Electronic Supplementary Information

Metal–organic frameworks at interfaces of hybrids perovskite solar cells towards enhanced photovoltaic properties

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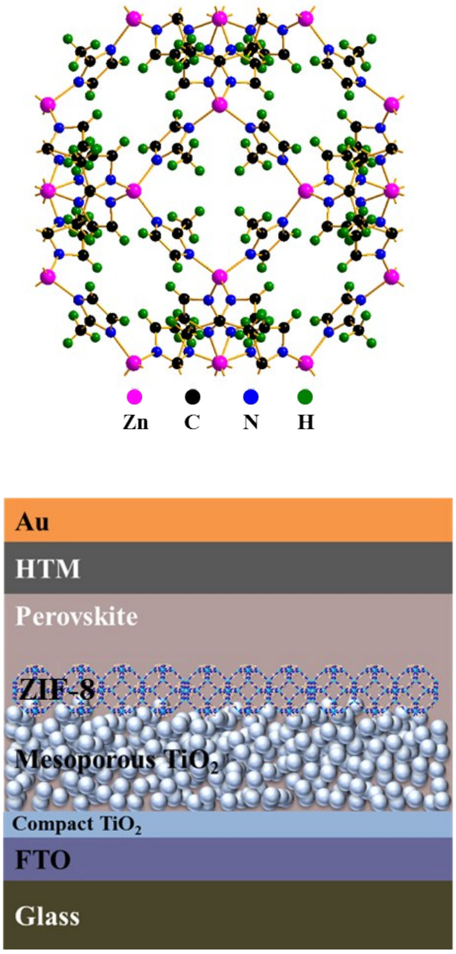


Fig. S1 (a) The chemical structure of ZIF-8 and (b) schematic illustration of the perovskite solar cell based on the surface of mesoporous TiO$_2$ film coated by ZIF-8 layer.

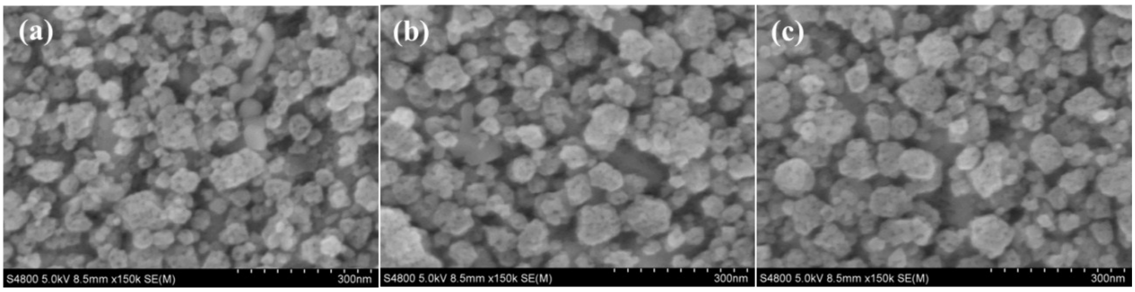


Fig. S2 SEM images of mesoporous TiO_2 film with ZIF-8 coating for (a) 0 min, (b) 10 min, (c) 20 min, respectively.

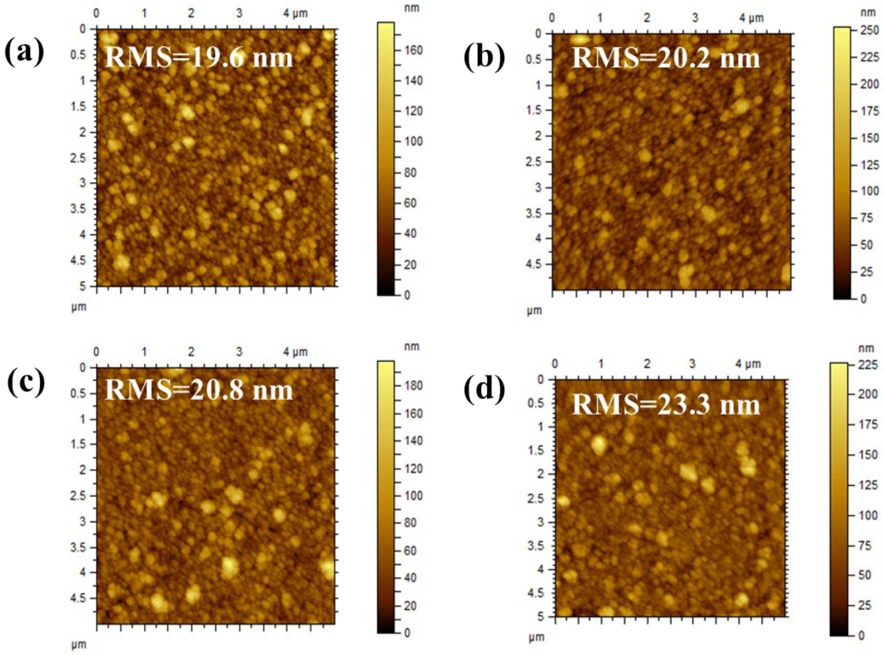
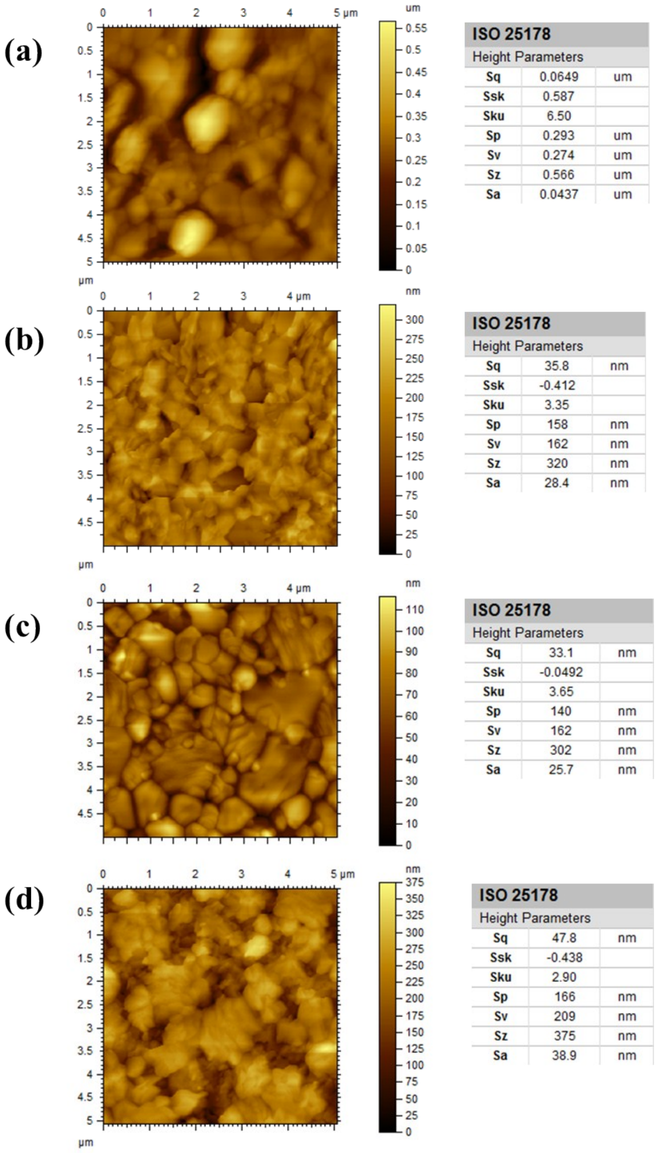


Fig. S3 AFM images of ZIF-8 layer on the surface of mesoporous TiO_2 deposited on compact TiO_2 and FTO substrates with different coating time: (a) 0, (b) 10, (c) 20, and (d) 40 min, respectively.



(a)

ISO 25178

Height Parameters

Sq	0.0649	um
Ssk	0.587	
Sku	6.50	
Sp	0.293	um
Sv	0.274	um
Sz	0.566	um
Sa	0.0437	um

(b)

ISO 25178

Height Parameters

Sq	35.8	nm
Ssk	-0.412	
Sku	3.35	
Sp	158	nm
Sv	162	nm
Sz	320	nm
Sa	28.4	nm

(c)

ISO 25178

Height Parameters

Sq	33.1	nm
Ssk	-0.0492	
Sku	3.65	
Sp	140	nm
Sv	162	nm
Sz	302	nm
Sa	25.7	nm

(d)

ISO 25178

Height Parameters

Sq	47.8	nm
Ssk	-0.438	
Sku	2.90	
Sp	166	nm
Sv	209	nm
Sz	375	nm
Sa	38.9	nm

Fig. S4 (a) AFM images of $MAPbI_3$ films based on different coating times of ZIF-8 on mesoporous TiO_2 electrodes: (a) 0 min, (b) 10 min, (c) 20 min and (d) 40 min, respectively.

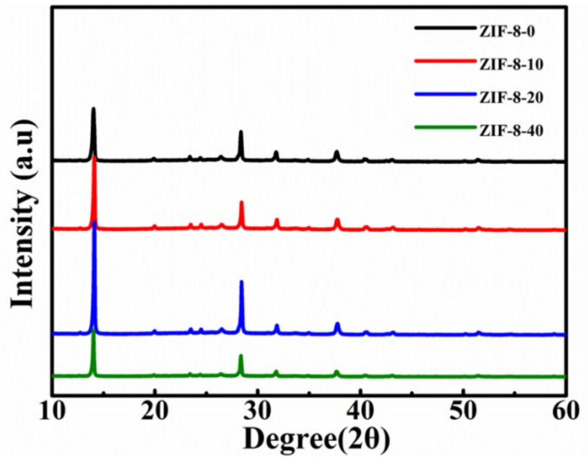


Fig. S5 XRD patterns of $MAPbI_3$ layers formed on the surface of mesoporous TiO_2 film with different coating time of ZIF-8: 0 (black), 10 (red), 20 (blue) and 40 min (green), respectively.

Table S1 Photovoltaic parameters of PSCs employing mesoporous TiO_2 with different coating time of ZIF-8 as the ETL: short-circuit current (J_{sc}), open-circuit voltage (V_{oc}), fill factor (FF), power conversion efficiency (PCE) extracted from the J–V curves in Fig. 4b.

ZIF-8 coating time/ min	**J_{sc}/mA·cm^{-2}**	**V_{oc}/V**	**FF**	**PCE/% (PCE_{max}/%)**
0	20.37±0.40	0.99±0.012	0.70±0.01	14.12±0.63 (14.75)
10	21.25±0.37	0.98±0.024	0.65±0.02	13.54±0.78 (14.32)
20	22.65±0.17	1.01±0.013	0.72±0.01	16.47±0.52 (16.99)
40	22.00±0.21	0.99±0.011	0.70±0.01	15.25±0.30 (15.55)

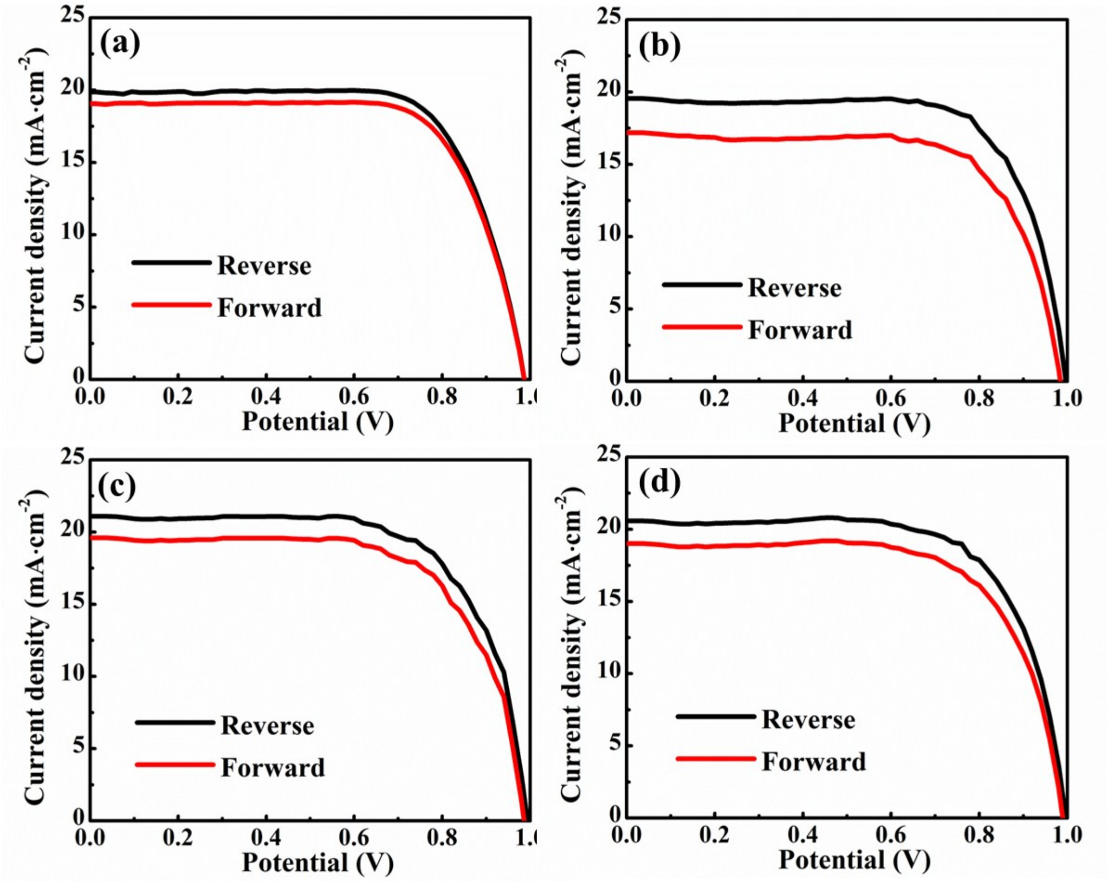


Fig. S6 J-V characteristics in the forward and reverse scanning directions of the PSCs employing mesoporous TiO_2 film with different ZIF-8 coating time: (a) 0 min, (b) 10 min, (c) 20 min and (d) 40 min, respectively.

Table S2 J-V parameters in the forward and reverse scanning directions of the PSCs employing mesoporous TiO_2 film with different ZIF-8 coating time.

ZIF-8 growth time/ min	**Scan direction**	**J_{sc}/mA·cm^{-2}**	**V_{oc}/V**	**FF**	**PCE/%**
0	Reverse	19.86	0.98	0.70	13.62
	Forwad	19.09	0.98	0.69	12.91
10	Reverse	19.55	0.99	0.72	13.94
	Forwad	17.18	0.98	0.65	10.94
20	Reverse	21.09	1.00	0.72	15.18
	Forwad	19.60	0.98	0.64	12.37
40	Reverse	20.58	1.00	0.69	14.20
	Forwad	19.00	0.99	0.67	12.60

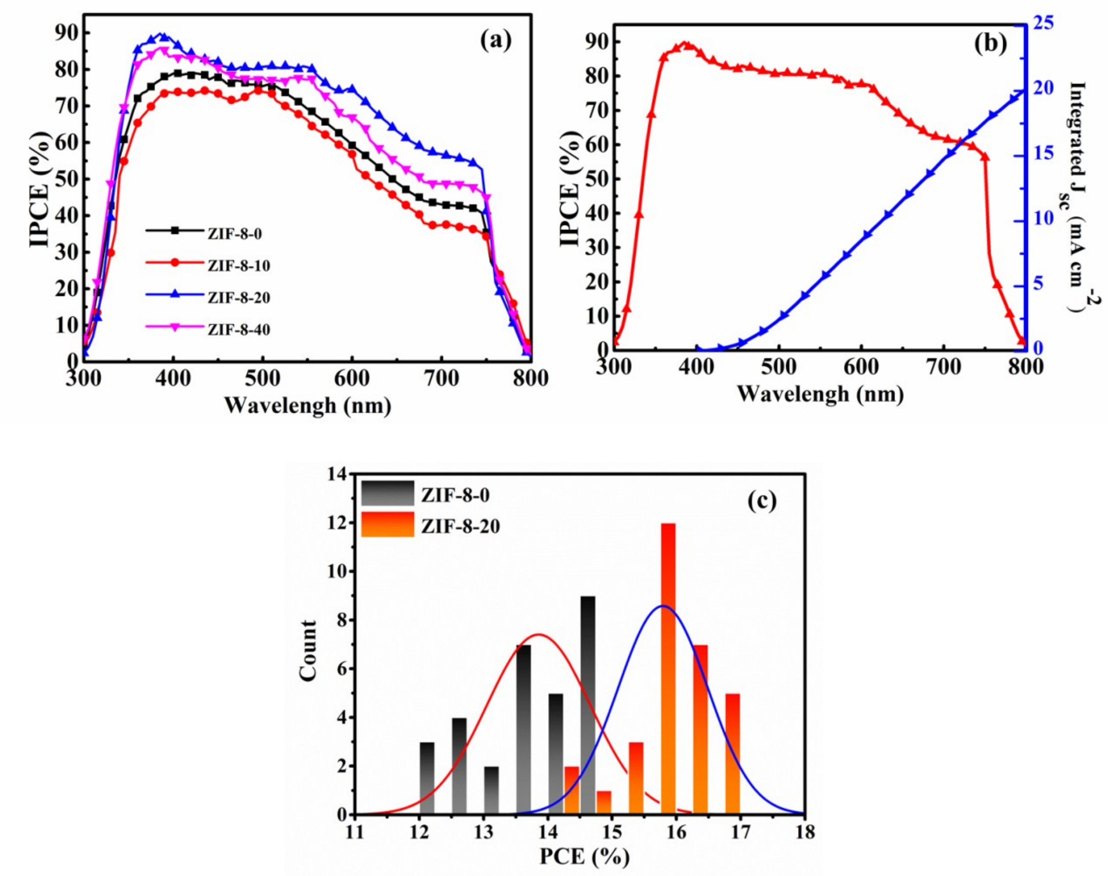


Fig. S7 (a) The incident photon-to-electron conversion efficiency (IPCE) spectra of the PSCs employing mesoporous TiO_2 with different ZIF-8 coating time as the ETL, (b) the IPCE curve of the PSC employing mesoporous TiO_2 with ZIF-8 coating time of 20 min as the ETL and the integrated current density of the same cell, (c) histograms of PCEs determined for 30 PSC devices based on mesoporous TiO_2 film with 0 min and 20 min ZIF-8 coating time, respectively.

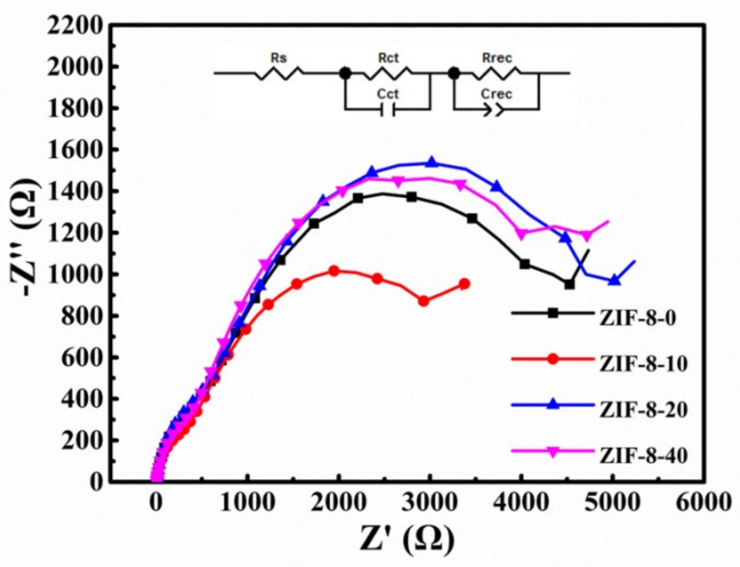


Fig. S8 Nyquist plots of the cells composed of the mesoporous TiO_2 film with different ZIF-8 coating time measured at -0.7 V, in the frequency range of 1 Hz to 1 MHz.

Table S3 EIS parameters of PSCs employing mesoporous TiO_2 with different ZIF-8 coating time as the ETL.

ZIF-8 coating time/ min	**R_s/Ω**	**R_{ct}/Ω**	**R_{rec}/Ω**
0	9.24	336.2	4286
10	9.72	357.6	2939
20	9.16	262.4	4810
40	9.18	287.5	4377

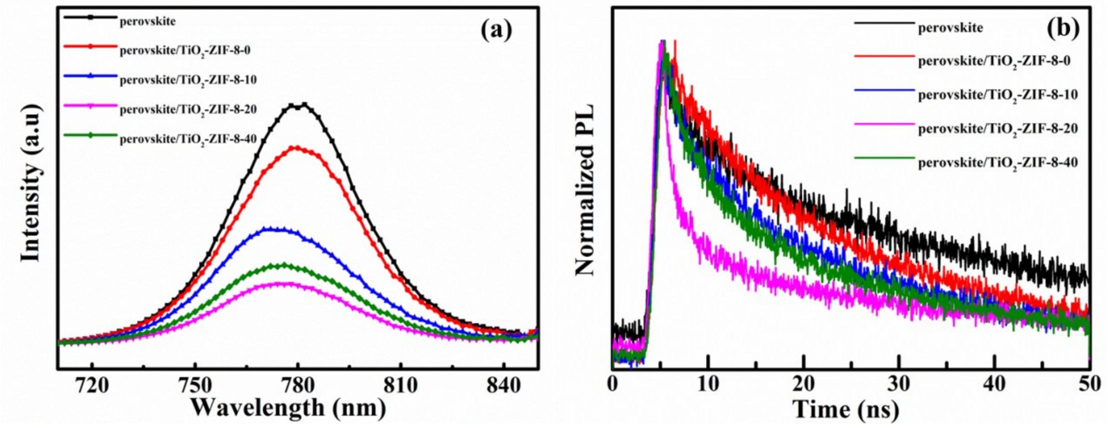


Fig. S9 (a) The photoluminescence (PL) spectra (excitation at 406 nm) and (b) time-resolved photoluminescence (TRPL) (excitation at 406 nm and emission at 760 nm) of the bare perovskite film and on the surface of mesoporous TiO_2 film with different ZIF-8 coating time.

Experimental Section

TiO_2 (25 nm) and 2-methyl imidazole were purchased from Aladdin Corp. The preparation of the paste for spin coating was according to our previous report.[1]

Preparation of substrates: SnO_2:F (FTO) substrates were patterned by etching with 2 M HCl and Zn powder. The cleaning of the patterned FTO was firstly executed by brushing the surface with detergent, and then cleaned in an ultrasonic bath with deionized water, ethanol, acetone and isopropanol for 30 min, respectively. The TiO_2 blocking layer (BL) was spin-coated on FTO substrate at 2000 rpm s^{-1} for 30 s using 0.15 M titanium diisopropoxide bis(acetylacetonate) (75 wt% in isopropanol, Alfa-Aesar) in 1-butanol (99.9%, Alfa-Aesar) solution, which was heated at 150 °C for 30 min. After cooling to room temperature, the homemade mp-TiO_2 paste was spin coated on the BL-TiO_2 at 2000 rpm s^{-1} for 30 s, where the pristine paste was diluted in ethanol (0.1 g ml^{-1}). After drying at 150 °C for 30 min, the film was annealed at 550 °C for 30 min, providing a layer thickness between 200-250 nm.

Surface treatment of mp-TiO_2 by ZIF-8: For depositing of ZIF-8, mp-TiO_2 film was immersed in a fresh methanol solution containing 2 mM $Zn(NO_3)_2$ and 4 mM 2-methyl imidazole for a given time. Then the film was rinsed with methanol and dried at 80 °C. The mp-TiO_2 film modified by ZIF-8 was denoted as mp-TiO_2/ZIF-8-x (x meant the coating time of ZIF-8), and the unit “min” was omitted to clarify. The powders left in the solution were centrifuged, rinsed by methanol 3 times, and then dried at 80 °C for XRD characterization.

Preparation of the perovskite solution: The perovskite layer was deposited in a Argon-filled glovebox by spin coating the perovskite precursor solution. The latter was prepared by dissolving a stoichiometric amount (1:1 molar ratio) of PbI_2 and CH_3NH_3I in dimethylsulfoxide (DMSO) at a concentration of 1.1 M of each component. The spin coating procedure included two steps, first at 1000 rpm for 10 s, and then at 6000 rpm for 30 s. 20 s after the beginning of the spin-coating program, chlorobenzene was gently dropped on the spinning substrate using an automatic dispenser. The substrate was then annealed at 90 °C for 30 min to obtain a dense $CH_3NH_3PbI_3$ film.

Preparation of the Spiro-OMeTAD solution and the gold layer: The hole transport material (HTM) was deposited on the top of the perovskite layer by spin coating at 4000 rpm s^{-1} for 20 s. HTM solution consisted of 72.3 mg (2,2’,7,7’-tetrakis(N,N-di-p-methoxyphenylamine)-9,9-spirobifluorene) (spiro-MeOTAD), 28.8 µl 4-tert-butylpyridine, 17.5µl of a stock solution of 520 mg ml^{-1} lithium bis(trifluoromethylsulphonyl)imide in acetonitrile in 1 ml chlorobenzene. Finally, Au was thermally evaporated on top of the device to form the back contact. The active area of devices were 0.12 cm^2 determined by the mask with dimensions of 4 mm × 3 mm.

Characterization of mp-TiO$_2$/ZIF-8 based PSC device: The photovoltaic performance of PSCs was recorded using a source meter (Keithley 2400). A PEC-L11 AM 1.5 solar simulator with a 1000 W Xe lamp and an AM 1.5 filter (Peccell,) was applied as the light source (100 mW cm^{-2}). J-V curves were measured at a scan rate of 20 mV s^{-1}. The incident photon-to-current conversion efficiency (IPCE) spectra were collected using a PEC-S20 (Peccell) Electrochemical Impedance Spectroscopy (EIS) was conducted employing an IM6 (Zahner). The impedance parameters were simulated by fitting of impedance spectrum through Z-view software.

The phase purity of the samples was characterized by powder X-ray diffraction (XRD) on a Rigaku Ultima IV using the Cu Kα radiation (λ=1.5418 Å). X-ray photo-electron spectroscopy (XPS) was recorded on a MUTILLAB 2000. The crystalline morphologies were examined by scanning electron microscope (S-4800 instrument). Atomic force microscopy (AFM) measurements were obtained using a SPA-300 AFM (Bruker) and scanning range of the AFM images was 5 µm × 5 µm. Steady-state photoluminescence (PL) (excitation at 406 nm) and time-resolved photoluminescence

(TRPL) (excitation at 406 nm and emission at 750 nm) were conducted with Edinburgn Instruments LTD (FLS 980).

References

1 F. Y. Xie, Y. F. Li, J. Dou, J. X. Wu and M. D. Wei, *Journal of Power Sources*, 2016, **336**, 143.