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Interface Engineering of Hybrid Perovskite Solar Cells with Poly(3-

thiophene acetic acid) under Ambient Condition

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Abstract:

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The properties of methyl ammonium lead iodide(MAPbI₃) perovskite solar cell with poly(3thiophence acetic acid)(P3TAA) as hole transporting material(HTM) and dense layer of ZnO nanoparticles film as electron transporting material(ETM) is described using the conventional ZnO(n)/Perovskite(i)/P3TAA(p) (n-i-p) architecture. The FT-IR spectra of MAPbI₃/P3TAA mixture indicates shift of N-H stretching and abolition of N-H bending peak indicating interaction between components. UV-Vis spectra of the mixture exhibit large red shift of π - π^* transition peak of the conjugated chain arising from the interaction causing increase of conjugation length. The cross-sectional SEM image of the device shows sequence of the individual layers of ZnO, MAPbI₃, P3TAA and Ag, respectively. The current density(J)voltage(V) curves on illumination with light of 100 mW/cm² indicate the average PCE to be 7.38±0.59% at ambient condition. The IPCE values of this cell reach about 63% across a broad range of wavelength (300-800 nm). The HOMO and LUMO of P3TAA is measured from cyclic voltammetry and optical band gap and the relative energy level of the components explain the operation of photocurrent in the cell. For comparison purposes a device using poly(3-hexyl thiophene)(P3HT) as HTM is fabricated under similar condition and it exhibits a lower $PCE(5.85\pm0.51 \text{ \%})$ than that of P3TAA based device. The longevity of the P3TAA based cell is also found to be better than that of P3HT based cell for storing in air. The UV-Vis and impedance spectral results clearly explain the above results, signifying the influence of interface on the performance of hybrid solar cells.

Introduction:

Recently organolead halide perovskites of the general formula ABX₃ (A= CH₃NH₃, B= Pb and X = Cl, Br or I) have attracted significant attention as an excellent material for solar energy conversion in the field of organic-inorganic hybrid solar cells. The initial report by Miyasaka and co-workers in 2009,¹ demonstrated power conversion efficiency (PCE) of \sim 4%. The exceptional optical and electronic properties of perovskite, for instance strong absorption bands that span over the whole visible region^{2,3} and large charge carrier diffusion lengths,⁴⁻⁶ make them ideal light absorbers towards photovoltaic application. Presently, the organolead halide based perovskite solar cell devices have improved the PCE from the initial ~4% to certified efficiencies of ~ 20%.^{1,7–9} Amongst the perovskite materials produced from methyl ammonium iodide and lead iodide, (MAPbI₃) has attracted significant attention because of ease of preparation, easy solution processability, cost effectiveness and high efficiency.⁸ The architecture of perovskites solar cell consist of a electron transfer material (ETM, n) / perovskites, a light absorbing material which is also an intrinsic semiconductor (i)/ hole transfer material (HTM, p) with n-i-p or the inverted p-i-n configuration. The efficiency of the cell depends on suitable choice of each component, the morphology of the material and on the interface between the layers.^{10,11}

Generally perovskite solar cells based on a mesoporous TiO_2 scaffold as ETM, a MAPbI₃ light-absorption layer and a 2,2',7,7'-tetrakis-(N,N-di-p-methoxyphenylamine)-9,9'-spirobifuorene (spiro-OMeTAD) as HTM have achieved PCEs of ~15.0%,¹² and several other reports suggest that solar cells with efficiencies up to 20% can be achieved by fabricating under controlled condition in glovebox.^{13,14} The TiO₂ perovskite solar cells require high temperature processing technique which is not compatible with the industry produce. Hence, high performance perovskite solar cells fabricated at low temperature is of special interest for the realistic application.¹⁵ Fullerene derivatives or other unstable organic materials as ETM are quite expensive whereas stable inexpensive ZnO compact layers can be prepared easily by spin coating of ZnO nanoparticles at room temperature without heat treatment steps.¹⁶ The development of ZnO nanoparticle as ETM for MAPbI₃-based solar cells, has achieved a PCE as high as 15.7% produced under controlled condition inside the glovebox.¹⁷

In perovskite solar cells, the use of spiro-OMeTAD as HTM has been extensively studied as it can infiltrate through the porous perovskite layer and afford a better contact for charge transportation.^{17–19} Alternatively less costly several conducting polymers such as PEDOT:PSS,²⁰ poly(3-hexylthiophene-2,5-diyl) (P3HT),^{21,22} poly-(triarylamine),²³ and graphene-based materials, ^{24,25} as well as some small molecules such as perylene-diimide derivatives, ²⁶ pyrene-core arylamine derivatives,²⁷ diacetylide-triphenylamine ²⁸ and inorganic material CuI²⁹ have been used as HTM in perovskite-based solar cells. Amongst the conducting polymer family, polythiophene is a good p-type semiconductor for its high crystallinity, charge mobility, conductivity and relative air stability and hence it has been widely studied for use as HTM in perovskite solar cell. In an inverted p-i-n device, ITO/polythiophene/MAPbI₃/C₆₀/BCP/Ag, where polythiophene is produced from electrochemical polymerization, a maximum PCE of 11.8 % is reported.³⁰ Photovoltaic devices fabricated through sequential vapor deposition of lead iodide and MAPbI₃ with undoped P3HT as a hole transporting layer exhibit a PCE of 13.7%.¹¹ In a TiO₂/ CH₃NH₃PbI₂Cl/ P3HT cell a maximum of 10.8% PCE is reported by Conings et al.³¹ In all these cases the fabrication of the devices have been made under stringent dry condition in glove box. Recently Namboopthiry and co-workers have fabricated a cell with TiO₂ as ETM, CH₃NH₃PbI_{3-x}Cl_x as light absorbing material and P3HT as HTM under ambient atmospheric condition and they have reported a maximum efficiency of 5.67%.²² In another TiO₂/CH₃NH₃PbI₂Br/P3HT cell produced under ambient condition the best PCE is reported

to be $6.64\%^{32}$ indicating the fabrication condition has significant effect on the PCE of the cell.

Interface between the different layers of the perovskite solar cell may have large effect on the PCE and in an attempt here we chose an acid derivative of polythiophene eg. poly(3thiophene acetic acid) (P3TAA) where the -COOH groups have a possibility to interact with perovskites through its NH₃ group, that may provide a good mixing at the interface facilitating easy transfer of holes. In this article, a solution processed planar heterojunction perovskite solar cell with MAPbI₃ as light absorbing material, P3TAA as HTM and a dense layer of ZnO nanoparticles film as ETM is described using the conventional ZnO (n)/Perovskite (i)/P3TAA HTM (p) (n-i-p) architecture. Here we have established that P3TAA can be efficiently used as a HTM that can enhance the photovoltaic performance of the perovskite-based solar cell and we have achieved an average PCE of 7.38%, a maximum reported efficiency so far, using polythiophene systems as HTM under ambient atmospheric condition with a satisfactory longevity for storing under ambient condition. In order to establish the interfacial effect on the PCE of perovskite solar cell we have fabricated another solar cell using poly(3-hexyl thiophene) (P3HT) as HTM under identical condition and a comparison of the results indicate that both PCE and longevity of the P3TAA cell are higher than those of P3HT based solar cell. Probable explanation of the results has been attempted through impedance spectroscopy.

Experimental:

Preparation of Ploy(3-thiophene acetic acid) (P3TAA):

3-thiophene acetic acid (3-TAA) was esterified with dry methanol by refluxing in presence of concentrated H_2SO_4 (0.05 ml) for 24 h to protect the oxidative decomposition of carboxylic

acid group during polymerization. It was then polymerized by using anhydrous FeCl₃ in dry chloroform. The molar ratio of FeCl₃ and monomer is 4:1 and the mixture was stirred for 24 h at 0 °C under N₂ atmosphere.³³ The polymer was precipitated into a large excess of methanol to produce poly(3-thiophene methyl acetate) (P3TMA). The precipitate was washed with methanol followed by deionized water. Then P3TMA was hydrolyzed by refluxing with 2 M NaOH solution for 24 h at 100 °C. The water-soluble part was then neutralized with dilute HCl and the precipitate was repeatedly washed with water and dried in vacuum at 60 °C for 3 days. Each step was characterized by ¹H NMR spectroscopy (Fig. S1). The regionegularity of P3TAA was measured from the ¹H NMR spectra presented in Fig. S1(b). The peak at 7.28 ppm is for a proton of H-H linkages and peak at 7.35 is for a proton of H-T linkages of thiophene rings.³³ From the ratio of peak area the % H-T linkage was calculated to be 42.3 mol%. The structures of P3TMA, and P3TAA were confirmed by ¹H NMR spectra. [P3TMA (Fig. S1a), (DMSO-d₆) δ 7.35-7.28 ppm (m, thiophene ring proton, 1H), 3.68 ppm (s, thiophene ring -CH₂-, 2H), 3.64 ppm (s, -CH₃, 3H); P3TAA (Fig. S1b), (DMSO-d₆) & 12.59 ppm (s, -COOH, 1H), 7.35-7.28 ppm (m, thiophene ring proton, 1H), 3.80 ppm (s, thiophene ring -CH₂-, 2H)]. P3HT is synthesized from the monomer 3-hexvlthiophene using the same procedure of polymerization described above. After 24 h of polymerization, the reaction mixtures were poured into methanol containing 10% HCl. The precipitate was re-dissolved in CHCl₃, and the filtrate was dried at 60 °C in air and finally in vacuum. The regioregularity of P3HT was measured from the ¹H NMR spectra presented in Fig. S1(c) in a similar way as above and the head-tail regioregularity was measured to be 81 mol %. The weight-average molecular weight (M_{w}) was estimated from gel-permeation chromatography. It was performed on a Waters instrument equipped with an ultra-styragel column with polystyrene standard as a reference using THF as an eluent at 35 °C at a flow rate of 0.6 ml/min. M_w and

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polydispersity were found as 1.1×10^4 and 1.83 for the P3TAA and 5.6×10^4 and 2.3 for P3HT, respectively.

Synthesis of ZnO nanoparticles:

ZnO nanoparticles were prepared according to a procedure reported in literature. 34,35 Zinc acetate dihydrate (2.95 g, 13.4 mmol) was dissolved in methanol (125 ml) with stirring at 65 °C. A solution of KOH (1.48 g, 23 mmol) in methanol (65 ml) was then added dropwise at 60–65 °C for 30 min. The reaction mixture was stirred for 2.5 h at 65 °C. After cooling to room temperature, the precipitate was collected by centrifugation. The precipitate was then washed three times with methanol, dispersed in methanol and chloroform mixture (1:1 v/v) to produce a ZnO nanoparticle solution with a concentration of 10 mg/ml.

Preparation of Methyl ammonium iodide (MAI):

The perovskite sensitizer methyl ammonium iodide was prepared according to a reported procedure.³⁶ An equimolar mixture of hydroiodic acid (57 wt% in water, Sigma-Aldrich) and methylamine (40% in water, Spectrochem) was stirred in an ice bath for 2 hours. After stirring at 0 °C for 2 hours, the resulting solution was evaporated using a rotary evaporator and MAI was obtained. The precipitate was washed three times with diethyl ether and dried in vacuum under dark conditions.

Solar cell fabrication:

Solar cells were fabricated on pre-cleaned ITO–coated glass substrates with a sheet resistance of 10 Ω /sq. First, a thin ZnO nanoparticle layer was spin coated onto the ITO surface at 3,000 r.p.m. for 30 s. The procedure was repeated two times to obtain a continuous smooth film. A PbI₂ solution (dissolved in N,N-dimethyl formamide at a concentration of 460 mg/ml) was then spin coated on top of the ZnO layer at 3,000 r.p.m. for 30 s. After short baking process at 90 °C for 20 minutes in air, the substrate was dipped into a solution of MAI in 2-propanol (10 mg/ml) for 30 s. The film was then annealed at 70 °C in air for 15 min. On top of the perovskite layer the hole transporting layer of P3TAA / P3HT was produced by spin coating from their respective solution in THF (15 mg/ml) at 1500 r.p.m. for 1 min. Finally, a silver layer was deposited by thermal evaporation at a base pressure of 2×10^{-6} mbar. All device fabrication steps were carried out under ambient conditions at the room temperature without encapsulation.

Device Characterization:

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The current-voltage (I-V) curves of solar cell devices were measured under ambient condition using a Keithley 2401 source meter. The cells were illuminated by a 150 W Xe-lamp equipped with an AM1.5G filter (Newport, 67005) at a calibrated intensity of 100 mW/cm², as determined by a standard silicon reference cell (91150V Oriel Instruments). The effective area of the cell was defined to be 0.4 cm² using a non-reflective mask. The incident photonto-current conversion efficiency (IPCE) as a function of wavelength was measured with a Newport 66902 150 Watt Xe-lamp in combination with an Oriel Cornerstone 130 monochromator and a Keithley 236 source measure unit controlled by Visual Basic software. Electrochemical impedance (EIS) measurements were performed under a 0.92 V DC bias and a 10 mV voltage perturbation conditions with Solartron SI1260 Impedance/Gain-phase analyzer in the frequency range from 1MHz to 0.1 Hz.

Materials Characterization:

The ¹H NMR spectra of the samples were made in DMSO-d₆ on a 500 MHz Bruker instrument. The X-ray diffraction data are recorded on a Philips X'Pert PRO diffractometer with Cu-K α radiation. The data were collected with a 0.05 step size (2 θ). Morphology and micro structural images were acquired on a scanning electron microscope (ZEISS EVO-MA

10). The FTIR spectra of the samples were taken using a Shimadzu FTIR instrument (model 8400S). UV-Vis absorption spectra were acquired on a UV-Vis- spectrophotometer (Cary 8454, Agilent Technologies). The photoluminescence spectra of the solid films cast on quartz plates was performed in a Fluoromax-3 instrument (Horiva Jovin Yvon). Cyclic voltammetry experiments were performed by an electrochemical station (CHI6002E) in a three-electrode cell configuration consisting of platinum working electrode, platinum wire counter electrode, and Ag/AgCl quasi reference electrode with ferrocence/ferrocenium (Fc/Fc⁺) as the internal standard during the measurement at a scan rate of 100 mV/s. P3TAA dissolved in THF and casted on the working electrode area followed by coating with Nafion. The measurements were carried out with 0.1 mol/L tetrabutyl ammonium perchlorate (TBAP) as supporting electrolyte in dry acetonitrile. All working solutions were thoroughly degassed with oxygen-free nitrogen and a nitrogen atmosphere was maintained above the solution throughout the experiments.

Results and Discussion:

Fig.1 shows the X-ray diffraction (XRD) patterns of PbI₂ (top panel) and that of perovskite (bottom panel) on ITO surface. The bottom panel XRD pattern of MAPbI₃ corresponds to 20 signals at 14.1°, 24.5°, 28.4°, 40.5°, 43.1°, and 50.2° respectively representing the (110), (202), (220), (314), and (404) diffraction planes of its tetragonal phase.^{37,38} This XRD pattern does not show any peak of PbI₂(top panel) suggesting complete conversion of PbI₂ to MAPbI₃ under the device preparation procedure.



Fig. 1: XRD patterns for PbI₂ films before and after dipping into MAI solution

In Fig. 2 the Fourier transform infrared (FTIR) spectra of MAPbI₃, P3TAA and the MAPbI₃/ P3TAA mixture in the ratio used for the cell fabrication is presented. In MAPbI₃ the characteristics peaks occur for N-H stretching vibration at 3088 cm⁻¹, C–H stretching vibration at 2920 cm⁻¹, N–H bending at 1571 cm⁻¹, 1463 and 1419 cm⁻¹ is for C–H bending vibration.^{39,40} P3TAA shows characteristics peaks at 1705 cm⁻¹ for >C=O, 2922 cm⁻¹ for C– H stretching, 1168 is for C-O stretching vibration.³³ In the MAPbI₃/ P3TAA mixture the N-H stretching peak at 3088 cm⁻¹ has shifted to 3126 cm⁻¹ and the N–H bending at 1571 cm⁻¹ is almost abolished, indicating interaction between P3TAA with NH₃ group of MAPbI₃ perovskite. Due to the use of very dilute concentration of P3TAA its characteristic vibration peaks are not prominent in the FTIR spectra of the mixture. These results therefore indicate the presence of interaction between the perovskite and P3TAA, which may cause a diffuse interface between the components.



Fig. 2: FTIR spectra of MAPbI₃, P3TAA and the MAPbI₃/P3TAA mixture

In Fig. 3a the UV-Vis spectra at solid state of P3TAA, MAPbI₃, and MAPbI₃/P3TAA made in a similar way to the device fabrication are compared. P3TAA shows a strong absorption peak at 453 nm with a hump at 559 nm and a broad absorption peak at 800 nm. The peak at 453 nm corresponds to π - π * transition of the conjugate chain and the hump at 559 nm corresponds to the vibronic side chain band.⁴¹ The broad absorption peak at 800 nm may appear for the vibronic coupling due to inter chain aggregation occurring at the solid state of the conjugated main chain. The perovskite shows two characteristic weak absorption peaks at 492 and 747 nm. However, in the perovskite/P3TAA hybrid the π - π * transition of the conjugated polythiophene chain at 453 nm has shifted to 546 nm with shift of the hump from 559 nm to 612 nm. The broad peak at 800 nm becomes sharper and it shifts to 911 nm. This spectral shift of P3TAA to lower energy region certainly indicates the interaction between the perovskite and P3TAA causing the P3TAA chain to be more extended increasing its conjugation lengths. This would certainly facilitate an easy movement of charge carriers (holes) inside the cell. Physical Chemistry Chemical Physics Accepted Manuscript



Fig. 3: UV-Vis spectra of (a) MAPbI₃, P3TAA and MAPbI₃/P3TAA (b) P3HT,

MAPbI₃/P3HT layers at the solid state

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To understand the state of P3HT in the P3HT/MAPbI₃ system the Uv-Vis spectra of P3HT and P3HT/MAPbI₃ are presented in Fig.3b. P3HT shows an absorption peak at 554 nm and a hump at 601 nm corresponding to π - π * transition of the conjugate chain and vibronic side chain band, respectively. In the hybrid these bands exhibit red shifts by 6 and 9 nm, respectively which is significantly lower than those of perovskite/P3TAA hybrid system. This result indicates that the P3HT chain remains at more coiled state than that of P3TAA chain in the perovskite system. In other words, it may be surmised that the interface is sharper in the P3HT/MAPbI₃ system than that of perovskite/P3TAA hybrid system.

In Fig. 4(a) the surface SEM image of MAPbI₃ film is presented. The surface image shows the formation of packed crystallites of MAPbI₃. A schematic presentation of the ITO/ZnO/MAPbI₃/P3TAA/Ag device structure is presented in Fig. 4(b) and the cross sectional image of perovskite based device is shown in Fig. 4(c). From the Fig. 4(c) it is apparent that the bottom layer is for ITO and the immediate upper layers sequentially indicate that for ZnO, perovskite, P3TAA and Ag electrodes. The cross sectional SEM image of the

device shows the thickness of the individual layers of ZnO, MAPbI₃, P3TAA and Ag which are measured to be 222, 228, 70 and 105 nm, respectively.



Fig. 4: (a) Surface SEM image of MAPbI₃ film, (b) schematic presentation of the ITO/ZnO/MAPbI₃/P3TAA/Ag device structure, (c) cross sectional image of perovskite based device.

Fig. 5(a) exhibits the J-V curves of ZnO/perovskite/P3TAA solar cell for the forward scan (from short circuit to forward bias) and the reverse scan along with that at dark condition for comparison purpose. It is apparent from the figure that compared to the dark current there is a large hike in current on illumination with a light intensity of 100 mW/cm² both in the forward and reverse bias conditions. The short circuit current (Jsc) has increased to 12.57 mA/cm² under the forward scan, however, in the reverse scan it increases to 12.73 mA/cm². This sharp increase of Jsc under the illumination condition certainly indicates a good performance of this inorganic-organic hybrid solar cells indicating ZnO is acting as a good ETM, and P3TAA as a good HTM in the MAPbI₃ perovskite solar cell produced under ambient condition (temperature 32 °C and humidity 62%). It is noteworthy that in the reverse scan there is some hysteresis which may cause an increase of fill factor (FF) and hence the PCE. In Table 1 the photovoltaic parameters (eg. J_{sc}, FF, open circuit V_{oc} and PCE) both for forward scan and

reverse scan are presented taking a mean from eight cells with their standard deviations for both the forward and reverse bias. The average value of efficiency is found to be $7.38\pm0.59\%$ which is higher than that of other perovskite solar cells produced at ambient conditions using P3HT as HTM.^{22,32} We have also fabricated a device using P3HT as HTM instead of P3TAA under similar condition as in P3TAA for comparison purposes and the PCE is found to be $5.85\pm0.51\%$ (Fig. 5b). All the Jsc, V_{oc} and FF (Table 1) are found to be lower in the P3HT based cell than those of the P3TAA based cell causing 1.53% lower efficiency. The PCE value of the present P3HT based solar cell is comparable to the values reported earlier under ambient condition.²² The probable reason for the large increase in PCE may be the good interaction between perovskite layer and the P3TAA used as HTM under ambient condition. The –COOH groups of P3TAA interact with MAPbI₃ through the lone pair of nitrogen atom of NH₃ group present in it as evident from FTIR spectroscopy. This causes the interface between perovskite and HTM to become more diffused causing an easy injection of holes to the P3TAA chains for its transport.



Fig. 5: J-V characteristics plots for the (a) ITO/ZnO/MAPbI₃/P3TAA/Ag (b) ITO/ZnO/MAPbI₃/P3HT/Ag based perovskire solar cell device under dark and AM 1.5G 100mW/cm² illumination measured with forward and reverse scan direction.

Table 1: Photovoltaic performance of ITO/ZnO/MAPbI₃/HTM/Ag based perovskire solar cell device under AM 1.5G 100mW/cm² illumination measured with forward and reverse scan.

HTM	Applied bias	Jsc	Voc (V)	FF	PCE, η	Average
	direction	(mA/cm ²)			(%)	PCE (%)
	Forward	12.57±0.4	0.90±0.02	0.61±0.02	6.90±0.56	
P3TAA	Reverse	12.73±0.3	0.92 ± 0.03	0.67 ± 0.04	7.85±0.62	7.38±0.59
	Forward	11.71±0.3	0.85±0.02	0.58±0.02	5.77±0.45	
						5.85 ± 0.51
P3HT	Reverse	11.74±0.2	0.87 ± 0.02	0.58±0.04	5.93±0.56	1

The incident-photon-to-current conversion efficiency (IPCE) spectrum (Fig. 6) for the ZnO/MAPbI₃/P3TAA device shows a response in the region from the UV-visible to near infrared range (300–800 nm). The IPCE values of this cell reach about 63% across a broad range of wavelength, indicating good light-harvesting by the device.



Fig. 6: IPCE spectrum of ZnO/MAPbI₃/HTM based device

The IPCE curve of ZnO/MAPbI₃/P3HT hybrid is also shown in the figure for comparison purpose and it is interesting that both P3TAA and P3HT show response in the same wavelength region but in the former case the IPCE values are higher than that of P3HT supporting the PCE data presented above.

The operation of the device can be understood from the relative energy levels of the each component of the device (Fig. 7). The excitons generated in the MAPbI₃ layer can be extracted or dissociated by transferring holes to the P3TAA layer and by transferring electrons to the ZnO layer, attaining high charge transport efficiencies to both the electrodes. Here, the energy levels for the ZnO and perovskite layer are taken from the literature.^{42,43} The corresponding HOMO and LUMO levels of P3TAA have been calculated from the onset oxidation potential in the cyclic voltammetry experiment and the optical band gap obtained from the Tauc's plot to be -4.86 eV and -2.78 eV vs. vacuum, respectively (Fig. S2 a, b).



Fig. 7: Schematic representation of the band energy diagrams for ITO/ZnO/MAPbI₃/P3TAA/Ag device.

The conduction band of ZnO is located in the closer proximity of the perovskite layer and the HOMO level of P3TAA is well matched for the separation of holes, which facilitates the charge separation process. The band gap offsets between the different components facilitating effective electron transport from the conduction band of MAPbI₃ to ZnO and then to the ITO electrodes and transport of holes from the valance band of the perovskite films to the P3TAA and then to the Ag electrodes. Since the HOMO level (-4.86 eV) of P3TAA is comparable to the valance band (-5.43 eV) of MAPbI₃, it facilitates the hole transfer to Ag electrode through P3TAA. The relatively high LUMO energy (-2.78 eV) of P3TAA compared with that of the conduction band of MAPbI₃ (-3.93 eV) prevents the electron transfer through the perovskite layer to the Ag electrode. This phenomenon suggests that P3TAA can be successfully used as an effective HTM for the MAPbI₃ based perovskite solar cell.

The longevity of the cell has been measured by keeping the cell under the ambient air condition without encapsulation and the PCE is measured at different time interval. In Fig. 8 the normalized PCE is plotted with storage time and after 10 days 55% value of PCE is retained. The longevity of P3HT based device made under similar condition as in P3TAA is lower as evident from the Fig. 8 and here after 10 days only 27 % value of PCE is retained. . This result indicates a fair stability of the P3TAA based cell under ambient atmospheric condition and it may be attributed to the controlled PbI₂ passivation.³⁸ The present system also exhibits much better stability than that of TiO₂ /MAPbI_{3-x}Cl_x/spiro-OMeTAD exposed to ambient air without encapsulation showing only 30 % PCE after 10 days of storing.⁴⁴ The better stability of P3TAA based cell that that of P3HT based cell may be due to mixing of MAPbI₃ with P3TAA causing diffuse interface.



Fig. 8: Normalized PCE with respect to storage time for ZnO/MAPbI₃/HTM based perovskite solar cells under ambient air condition without encapsulation.

Electrochemical impedance spectroscopy (EIS) is a non destructive powerful technique to elucidate the charge transport process in the solar cells. The Nyquist plot of ITO/ZnO/MAPbI₃/HTM/Ag cell is presented in Fig. 9. From the figure it is apparent that in each case there are two semicircles characterizing the impedance spectra of the cell. The data can be fitted in an equivalent resistance (R) – capacitance (C) circuit shown in Fig. 9 (Inset).



Fig. 9: Typical Nyquist plot of the hybrid perovskite solar cells based on ZnO/MAPbI₃/HTM. The simulation result (line) is fitted to experimental data (symbols). Inset is the equivalent circuit applied to fit the Nyquist plot.

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The semicircle at the higher frequency region corresponds to the charge-transfer resistance (R_{HTM}) at the hole transporting layer and the C_{HTM} is the interfacial capacitance between electrode (Ag) and HTM.²⁹ The semicircle at the low frequency region corresponds to the recombination resistance (R_{rec}) of the ETM (ZnO)/perovskite interface and the CPE yields the chemical capacitance which is related to the Fermi level of ETM.^{29,45,46} An additional resistance (R_s) appears in the equivalent circuit drawn from Z-view software and it may be attributed to the additional contribution of the series resistance. The fitting parameters of EIS data are presented in Table 2. The impedance analysis of the P3TAA based cell yields lower R_{HTM} and higher R_{rec} value compared to those of P3HT based cell. The lower R_{HTM} value indicates lower resistance experienced by the holes to flow along the HTM material and the higher R_{rec} indicate a lower recombination of photo-injected electrons. Thus the combined effects of lower R_{HTM} and higher R_{rec} value cause higher PCE in the P3TAA than that of P3HT based solar cell. So, this result supports that the diffuse interface between the components of perovskite solar cell yield higher efficiency due to easier transport processes.

Table 2: Fitting parameters for EIS data of ITO/ZnO/MAPbI₃/HTM/Ag based perovskire solar cell device.

HTM	Rs	R _{RHM}	C _{HTM}	Rrec	CPE-P	CPE-T	Cµ*
	(Ω/cm^2)	(Ω/cm^2)	(µF)	(Ω/cm^2)		$(\Omega^{-1}s^{CPE-P})$	(µF)
P3TAA	60.5	69.0	0.82	242.0	0.8	5.1×10 ⁻⁵	15.8
P3HT	44.0	90.5	0.18	180.8	0.7	0.8×10 ⁻⁵	0.34

*[Cµ is calculated from the CPE-T and CPE-P values using the equation.

$$C_{\mu} = \frac{(CPE - T \times R_{rec})^{\frac{1}{CPE - P}}}{R_{rec}}$$

To understand the charge recombination and dissociation process in the device photoluminescence spectra (PL) of individual and mixed layers are presented in Fig. 10. The PL spectra of MAPbI₃ show emission peaks at 740 nm and 763 nm for excitation at 490 nm. On addition of P3TAA the emission peak at 740 nm is fully quenched but that of 763 nm is slightly quenched and similar reports are also observed in these types CH₃NH₃PbI₂Br/P3HT systems ³² where it is suggested that photo-generated holes are quickly extracted to the P3HT layer before bulk recombination.⁵ On the other hand, addition of ZnO to MAPbI₃ the intensity of all the emission peaks of MAPBI₃ are totally quenched. This is also true for the ZnO/MAPbI₃/P3TAA hybrid system. The complete quenching of fluorescence intensity of MAPbI₃ by ZnO indicates ZnO is a very effective ETM for transfer of photo-generated electrons by dissociation of the hole-electron pair generated from white light illumination on MAPbI₃ system. Hence ZnO is a very effective ETM and P3TAA act as a good HTM for perovskite solar cell application yielding a moderate average PCE of 7.38±0.59% under ambient condition.



Fig. 10: Solid state photoluminescence spectra of indicated components and their mixtures as present in the device.

Conclusion:

In conclusion it may be inferred that P3TAA can act as an effective HTM in the conventional ZnO (n)/Perovskite (i)/P3TAA (p) (n-i-p) solar cell even produced in air under ambient condition. The FTIR spectra of MAPbI₃/P3TAA mixture indicate shifts of N-H stretching peak and abolition of N-H bending peak suggesting an interaction between the components. The UV-V is spectra of the mixture exhibit a large red shift of π - π * transition peak of the conjugated chain arising from the interaction causing increase of conjugation length. These results suggest that the interface between the MAPbI₃/P3TAA is diffused which facilitates the hole transfer process. The current density (J) – voltage (V) curves on illumination with a light intensity of 100 mW/cm² indicate a hysteresis in the reverse bias than that of forward bias and the average PCE is measured to be 7.38±0.59%. The IPCE values of this cell reach about 63% across a broad range of wavelength (300-800 nm). The HOMO and LUMO energy levels of P3TAA are measured from cyclic voltammetry and optical band gap and the relative energy levels of the components explain the operation of P3TAA as HTM and ZnO as ETM. The Nyquist plot of the ITO/ZnO/MAPbI₃/P3TAA/Ag cell show two semicircles and the recombination resistance is calculated to be 96.8 Ω . From the photoluminescence spectra of individual and mixed layers it is proved that ZnO is a very effective ETM and P3TAA acts as a good HTM for MAPbI₃ hybrid perovskite solar cell produced under ambient condition yielding an average PCE of 7.38±0.59%. We have also fabricated a device using P3HT as HTM instead of P3TAA under similar condition for comparison purposes and the PCE is found to be 5.85±0.51 % which is 1.53% lower than that of P3TAA system. The longevity of the P3TAA based cell is found to be better that that of P3HT based cell for storing under ambient condition in air. The UV-Vis and impedance spectral results clearly explain the influence of interface on the PCE value of the hybrid solar cells.

Electronic supplementary information (ESI) available:

¹H NMR spectra of P3TMA, P3TAA and P3HT, Cyclic voltammetry curve and Tauc's plot for P3TAA. This material is available free of charge via the Internet at http://pubs.rsc.org/.

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References:

- A. Kojima, K.Teshima, Y. Shirai and T. Miyasaka, J. Am. Chem. Soc., 2009, 131, 6050–6051.
- D. B. Mitzi, In Progress in Inorganic Chemistry, Ed. K. D. Karlin, Wiley-Interscience, New York, 1999; Vol. 48, pp 1–121.
- 3. T.-C. Sum and N. Mathews, Energy Environ. Sci., 2014, 7, 2518–2534.
- S. D. Stranks, G. E. Eperon, G. Grancini, C. Menelao, M. J. P. Alcocer, T. Leijtens, L. M. Herz, A. Petrozza and H. J. Snaith, *Science*, 2013, **342**, 341–344.
- G. Xing, N. Mathews, S. Sun, S. S. Lim, Y. M. Lam, M. Grätzel, S. Mhaislkar and T. C. Sum, *Science*, 2013, **342**, 344–347.
- C. Wehrenfennig, G. E. Eperon, M. B. Johnston, H. J. Snaith and L. M. Herz, *Adv. Mater.*, 2014, 26, 1584–1589.
- C. G. Wu, C. H. Chiang, Z. L. Tseng, M. K. Nazeeruddin, A. Hagfeldt and M. Grätzel, *Energy Environ. Sci.*, 2015, 8, 2725–2733.

- H. Zhou, Q. Chen, G. Li, S. Luo, T. B. Song, H. S. Duan, Z. Hong, J. You, Y. Liu and Y. Yang, *Science*, 2014, 345, 542–546.
- NREL. Best Research Cell Efficiency. http://www.nrel.gov/ ncpv/images/efficiency chart.jpg (accessed August, 2015).
- 10. D. Forgács, M. Sessolo and H. J Bolink, J. Mater. Chem. A, 2015, 3, 14121-14125.
- H. A. Abbas, R. Kottokkaran, B. Ganapathy, M. Samiee, L. Zhang, A. Kitahara, M. Noack and V. L. Dalal, *APL Mater.*, 2015, 3, 016105.
- J. Burschka, N. Pellet, S.-J. Moon, R. Humphry-Baker, P. Gao, M. K. Nazeeruddin and M. Grätzel, *Nature*, 2013, 499, 316–319.
- 13. M. D. Mcgehee, Nature, 2013, 501, 323-325.
- 14. N.-G. Park, J. Phys. Chem. Lett., 2013, 4, 2423-2429.
- L. Q. Zhang, X. W. Zhang, Z. G. Yin, Q. Jiang, X. Liu, J. H. Meng, Y. J. Zhao and H. L. Wang, *J. Mater. Chem. A*, 2015, **3**, 12133–12138.
- 16. Y. Jin and G. Chumanov, ACS Appl. Mater. Interfaces, 2015, 7, 12015–12021.
- 17. D. Liu and T. L. Kelly, Nat. Photonics, 2014, 8, 133-138.
- M. M. Lee, J. Teuscher, T. Miyasaka, T. N. Murakami and H. J. Snaith, *Science*, 2012, **338**, 643–647.
- 19. J. M. Ball, M. M. Lee, A. Hey and H. J. Snaith, *Energy Environ. Sci.*, 2013, 6, 1739–1743.
- J.-Y. Jeng, Y.-F. Chiang, M.-H. Lee, S.-R. Peng, T.-F. Guo, P. Chen and T.-C. Wen, *Adv. Mater.*, 2013, 25, 3727–3732.
- S. N. Habisreutinger, T. Leijtens, G. E. Eperon, S. D. Stranks, R. J. Nicholas and H. J. Snaith, *Nano Lett.*, 2014, 14, 5561–5568.

- 22. M. Seetharaman, P. Nagarjuna, P. N. Kumar, S. P. Singh, M. Deepa and M. A. G. Namboothiry, *Phys. Chem. Chem. Phys.*, 2014, **16**, 24691–24696.
- 23. J. H. Heo, S. H. Im, J. H. Noh, T. N. Mandal, C.-S. Lim, J. A. Chang, Y. H. Lee, H.-J. Kim, A. Sarkar, M. K. Nazeeruddin, M. Grätzel and S. I. Seok, *Nat. Photon.*, 2013, 7, 486–491.
- 24. Z. Wu, S. Bai, J. Xiang, Z. Yuan, Y. Yang, W. Cui, X. Gao, Z. Liu, Y. Jin and B. Sun, *Nanoscale*, 2014, 6, 10505–10510.
- J. S. Yeo, R. Kang, S. Lee, Y. J. Jeon, N. Myoung, C. L. Lee, D. Y. Kim, J. M. Yun,
 Y. H. Seo, S. S. Kim and S. I. Na, *Nano Energy*, 2015, **12**, 96–104.
- J. Min, Z. G. Zhang, Y. Hou, C. O. R. Quiroz, T. Przybilla, C. Bronnbauer, F. Guo, K. Forberich, H. Azimi, T. Ameri, E. Spiecker, Y. F. Li and C. J. Brabec, *Chem. Mater.*, 2015, 27, 227–234.

- 27. N. J. Jeon, J. Lee, J. H. Noh, M. K. Nazeeruddin, M. Grätzel and S. I. Seok, J. Am. Chem. Soc., 2013, 135, 19087–19090.
- 28. A. Abate, M. Planells, D. J. Hollman, V. Barthi, S. Chand, H. J. Snaith and N. Robertson, *Phys. Chem. Chem. Phys.*, 2015, 17, 2335–2338.
- J. A. Christians, R. C. M. Fung and P. V. Kamat, J. Am. Chem. Soc., 2014, 136, 758–764.
- W. Yan, Y. Li, W. Sun, H. Peng, S. Ye, Z. Liu, Z. Bian and C. Huang, *RSC. Adv.*, 2014, 4, 33039–33046.
- B. Conings, L. Baeten, C. De Dobbelaere, J. D'Haen, J. Manca and H.-G. Boyen, *Adv. Mater.*, 2014, 26, 2041–2046.
- 32. M. Zhang, M. Lyu, H. Yu, J.-H. Yun, Q. Wang and L. Wang, *Chem.-Eur. J.*, 2015, 21, 434–439.
- 33. B. S. Kim, L. Chen, J. P. Gong and Y. Osada, *Macromolecules*, 1999, 32, 3964–3969.

- 34. Q. Zhang, C. S. Dandeneau, X. Zhou and G. Cao, Adv. Mater., 2009, 21, 4087-4108.
- 35. W. J. E. Beek, M. M. Wienk, M. Kemerink, X. N. Yang and R. A. J. Janssen, J. Phys. Chem. B, 2005, 109, 9505-9516.
- G. E. Eperon, V. M. Burlakov, P. Docampo, A. Goriely and H. J. Snaith, *Adv. Funct. Mater.*, 2014, 24, 151–157.
- 37. Q. Chen, H. Zhou, Z. Hong, S. Luo, H.-S. Duan, H.- H. Wang, Y. Liu, G. Li and Y. Yang, J. Am. Chem. Soc., 2014, 136, 622–625.
- 38. J. Song, J. Bian, E. Zheng, X.-F. Wang, W. Tian and T. Miyasaka, *Chem. Lett.*, 2015, 44, 610–612.
- 39. A. Cabana and C. Sandorfy, Spectrochim. Acta, 1962, 18, 843-861.
- 40. N. J. Jeon, J. H. Noh, Y. C. Kim, W. S. Yang, S. Ryu and S. I. Seok, *Nat. Mater*. 2014, **13**, 897–903.
- 41. S. D. D. V. Rughooputh, S. Hotta, A. J. Heeger and F. J. Wudl, *Polym. Sci., Part B: Polym. Phys.*, 1987, 25, 1071–1078.
- 42. D. I. Son, B. W. Kwon, J. D. Yang, D. H. Park, B. Angadi and W. K. Choi, J. Mater. Chem., 2012, 22, 816–819.
- 43. W. Ke, D. Zhao, C. R. Grice, A. J. Cimaroli, J. Ge, H. Tao, H. Lei, G. Fang and Y. Yan, *J. Mater. Chem. A*, 2015, **3**, 17971–17976.
- 44. J.-F. Li, Z.-L. Zhang, H.-P. Gao, Y. Zhang and Y.-L. Mao, *J. Mater. Chem. A*, 2015, **3**, 19476–19482.
- 45. Q. Zhu, X. Bao, J. Yu, D. Zhu, M. Qiu, R. Yang and L. Dong, *ACS Appl. Mater. Interfaces*, 2016, **8**, 2652–2657.

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46. J. Zhang, Z. Hu, L. Huang, G. Yue, J. Liu, X. Lu, Z. Hu, M. Shang, L. Han and Y.

Zhu, Chem. Commun., 2015, 51, 7047-7050.

Table of Content

Interface Engineering of Hybrid Perovskite Solar Cells with Poly(3thiophene acetic acid) under Ambient Condition

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 $ZnO/MAPbI_3$ based perovskite solar cell with poly(3-thiophene acetic acid) shows higher efficiency(7.38%) and stability than P3HT based cell(5.85%) in air.