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A swivel-cruciform thiophene based hole-transporting material for efficient perovskite solar cells

Thirumal Krishnamoorthy, Fu Kunwu, Pablo P. Boix, Hairong Li, Teck Ming Koh, Wei Lin Leong, Satvasheel Powar, Andrew Grimsdale, Michael Grätzel, Nripan Mathews* and Subodh G. Mhaisalkar*

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A novel swivel-cruciform 3,3'-bithiophene based hole-transporting material (HTM) with a low lying highest occupied molecular orbital (HOMO) level was synthesized. This new HTM (KTM3) in CH₃NH₃PbI₃ perovskite solar cells showed a higher V_{oc} (1.08 V) 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 Gratzel in 1991 is an attractive alternative to the silicon solar cell.¹ Recent research in this area has focused on solid state DSCs where the liquid electrolyte is replaced by an organic hole transport layer^{2,3} for higher stability, but which is accompanied by lower power conversion efficiencies. Hybrid organic-inorganic perovskites with their direct band gaps, large absorption coefficients, and high carrier transport lengths have attracted attention as alternate light harvesters in solid state mesoscopic solar cells.^{4–9} Solid-state solar cells with this novel perovskite material (CH₃NH₃PbI₃) are promising alternatives to conventional liquid electrolyte DSCs in terms of performance and stability.¹⁰ It is remarkable that perovskite solar cells have already achieved over 15% efficiency within such a short development lifetime.¹¹ 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.¹² Additionally, the design of the HTM with an appropriate structure can inhibit back electron transfer, which will result in a solar cell with a higher fill factor and open circuit voltage.¹³ Tuning the energy levels of the HTM is also a methodology to enhance the V_{oc} . Specifically, shifting the highest occupied molecular orbital (HOMO) level of the HTM towards that of the lead iodide perovskite will result in higher open circuit potentials.¹⁴ Previous studies on perovskite solar cells using different HTMs^{15,16} have indicated that poly-triarylamine PTAA and spiro-OMeTAD (see Fig. 1), which contain amine groups, 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 an amine moiety.

The tedious synthesis of spiro-OMeTAD results in its increased cost that limits its scale-up. Thus the 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.¹⁷ However, the direct application of thiophene based hole transport layers to perovskite solar cells has

^aEnergy Research Institute @ NTU (ERI@N), Research Techno Plaza, X-Frontier Block, Level 5, 50 Nanyang Drive, 637553, Singapore. E-mail: Nripan@ntu.edu.sg; Subodh@ntu.edu.sg

^bSchool of Materials Science and Engineering, Nanyang Technological University, Nanyang Avenue, 639798, Singapore

^cInstitute of Materials Research and Engineering, 3 Research Link, Singapore 117602

^dLaboratory of Photonics and Interfaces, EPFL, Lausanne, Switzerland

^{*}Singapore-Berkeley Research Initiative for Sustainable Energy, 1 Create Way, Singapore 138602, Singapore

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

been shown to be unfavourable.¹⁶ Swivel-cruciform thiophene based materials display superior solubility while allowing for tuning of the molecular properties by manipulating the pendant group.¹⁸ In this work we introduce the swivel-cruciform thiophene between the two phenyl groups of each fluorene unit in spiro-OMeTAD as shown in Fig. 1.

The synthetic procedure for the preparation of 2,2',5,5'-tetrakis[*N,N*-di(4-methoxyphenyl)amino]-3,3'-bithiophene (KTM3) is shown in Fig. 2. Detailed procedures are provided in the ESI.† The key step for its synthesis is the Suzuki coupling reaction using [Pd(PPh₃)₄] between boronic acid and tetrabromo-3,3'-bithiophene. Boronic acid was prepared from bis(4-methoxyphenyl)aminebromophenyl using a catalyst previously reported.¹⁹ The target product 2,2',5,5'-tetrakis[*N,N*-di(4-methoxyphenyl)amino]-3,3'-bithiophene was successfully isolated with 25% yield by column chromatography.

The HOMO energy levels of 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. Fig. 3a shows evidence of two oxidation peaks of 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 the 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 KTM3 is measured to be 5.29 eV by PESA as shown in Fig. 3b which is 70 mV deeper than that of spiro-OMeTAD. The extension of the conjugation length using the thiophene unit in between the two phenyl groups in spiro-OMeTAD brings down the HOMO level. KTM3 with its low lying HOMO level can thus possibly give higher V_{oc} values compared to spiro-OMeTAD.

Fig. 2 Synthetic scheme for the preparation of KTM3.

Table 1 Summary of the electrochemical, photophysical, and thermal properties of spiro-OMeTAD and KTM3

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

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

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

The absorption spectrum of the HTMs is shown in Fig. 4. KTM3 in chlorobenzene displays an absorption spectrum which is similar to that of spiro-OMeTAD with absorption peakings 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

Fig. 4 Normalised absorption spectra of KTM3, spiro-OMeTAD and doped KTM3. The inset shows the KTM3 solution.

provide additional charge carriers through charge transfer doping are also added.³ 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 the redox potential of KTM3 and FK102 is only 240 mV which may not be adequate to effectively oxidize KTM3.^{3,20} Hence FK269 which has a deeper HOMO value (5.65 eV) compared to FK102 (5.37 eV) has been employed to dope KTM3 (see ESI, Fig. S1†).²¹ 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 Fig. 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.

Fig. 5 shows the current density–voltage (j - V) curves for $\text{TiO}_2/\text{CH}_3\text{NH}_3\text{PbI}_3/\text{HTM}/\text{Au}$ solar cells fabricated using KTM3 and spiro-OMeTAD with detailed parameters presented in Table 2. The samples were fabricated using a sequential deposition methodology for the deposition of $\text{CH}_3\text{NH}_3\text{PbI}_3$. Devices with KTM3 (without a cobalt dopant) displayed a V_{oc} of 0.99 and a fill factor of 70.9% which is noteworthy. The addition of the dopant FK102 (15 mol%) 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} , a V_{oc} of 1.08 V, a fill factor of 78.3% and an overall performance of 11.0%. I - V measurements at a slow scan rate show a small hump close to the maximum power point as has been observed in other $\text{CH}_3\text{NH}_3\text{PbI}_3$ solar cells.⁴ However this small hump does not affect the fill factor of the device. We recalculated the fill factor by manually drawing a straight line from J_{sc} ($V = 0$) to the P_{max} point as shown in Fig. 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 the standard spiro-OMeTAD based device (62.5%). Thus we do not believe that 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.

IPCE spectra of these devices with new HTMs revealed that the increased optical absorption between 500 nm and 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 dopants suggesting that the new absorption peak of doped KTM3 has a negligible effect on the solar cell (see ESI Fig. S3†). Further optimization of the 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 voltage attributed to the KTM3 solar cells is supported by the deep HOMO level of the new HTM.

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 (Fig. 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.^{22,23} The high frequency part of the impedance spectrum of perovskite solar cells is generally attributed to the hole transport.^{23–25} 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 (Fig. 6a).²⁶ 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 kinds of solar cells.^{27,28} Recently, it has been applied to perovskite devices for the estimation of the recombination losses.²⁹ In contrast to the similar results for both kinds of devices obtained from the IS measurements, the TPV analysis (Fig. 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

Fig. 5 j - V characteristics of spiro-OMeTAD and KTM3 devices measured under AM1.5G solar irradiation (100 mW cm^{-2}).

Table 2 Summary of the electrochemical, photophysical, and thermal properties of spiro-OMeTAD and KTM3

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 mol%)	13.0	1.08	78.3	11.0
Spiro-OMeTAD + FK269 (12 mol%)	17.2	1.06	62.5	11.4

Fig. 6 (a) Total series resistance of 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 $V_{\text{oc}} = 850$ mV.

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 cells exhibited a higher V_{oc} and fill factor than spiro-OMeTAD. The present finding shows the possibility of developing new HTMs based on swivel-cruciform thiophenes with an optimum HOMO level and low recombination rates for application in solid-state perovskite solar cells.

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