to the protocol previously described in the literature.[\textsuperscript{17}] As a summary, the perovskite precursor solution was spin-coated at 4000 rpm for 30 s. 10 s prior to the end of the spinning program, 120 µl of chlorobenzene were poured onto the spinning substrate to obtain a homogeneous dense perovskite film after annealing for 1 h at 100°C. Compared to the standard perovskite devices, the composite material has a thicker capping layer of around 400 nm, three times larger than the value observed around 400 nm, three times larger than the value observed.
when using the standard perovskite. The hole-transporting materials presented in this study were then spin-coated on top of the perovskite layer at 4000 rpm for 15 s. The detailed procedure for the device fabrication is given in the SI.

The photovoltaic performance of the devices under AM 1.5 G conditions are shown in Figure 3 and the detailed results are summarized in the table below. Current-voltage (J-V) curves were recorded by applying a forward bias with a scan rate of 10 mVs−1 in order to minimize the hysteresis effects stemming from the perovskite material.[38] Hysteresis scans showing the performance under forward and reverse bias can be found in the SI. The results show excellent performances for all the benzothiophene derivatives, being BTT-3 slightly better than its analogous BTT-1 and BTT-2. Power conversion efficiencies (PCE) above 18.2% were observed on standard MAPbI3 perovskite solar cells, with almost no hysteresis when tested under the described conditions. The average PCE of 17.7 ± 0.4% indicates a very good reproducibility for this molecule. Up to date such a high PCE value could be only achieved when using either spiro-OMeTAD or PTAA as hole-transporting materials. Comparing the results obtained for the three derivatives, the main difference when using BTT-3 is the high short circuit current density ($J_\text{sc} = 21.9 \text{mAcm}^{-2}$). In fact these values are very close to those obtained with the spiro-OMeTAD reference. Devices with BTT-2, on the other hand, show a remarkably high open circuit voltage of almost 1.1 V, resulting in PCEs up to 17% (average: 15.6 ± 1.1%).

BTT-1 shows the lower performance, which might be also related to its low solubility in chlorobenzene compared to BTT-2 and BTT-3, making it more difficult to obtain uniform films and reproducible results, which can be seen from the relatively high standard deviation on the average PCE value of 13.9 ± 1.5%. Nevertheless, PCE values of up to 16% are still possible to be obtained by using this molecule. Comparing the devices prepared with the composite perovskite (FAPbI3)0.85(MAPbBr3)0.15 and BTT-HTM molecules, the resulting performances are very similar. As previously observed, BTT-1 is the least effective HTM, leading to lower fill factor and $J_\text{sc}$. On the contrary, compounds BTT-2 and BTT-3 behave similarly and excellent PCE values of up to 17.5% are obtained. As a general trend, the presented chemical structures seem to favor the formation of homogeneous thin films with a good morphology and conductivity, which lead to excellent fill factor values (FF > 70%) comparable to those obtained for spiro-OMeTAD. These experimental findings suggest a high carrier mobility in these new materials.

The electrical conductivity of the BTT-based thin films was measured in a lateral configuration between 2.5 μm spaced gold contacts. Thin films of the BTT molecules were deposited onto substrates having interdigitated gold electrodes by using the same procedure as for device preparation, adding 3 mol% of FK209 as a dopant in all of them. Figure 4 shows the comparison of the conductivity determined for the three derivatives. The values were extracted using a linear fit to Ohm’s law. As can be observed in the inset of Figure 4, BTT-1 exhibits the lowest conductivity ($6.0 \times 10^{-6} \text{Scm}^{-1}$), followed by BTT-2 ($1.3 \times 10^{-5} \text{Scm}^{-1}$). The conductivity of BTT-3 is the highest, reaching $2.79 \times 10^{-5} \text{Scm}^{-1}$. Although this value is still about one order of magnitude lower than that of Spiro-OMeTAD,[39] it seems to be sufficient for obtaining a high performance when a thin HTM layer is used.

The trend in conductivity clearly supports the observation of the device performance obtained for the three different BTT molecules. The thickness of the individual BTT layers was adjusted to obtain the best efficiencies. According to the results, the lower conductivity of BTT-1 requires a very thin layer in order to have a good performance. Values for the shunt resistance of the three derivatives, estimated from the slope close to short circuit current, are very similar for the champion devices ($>2k \text{M}Ω$ Do you mean $2000\text{M}Ω$?) Nevertheless, using a thinner HTM layer, it is more likely to generate shunting paths due to for example, roughness of the
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Promising new candidates: Benzothiophene (BTT) with different donor moieties are introduced as hole-transporting materials for perovskite solar cells. The incorporation of these new derivatives in photovoltaic devices leads to power conversion efficiencies (PCE) up to 18.2%, thus paving the way to very efficient and highly versatile materials for light energy conversion.

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