

# Effect of Different Hole Transport Materials on Recombination in CH<sub>3</sub>NH<sub>3</sub>Pbl<sub>3</sub> Perovskite-Sensitized Mesoscopic Solar Cells

Dongqin Bi, Lei Yang, Gerrit Boschloo, Anders Hagfeldt, and Erik M. J. Johansson\*

Department of Chemistry-Ångström, Physical Chemistry, Uppsala University, Uppsala, Sweden

Supporting Information

ABSTRACT: We report on perovskite (CH<sub>2</sub>NH<sub>2</sub>)PbI<sub>3</sub>-sensitized solid-state solar cells using spiro-OMeTAD, poly(3-hexylthiophene-2,5-diyl) (P3HT) and 4-(diethylamino)benzaldehyde diphenylhydrazone (DEH) as hole transport materials (HTMs) with a light to electricity power conversion efficiency of 8.5%, 4.5%, and 1.6%, respectively, under AM 1.5G illumination of 1000 W/m<sup>2</sup> intensity. Photoinduced absorption spectroscopy (PIA) shows that hole transfer occurs from the (CH<sub>3</sub>NH<sub>3</sub>)PbI<sub>3</sub> to HTMs after excitation of  $(CH_3NH_3)PbI_3$ . The electron lifetime  $(\tau_e)$  in these devices are in the



order Spiro-OMeTAD > P3HT > DEH, while the charge transport time  $(t_{tr})$  is rather similar. The difference in  $\tau_e$  can therefore explain the lower efficiency of the devices based on P3HT and DEH. This report shows that the nature of the HTM is essential for charge recombination and elucidates that finding an optimal HTM for the perovskite solar cell includes controlling the perovskite/HTM interaction. Design routes for new HTMs are suggested.

SECTION: Energy Conversion and Storage; Energy and Charge Transport

lthough dye-sensitized solar cells (DSCs) is a very attractive low-cost technology for sustainable power conversion, 1,2 solid-state dye-sensitized solar cells (ssDSCs) show a promising alternative to conventional DSCs based on liquid electrolyte in terms of stability.<sup>3</sup> Recently, an impressive record efficiency of 7.2% and improved cell stability have been obtained.4 However, the efficiency is still lower than the conventional DSCs based on liquid electrolyte. Generally, the lower performance of ssDSCs is attributed to reasons such as the limited pore-filling of the mesoporous TiO2 with the hole transport material (HTM),<sup>5</sup> and the absorption of light, which is currently limited by the rather low maximal film thickness of well-performing ssDSCs compared to the liquid electrolyte DSCs.6 The utilization of quantum dots (QDs) as lightharvesters in place of dye molecules has recently drawn great attention. Their advantages include a good light-harvesting capability, a tunable band gap over a wide range, and a large intrinsic dipole moment. Because of this, a variety of QDs have been investigated, including CdS, CdSe, PbS, PbSe, PbSe, PbSe, Date of CdSe, D InP, <sup>13</sup> InAs, <sup>14</sup> and Sb<sub>2</sub>S<sub>3</sub>. <sup>15</sup> Although such heterojunction QD solar cells show promising photovoltaic performance, they still face problems such as low stability, low  $V_{\rm oc}$  and fast carrier recombination, which prevent them from achieving higher efficiencies.

Hybrid organic-inorganic perovskites based on lead iodide inorganic layers with a direct band gap, large absorption coefficient, <sup>16</sup> and high carrier mobility, <sup>17</sup> is an attractive class of materials as light harvesters in heterojunction solar cells. The layered hybrid perovskites can also be viewed as multilayer quantum well structures, with semiconducting inorganic sheets alternating with wider band gap (i.e., highest occupied molecular orbital to lowest unoccupied molecular orbital (HOMO-LUMO) gap) organic layers. 18 Making substitutions

on either the metal or halogen site modifies the band gap of the inorganic layers (well depth), while the width of the barrier and well layers can easily be adjusted by changing the length of the organic cations and the number of perovskite sheets between each organic layer, respectively. Previous studies reported (CH<sub>3</sub>NH<sub>3</sub>)PbI<sub>3</sub>/(CH<sub>3</sub>NH<sub>3</sub>)PbBr<sub>3</sub> as sensitizers in DSCs based on liquid electrolytes. However, the perovskite sheets tend to dissolve easily in the electrolytes, which degrades the solar cell performance rapidly. Recently, a solid-state solar cell using (CH<sub>3</sub>NH<sub>3</sub>)PbI<sub>3</sub> as the light harvester has drawn great interest, reaching above 10% efficiency with low-cost.<sup>22-24</sup> One important limitation in the performance of perovskite/HTM solar cells at present is a balance between series and shunt resistance. The perovskite is very conductive, on the order of 10<sup>-3</sup> S cm<sup>-3</sup>, requiring a thick layer of HTM to avoid pinholes.<sup>24</sup> While most HTMs, for example, spiro-OMeTAD, are less conductive (~10<sup>-5</sup> S cm<sup>-1</sup>), a thicker capping layer results in high series resistance. Therefore, it would be meaningful to investigate perovskite solar cells using different HTMs, not only to afford more convincing understanding for the charge transfer but also to understand the effect of HTM on the solar cell performance. Previous results for CH<sub>3</sub>NH<sub>3</sub>PbBr<sub>3</sub> solar cells with different HTMs showed that a high open-circuit voltage can be obtained.<sup>25</sup>

Here, we report on the photovoltaic properties of HTM/ (CH<sub>3</sub>NH<sub>3</sub>)PbI<sub>3</sub>/TiO<sub>2</sub> solar cells using spiro-OMeTAD, poly(3hexylthiophene-2,5-diyl) (P3HT), and 4-(diethylamino)benzaldehyde diphenylhydrazone (DEH) as HTMs (see Figure 1) and investigate the differences in the charge recombination,

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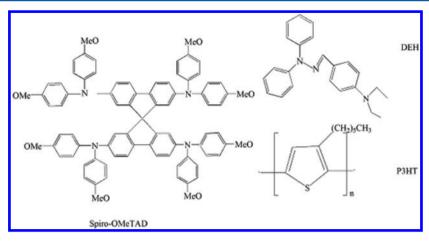


Figure 1. Molecular structures of the different HTMs.

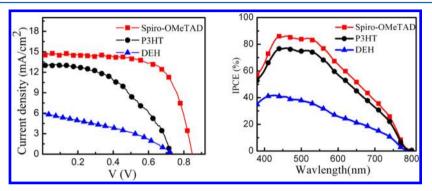


Figure 2. J-V curve under AM 1.5G illumination of 1000 W/m<sup>2</sup> intensity and IPCE spectra of HTM/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/TiO<sub>2</sub> solar cells.

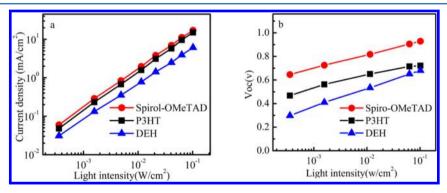


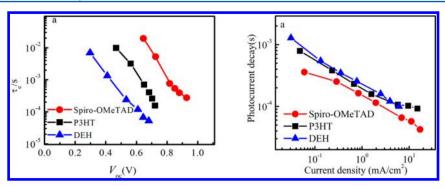
Figure 3. The light intensity dependence of  $J_{\rm sc}$  and  $V_{\rm oc}$  in HTM/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/TiO<sub>2</sub> solar cells.

charge transport, and the light-to-current conversion process, to understand how to choose an optimal HTM for the perovskite solar cell.

The photovoltaic performance and the incident photon-to-current conversion efficiency (IPCE) of the  $HTM/CH_3NH_3PbI_3/TiO_2$  solar cell devices are shown in Figure 2.

A power conversion efficiency of 8.5%, 4.5%, and 1.6% was achieved for spiro-OMeTAD, P3HT and DEH, respectively. All the devices show photocurrent in the visible region between 400 and 750 nm, which shows that the perovskite light absorber is efficient for these thin solar cells. P3HT absorbs light in the visible region compared to spiro-OMeTAD and DEH, which have negligible light absorption in the visible region. <sup>26–28</sup> This might effect the photoconversion efficiency, however, the IPCE spectra have very similar shape for the different solar cells, which suggests that the HTM light absorption has negligible effect on the solar cell.

The dependence of short-circuit current  $(J_{sc})$  on light intensity (I) is shown in Figure 3a. A power law dependence of  $J_{\rm sc}$  on I, i.e.,  $J_{\rm sc} \propto I^{\alpha}$ , where  $\alpha$  is close to 1 for all three HTMs is observed, indicating that charge collection efficiency is independent of light intensity, which also may indicate sufficient electron and hole mobility, and non space-charge limited photocurrents. <sup>29</sup> In ssDSCs, the  $V_{\rm oc}$  is determined by the difference between the quasi Fermi level of electrons in TiO<sub>2</sub> under illumination and the quasi Fermi level of holes in the HTM. Figure 3b shows that the  $V_{oc}$  increases with the light intensity, the slope in  $V_{\rm oc}$  versus intensity varied with different hole conductors: it was about 114 mV/decade for spiro-OMeTAD, 102 mV/decade for P3HT, with a decrease in the slope at higher light intensity, and 154 mV/decade for DEH. Notably, it is significantly higher than the value of 59 mV per decade that is expected in DSCs, when recombination of the conduction band electron from the metal oxide to the redox



**Figure 4.** (a) Electron lifetime as a function of open circuit voltage in CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/TiO<sub>2</sub> solar cells, measured from the transient photo voltage at modulated light intensity. (b) Transient photocurrent decay time as a function of short-circuit current in CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/TiO<sub>2</sub> solar cells, measured from the transient photocurrent at modulated light intensity.

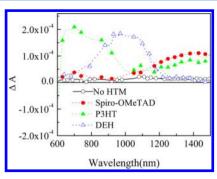
electrolyte shows first-order kinetics. It seems a reasonable approximation that the doping level of the spiro-OMeTAD does not change much when the light intensity is varied, and that the Fermi level in the HTM can be considered rather constant for these concentrations of LiTFSI added.<sup>30</sup> Deviation from first-order recombination kinetics can be attributed to trap-assisted recombination, or inhomogeneous recombination due to the variations in pore-filling.

The transient  $V_{oc}$  decay experiment was used to measure the electron lifetime  $(\tau_e)$ . The measured  $\tau_e$  is shown as a function of light intensity, and the decrease in  $\tau_e$  at higher light intensity is attributed to relatively faster recombination. This is usually observed in DSCs and is caused by the increased concentration of electrons in TiO2 at a higher light intensity and device potential. In Figure 4, we can see that the  $\tau_e$  for the solar cells with DEH and P3HT is clearly lower than that with spiro-OMeTAD HTM. The different electron lifetimes is due to different rates of electron transfer to the oxidized hole conductor (a recombination process). Therefore the recombination in the solar cells using DEH or P3HT is faster compared to the recombination in the solar cells using spiro-OMeTAD. The recombination rate of the device with spiro-OMeTAD is more than 10 times lower compared to that in the device with P3HT, and more than 100 times lower than in the device with DEH. The faster recombination explains the lower short-circuit current, the lower open-circuit voltage, and the lower fill-factor of the solar cells based on P3HT and DEH. The difference in recombination rate may be due to several reasons. Electron transfer reactions are dependent on the electronic coupling, which is dependent on the electronic structure of the materials and the distance between the materials.<sup>31</sup> The bulky molecular structure of spiro-OMeTAD with the twisted spiro center, probably makes the electronic coupling to the perovskite lower compared to DEH, which have a more flat molecular structure and therefore may have a more close position to the perovskite surface. This may therefore explain the short  $\tau_e$  of the solar cell based on DEH compared to the spiro-OMeTAD-based solar cell. Also, P3HT has a rather flat molecular structure in comparison to spiro-OMeTAD, and the thiophene units may be in close contact with the perovskite surface, which may be the reason for the lower electron lifetime for the solar cell based on P3HT compared to the solar cell based on spiro-OMeTAD. We therefore suggest that for perovskite solar cells, the molecular structure of the HTM should be designed to avoid close contact between the perovskite and the hole on the HTM. For example, a bulky three-dimensional structure of the HTM with alkyl chains protecting the hole can specifically be of interest for future HTMs. Also the energies of the HOMO levels for the different HTMs may affect the charge recombination. Electrochemical measurements show that the oxidation potential of DEH is approximately 0.12 V versus Fc/Fc<sup>+</sup> (see Supporting Information), which is very similar to spiro-OMeTAD and P3HT, which have onset of oxidation potentials of approximately 0.15 V versus Fc/Fc<sup>+</sup> and 0.05 V versus Fc/Fc<sup>+</sup>, respectively, according to our previous measurements. <sup>26,27</sup> This suggests that the energy levels and the driving forces for charge transfer are rather similar in the different solar cells.

In Figure 4b, the transient photocurrent decay time is measured for the solar cells with different HTMs. The results are rather similar for the different solar cells, which indicate that the charge transport time  $(t_{\rm tr})$  is rather similar for the different solar cells. The lower solar cell performance of the DEH and P3HT-based solar cells compared to the spiro-OMeTAD-based solar cells is therefore attributed to the lower electron lifetime of the solar cells based on DEH and P3HT. It is interesting to note that, although P3HT possesses a high hole mobility of up to 0.1 cm²/V/s, 32 which is several orders of magnitude higher than that for spiro-OMeTAD  $(10^{-4} {\rm cm}^2/{\rm V/s})^{33}$  and DEH  $(10^{-6} {\rm cm}^2/{\rm V/s})^{34}$  the transport times were rather similar.

Another factor that may be important for the solar cell efficiency is the pore filling of the HTM into mesoporous  ${\rm TiO_2}$  film. Spiro-OMeTAD has a much smaller molecular size than P3HT, and the pore filling and dye regeneration in ssDSCs is therefore better. <sup>27,35</sup> DEH, which has an even smaller molecular size, can probably infiltrate the mesoporous  ${\rm TiO_2}$  layer efficiently. However, the smaller size also enables closer approach to the titania surface, which may increase electronhole recombination at the  ${\rm TiO_2}$  interface, lowering the solar cell performance as discussed above. <sup>27</sup>

To understand in more detail the charge transfer processes occurring in the solar cells, photoinduced absorption spectroscopy (PIA) measurements were performed. For perovskite solar cells, the charge transfer processes between the perovskite and the TiO<sub>2</sub> and the HTMs have been discussed, <sup>23</sup> but the exact processes occurring are still not certain. In order to investigate the charge generation in the devices with the different HTMs, we performed PIA on the TiO<sub>2</sub> film with perovskite coated without and with different HTMs, and the results are shown in Figure 5. For the mesoporous TiO<sub>2</sub> film coated with perovskite and no HTM, the PIA spectrum revealed only weak features in the range of 1000–1400 nm, which is assigned to free electrons in the TiO<sub>2</sub>, <sup>35,36</sup> but could also be an effect of charges in the perovskite. After addition of



**Figure 5.** PIA of samples with  $TiO_2$ /perovskite and the different HTMs: Spiro-OMeTAD, P3HT and DEH. Also the PIA spectrum for the sample without any HTM is shown. The excitation wavelength is 460 nm.

HTM, we could efficiently monitor the oxidized species of HTM created after photoexcitation of the perovskite. For the sample with spiro-OMeTAD HTM, the spectrum shows absorption features at 750 nm, as well as a broad band around 1300 nm, which is assigned to the hole located on the Spiro-OMeTAD. <sup>23,26,27</sup> For P3HT, several absorption bands were observed. The band at 700-1100 nm is assigned to positively charged P3HT (polarons) but may also have contributions from excitons in P3HT,<sup>37</sup> the absorption band over 1200 nm is suggested to result from delocalized polarons in P3HT.<sup>38</sup> For the sample with DEH, the band between 700 and 1200 nm is assigned to the oxidized DEH.<sup>39</sup> We may therefore conclude that the hole transfer from the perovskite to the HTM is possible to measure for all the HTMs. Although the PIA spectrum for the sample without HTM was very weak, the result suggests that we may have an electron transfer from the perovskite to the TiO2 which was also observed for the CH<sub>3</sub>NH<sub>3</sub>PbI<sub>2</sub>Cl perovskite on TiO<sub>2</sub>. <sup>23</sup> We note that the PIA signal depends both on the concentration and lifetime of the species monitored, hence from this measurement alone, quantification of the relative charge generated yield is not possible.<sup>23</sup> However, rather strong signals were observed in the PIA spectra when the different HTMs were deposited, which suggest that the hole transfer from the perovskite to the HTM is efficient, and that the low efficiency of the device with DEH HTM instead is a result of the faster recombination measured above.

In summary, perovskite (CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>)-sensitized solid state solar cells using different HTMs (spiro-OMeTAD, P3HT, and DEH) were investigated. Among the three HTMs, spiro-OMeTAD results in devices that show the best efficiency of 8.5% under AM 1.5G illumination of 1000 W/m<sup>2</sup> intensity. PIA showed that there is obvious hole transfer to the HTM from the perovskite in all devices. Electron lifetime measurements showed that the recombination of the separated charges in the device using spiro-OMeTAD HTM is more than 10 times slower compared to that in the device with P3HT, and more than 100 times slower than that in the device with DEH HTM. Charge transport was, on the other hand, rather similar for the devices, and the difference in electron lifetime can therefore explain the large difference in efficiency of the devices.

## ASSOCIATED CONTENT

### S Supporting Information

The Supporting Information includes material synthesis, device preparation procedures, and description of experimental setups.

This material is available free of charge via the Internet at http://pubs.acs.org.

#### AUTHOR INFORMATION

#### **Corresponding Author**

\*E-mail: erik.johansson@kemi.uu.se.

#### Notes

The authors declare no competing financial interest.

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