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## Swivel-Cruciform Thiophene Based Hole-Transporting Material for Efficient Perovskite Solar Cells

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**A novel swivel-cruciform 3,3'-bithiophene based hole-transporting material (HTM) with low lying highest occupied molecular orbital (HOMO) level was synthesized. This new HTM (KTM3) in CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> perovskite solar cell, showed higher Voc (1.08V), and fill factor (78.3%) compared to solar cells fabricated using the widely used spiro-OMeTAD.**

The mesoscopic dye-sensitized solar cell (DSC) invented by Michael Grätzel in 1991 is an attractive alternative to the silicon solar cell.<sup>1</sup> Recent research in this area has focused on solid state DSCs where the liquid electrolyte is replaced by an organic hole transport layer<sup>2-3</sup> for higher stability, but which is accompanied by lower power conversion efficiencies. Hybrid organic-inorganic perovskites with its direct band gap, large absorption coefficient, and high carrier transport lengths have attracted attention as alternate light harvesters in solid state mesoscopic solar cells.<sup>4-9</sup> Solid-state solar cells with this novel perovskite material (CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>) are a promising alternative to conventional liquid electrolyte DSCs in terms of performance and stability.<sup>10</sup> It is remarkable that perovskite solar cells have already achieved over 15% efficiency within such a short development lifetime.<sup>11</sup> Despite the high efficiencies already achieved by this technology, further improvement could push the cell performance to ~20%.

The exploration of newer hole transporting layers is essential for future perovskite solar cell development. It has been previously demonstrated that interfacial chemical interactions may play a significant role in determining efficiencies in solid state sensitized solar cells.<sup>12</sup> Additionally, the design of the HTM with the appropriate structure can inhibit back electron transfer, which will result in a solar cell with higher fill factor and open circuit voltage.<sup>13</sup> Tuning the energetic levels of the HTM is also a methodology to enhance the Voc. Specifically, shifting the highest occupied molecular orbital (HOMO) level of the HTM

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towards that of the lead iodide perovskite will result in higher open circuit potentials.<sup>14</sup> Previous studies on perovskite solar cells using different HTMs<sup>15-16</sup> have indicated that polytriarylamine PTAA and spiro-OMeTAD (see figure 1), which contain amine group, have shown the best performance. This has been tentatively attributed to the favourable molecular interaction between the amine groups and the lead perovskite. Thus it is fair to explore other HTMs which also possess the amine moiety.

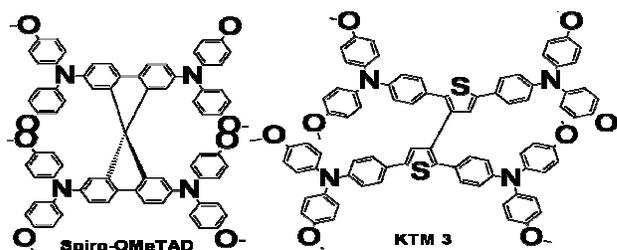


Fig. 1. Chemical Structure of spiro-OMeTAD and KTM3.

The tedious synthesis of Spiro-OMeTAD results in its increased cost that limits its scale-up. Thus exploration of low-cost and high-

efficiency HTMs is important. As a very important class of organic semiconducting materials, thiophenes have been extensively investigated owing to their high charge-carrier mobility. Thiophene-based materials have shown strong performance in organic photovoltaic devices as well as organic transistors.<sup>17</sup> However, the direct application of thiophene based hole transport layers to perovskite solar cells have been shown to be unfavourable.<sup>16</sup> Swivel-cruciform thiophene based materials display superior solubility while allowing for tuning of the molecular properties by manipulating the pendant group.<sup>18</sup> In this work we introduce the swivel-cruciform thiophene between the two phenyl groups of each fluorene unit in spiro-OMeTAD as shown in figure 1.

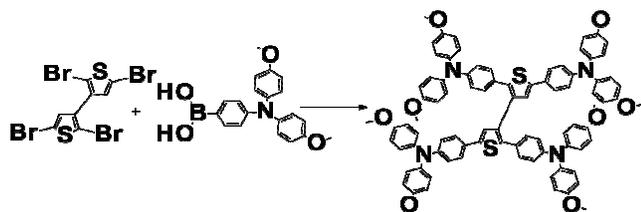


Fig. 2. Synthetic scheme for the preparation of KTM3

The synthetic procedure for the preparation of the 2,2',5,5'-Tetrakis [N,N-di(4-methoxyphenyl)amino]-3,3'-bithiophene (KTM3) is shown in Figure 2. Detailed procedures are provided in Supporting Information. The key step for its synthesis is the Suzuki coupling reaction using  $[Pd(PPh_3)_4]$  between the boronic acid and tetra bromo 3,3'-bithiophene. The boronic acid was prepared from the bis(4-methoxy phenyl amino)bromo phenyl using the catalyst previously reported.<sup>19</sup> The target 2,2',5,5'-Tetrakis [N,N-di(4-methoxyphenyl)amino]-3,3'-bithiophene product was successfully isolated with 25% yield by column chromatography.

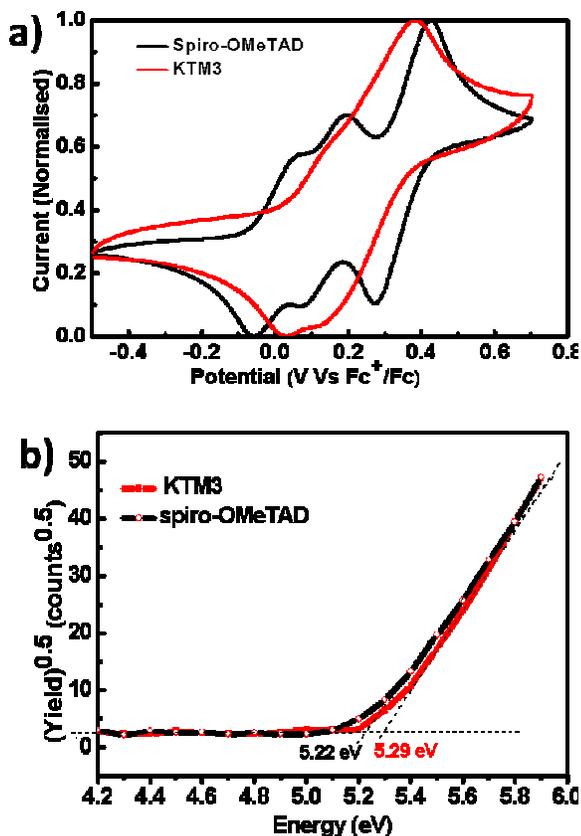


Fig. 3. A. Photoelectron spectroscopy in air (PESA) of HTMs. B. Cyclic voltammetry of HTMs

The HOMO energy levels of the KTM3 and spiro-OMeTAD (reported in Table 1) were determined using photoelectron spectroscopy in air (PESA) on thin films and using cyclic voltammetry (CV) in dilute solutions. Figure 3a shows evidence of two oxidation peaks for KTM3, compared to three oxidation peaks of spiro-OMeTAD. The disappearance of the 22 meV gap between the first and second peaks in spiro-OMeTAD is a manifestation of the increasing N-N distance and a decrease in electronic interaction between the two redox active moieties. The limited electronic interaction between the two arms of the molecule through 3,3'-bithiophene does not affect the HOMO level of the molecule. The HOMO level of the KTM3 is measured as 5.29eV by PESA as shown in Figure 3b which is 70 mV deeper than the spiro-OMeTAD. The extension of conjugation length using the thiophene unit in between the two phenyl groups in spiro-OMeTAD brings down the HOMO level. The KTM3 with its low lying HOMO level can thus possibly give higher  $V_{oc}$  compared to spiro-OMeTAD.

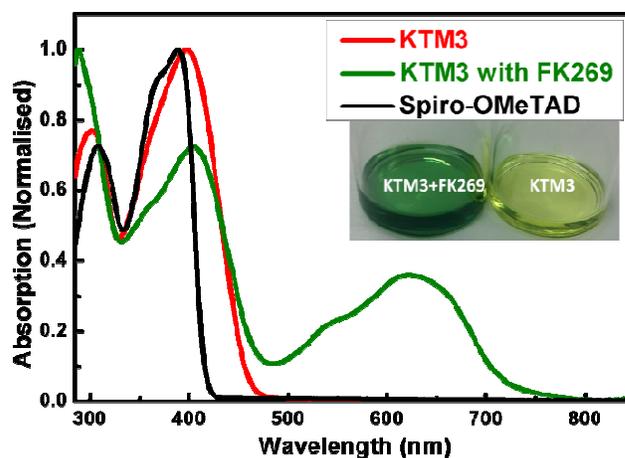


Fig. 4. Normalised absorption spectra for KTM3, spiro-OMeTAD and doped KTM3. Inset shows the KTM3 solution.

The absorption spectrum of the HTMs is shown in Figure 4. KTM3 in chlorobenzene displays an absorption spectrum which is similar to that of spiro-OMeTAD with absorption peaking at 302 and 397 nm. As expected, the extended conjugation in KTM3 results in a clear red-shift of the absorption onset with respect to spiro-OMeTAD. When HTMs are employed in solid state mesoscopic solar cells, cobalt based dopants which provide additional charge carriers through charge transfer doping are also added.<sup>3</sup> Chief among these dopants is FK102 which is employed along with Spiro-OMeTAD. The addition of this dopant FK102 to the solution of KTM3 along with other additives such as Li salt and TBP causes only a temporary color change. The difference in redox potential of KTM3 and FK102 is only 240mV which may not be adequate to effectively oxidize KTM3.<sup>3,20</sup> Hence FK269 which has a deeper HOMO value (5.65 eV) compared to FK102 (5.37 eV) has been employed to dope KTM3 (see supporting information Fig. S1).<sup>21</sup> The color of the solution turns green with the rise of two new absorption bands at 540 and 620 nm corresponding to the formation of the KTM3 cation accompanied by the decrease in the absorption band of KTM3 situated at 397 nm (see figure 4). The thermal property of the KTM3 was also analysed using differential scanning calorimetry (DSC) which showed that

replacing the central spiro unit by swivel-cruciform 3,3'-bithiophene reduces the  $T_g$  to 65 °C.

HTM	HOMO (eV) <sup>a, b</sup>	LUMO (eV) <sup>c</sup>	$E_{opt}^{Gap}$ (eV) <sup>d</sup>	UV (nm)	$T_g$ (°C)
spiro-OMeTAD	5.22 <sup>a</sup> (5.04) <sup>b</sup>	2.05	2.99	309, 389	125
KTM3	5.29 <sup>a</sup> (5.13) <sup>b</sup>	2.42	2.71	302, 397	65

Table 1. Summary of the Electrochemical, Photophysical, and Thermal Properties of the spiro-OMeTAD, and KTM3

<sup>a</sup> Determined by photoelectron spectroscopy in air. <sup>b</sup> Determined by cyclic voltammetry. <sup>c</sup> LUMO = HOMO +  $E_{opt. gap}$ . <sup>d</sup> Determined at the UV absorption onset.

Figure 5 shows the current density-voltage ( $j$ - $V$ ) curves for  $TiO_2/CH_3NH_3PbI_3/HTM/Au$  solar cells fabricated using KTM3 and spiro-OMeTAD with detailed parameters presented in Table 2. The samples were fabricated using sequential deposition methodology for the deposition of the  $CH_3NH_3PbI_3$ . Devices with KTM3 (without Cobalt dopant) displayed a  $V_{oc}$  of 0.99 and fill factor of 70.9% which is noteworthy. The addition of dopant FK102 (15 mole%) to KTM3 resulted in an overall performance increase from 7.3 to 8.7%. As expected, the ineffective doping of KTM3 by FK102 did not cause a significant efficiency improvement. Solar cells fabricated with the deeper dopant FK269 showed a remarkable performance with a  $J_{sc}$  of 13.0 mA  $cm^{-2}$ ,  $V_{oc}$  of 1.08 V, fill factor of 78.3% and an overall performance of 11.0%. I-V measurements at slow scan rate shows a small hump close to the maximum power point as has been observed in other  $CH_3NH_3PbI_3$  solar cells.<sup>4</sup> However this small hump does not affect the fill factor of the device. We recalculated the fill factor by manually drawing the straight line from  $J_{sc}$  ( $V=0$ ) to the  $P_{max}$  point as shown in figure S2 and calculated the fill factor at the  $P_{max}$  point, which indicated a non-variant FF. Therefore the hump may originate from other reasons than the HTM. In addition, the fill factor of the undoped device (which does not show any hump) is 70.1% which is better than standard spiro-OMeTAD based device (62.5%). Thus we do not believe the "hump" plays a significant role. This result is comparable to that obtained from spiro-OMeTAD based solar cells (11.4%) for the same amount of doping.

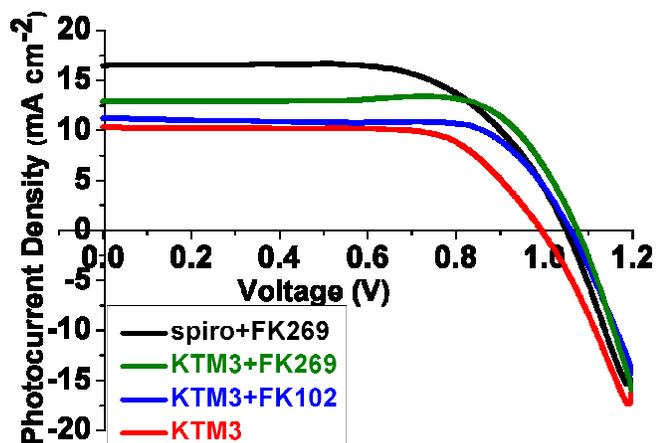


Fig. 5.  $j$ - $V$  Characteristics for spiro-OMeTAD and KTM3 devices measured under AM1.5G solar irradiation (100mW/cm<sup>2</sup>)

IPCE spectra of these devices with new HTMs revealed that the increased optical absorption between 500 nm-750 nm within the KTM3 layers due to doping did not affect the photoconversion efficiency. The IPCE spectra have very similar shapes for solar cells with and without dopant suggesting that the new absorption peak of doped KTM3 has negligible effect on the solar cell (see Supporting Information Fig. S3). Further optimization of dopant level and understanding of the interaction of the sensitizer with the new HTM can possibly improve the efficiency of the solar cell device. The high open circuit voltages attributed to the KTM3 solar cells is supported by the deep HOMO level of the new HTM.

Device	$J_{sc}$ (mA $cm^{-2}$ )	$V_{oc}$ (V)	FF (%)	PCE (%)
KTM3	10.3	0.99	70.9	7.3
KTM3+FK102	11.2	1.06	73.1	8.7
KTM3+FK269(12 mole%)	13.0	1.08	78.3	11.0
spiro-OMeTAD +FK269 (12 mole%)	17.2	1.06	62.5	11.4

Table 2. Summary of the Electrochemical, Photophysical, and Thermal Properties of the spiro-OMeTAD, and KTM3

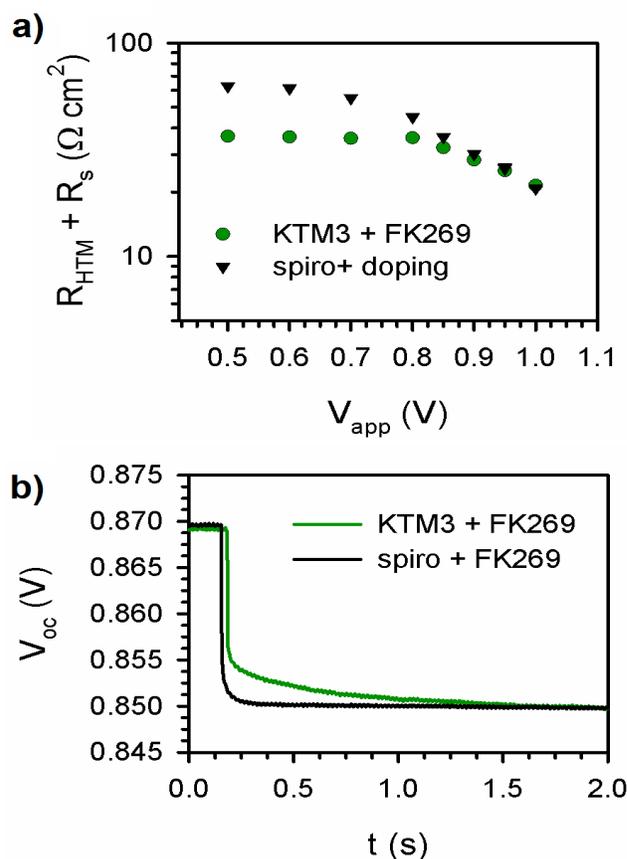


Fig. 6. (a) Total series resistance for spiro-OMeTAD +FK269 and KTM3+FK269 extracted from impedance spectroscopy measurements at different potentials under LED illumination. (b) Photovoltage decay measured for the same samples at  $V_{oc} = 850$  mV

The FF is determined by two aspects: the recombination of photogenerated charge and the series and transport resistances. In order to elucidate the processes which lead to higher FF in the KTM3+doping sample, transient photovoltage decay (TPV) and impedance spectroscopy (IS) measurements (Figure S4) were conducted. For solid state perovskite devices it is accepted that the information regarding hole transport and extraction can be gleaned from the highest frequency features of the impedance spectra.<sup>22-23</sup> The high frequency part of the impedance spectrum of perovskite solar cells is generally attributed to the hole transport.<sup>23-25</sup> Since the charge recombination and electron transport processes are not the scope of this manuscript, we fitted exclusively a series resistance plus the high frequency feature with a parallel R-C circuit. In addition to the high frequency arc, the bulk HTM as well as its interfaces can contribute to the pure series resistance ( $R_s$ ). Since the FF depends on the total series resistance the representation of  $R_{HTM} + R_s$  results in the fairest comparison between the devices (Figure 6(a)).<sup>26</sup> The similar values obtained for both samples cannot justify the large difference in the FF. TPV is a well-established technique to measure the recombination kinetics in different kind of solar cells<sup>27-28</sup>. Recently, it has been applied to perovskite devices for the estimation of the recombination losses<sup>29</sup>. In contrast to the similar results for both kind of devices obtained from the IS measurements, the TPV analysis (figure 6b) exhibits a significant slower decay for the KTM3+FK269 sample, presumably related to a decrease in the recombination -explaining the better FF. The reduced recombination may be related to the torsional relaxation in the KTM3 that may allow for a better interaction with the perovskite surface, as well as the extended delocalization length for the radical cation.

In summary, we successfully synthesized a novel HTM, KTM3 which has a swivel 3,3'-bithiophene as the central unit. This novel HTM in perovskite solar cell exhibited higher  $V_{oc}$  and fill factor than the spiro-OMeTAD. The present finding shows the possibility of developing new HTMs based on swivel-cruciform thiophene with an optimum HOMO level and low recombination rates for application in solid-state perovskite solar cells.

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