Supporting information

Mesoscopic $TiO_2/CH_3NH_3PbI_3$ perovskite solar cells with new hole-transporting materials containing butadiene derivatives

Songtao Lv,[a] Liying Han,[b] Junyan Xiao,[a] Lifeng Zhu,[a] Jiangjian Shi,[a] Huiyun Wei,[a] Yuzhuan Xu,[a] Juan Dong, [a] Xin Xu,[a] Dongmei Li,*[a] Yanhong Luo, [a] Qingbo Meng*[a] and Xianggao Li*[b]

[a] Key Laboratory for Renewable Energy (CAS), Beijing Key Laboratory for New Energy Materials and Devices, Beijing National Laboratory for Condense Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China. Fax: +86-10-8264-9242; Tel: +86-10-8264-9242; E-mail: qbmeng@iphy.ac.cn, dmli@iphy.ac.cn.

[b] The Co-Innovation Center of Chemistry and Chemical Engineering of Tianjin, School of chemical Engineering and Technology, Tianjin University, Tianjin 300072, China. Fax: +86-22-27404208; Tel: +86-22- 27892279; E-mail: lixianggao@hotmail.com.

1. Materials

PbI_2 was purchased from Aldrich, N,N-dimethylformamide (DMF) and chlorobenzene from Alfar Aesar, hydroiodic acid (AR, 45 wt% in water), methylamine (AR, 27% in methanol) from Sinopharm Chemical Reagent Co. Ltd. and *spiro*-OMeTAD from Luminescence Technology Corp., Taiwan. All the chemicals were directly used without further purification. CH_3NH_3I was synthesized by following the literature. 4-(4-Phenyl-4-α-naphthylbutadienyl)-N,N-di(4-tolyl)-phenylamine (denoted as HTM_1) and 4-(4-phenyl-4-α-naphthylbutadienyl)-N,N-di(4-methoxyphenyl)-phenylamine (denoted as HTM_2) were prepared according to our previous work. Substrates are fluorine-doped tin oxide conducting glass (FTO, Pilkington, thickness: 2.2 mm, sheet resistance 14 Ω/square). Before use, FTO glass was first washed with mild detergent, rinsed with distilled water for several times and subsequently with ethanol in an ultrasonic bath, finally dried under air stream.

2. Characterization

The surface morphology of the $TiO_2/CH_3NH_3PbI_3$/HTM/Au film was obtained by using a scanning electron microscope (SEM, FEI XL30S-FEG). The film thickness was determined by a

surface profiler (KLA-Tencor, P-6). Electrochemical impedance spectra (EIS) of the perovskite solar cells were performed on a ZAHNER IM6e electrochemical workstation in the dark in the frequency ranging from 0.1 to 10^5 Hz with a perturbation amplitude of 10 mV. The obtained impedance spectra were fitted with *Zview* software based on appropriate equivalent circuit. The cells were illuminated under 100 mW·cm^{-2} (AM 1.5) by an Oriel solar simulator 91192, and the *J-V* characteristics of the cells were recorded on Princeton Applied Research, Model 263A. For *J-V* characteristics, a mask with a window of 0.08 cm^2 was clipped on the TiO_2 side to define the active area of the cell. Photoluminescence spectra were obtained on a PL Spectrometer (Edinburgh Instruments, FLS 900), excited with a picosecond pulsed diode laser (EPL-445). The time-of-flight (TOF) measurements were conducted on TOF401 (Sumitomo Heavy Industries. Ltd., Japan). Samples were prepared through vacuum deposition using a structure ITO/HTM (about 1 μm)/Al (150 nm) having an active area of 3 mm × 10 mm.

Figures

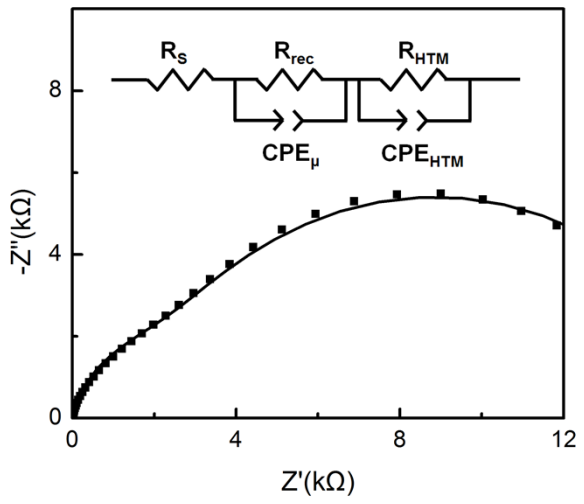

Fig. S1 Nyquist plot of the device with 60 mg·mL^{-1} HTM_2 in the dark over 600 mV forward bias, scattered point: experimental data, solid line: fitted curves. Inset: Equivalent circuit model for fitting the EIS. R_s: series resistance; R_{rec}: recombination resistance and CPE_μ is the chemical capacitance of the film; R_{HTM} and CPE_{HTM}: HTM resistance, capacitance and the extraction in the Au electrode.

As shown in Fig. S1, the obtained EIS spectra can give two arcs in the dark in the frequency ranging from 0.1 to 10^5 Hz. In terms of Ref. 17, 22 and 23, the first arc at higher frequencies, is related to the HTM transport and extraction in the Au electrode, which have a similar effect in the different thickness HTM layers. The main arc is due to the combination of the recombination resistance (R_{rec}) and the chemical capacitance of the film (CPE_{μ}). Here, more attention has been focused on the main arc related to the HTM/$CH_3NH_3PbI_3$/TiO_2 film, which is fitted by *Zview* software based on Equivalent circuit model shown in the Inset of Fig. S1.

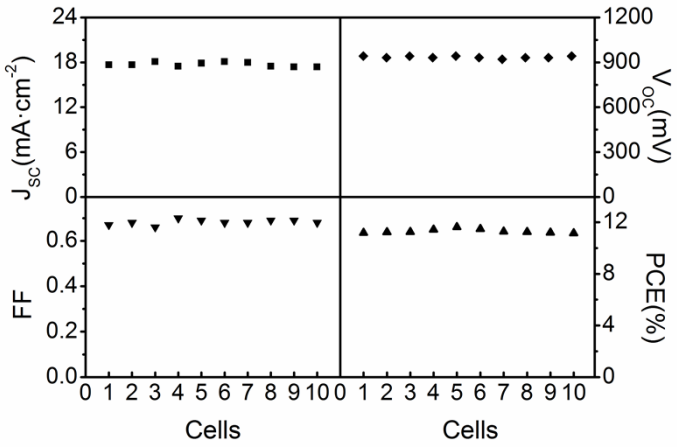

Fig. S2 A histogram of device efficiencies from a batch of ten perovskite solar cells with HTM_2.

Table. S1 Photovoltaic parameters from a batch of ten cells with HTM_1 and HTM_2

HTM	Cell	J_{sc} (mA·cm^{-}	V_{oc} (mV)	*FF*	PCE (%)
HTM_1	1	17.8	921	0.68	11.15
	2	18.2	921	0.66	11.06
	3	18.1	921	0.68	11.34
	4	18	921	0.67	11.11
	5	17.9	921	0.68	11.21
HTM_2	1	17.4	942	0.68	11.15
	2	17.7	942	0.67	11.17
	3	18.1	942	0.66	11.25
	4	17.9	942	0.69	11.63
	5	18.1	932	0.68	11.47