Supporting information

Zeolitic-Imidazolate-Framework (ZIF-8)/PEDOT: PSS Composite Counter Electrode for Low Cost and Efficient Dye-Sensitized Solar Cells

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1 Materials and reagents

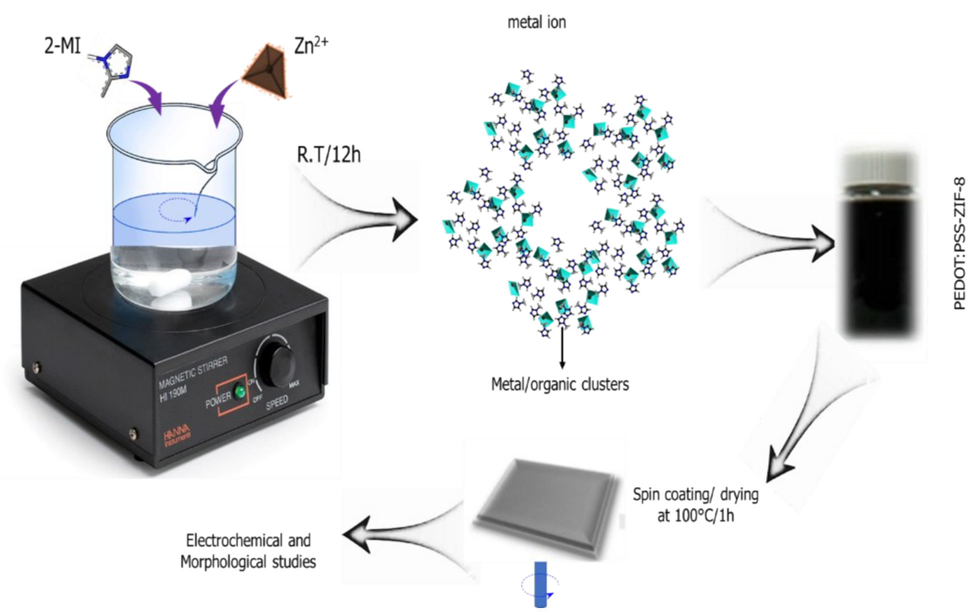
All used reagents and solvents were obtained from commercial sources. Both of PEDOT:PSS (1.3 wt % dispersed in H_2O), lithium iodide (LiI, 99%), Iodine (I_2, 99.8%), 4-*tert*-butylpyridine (4-tBP, $C_9H_{13}N$, 96%), titanium di-isopropoxide bis (acetylacetonate) (TAA) $[(CH_3)_2CHO]_2Ti(C_5H_7O_2)_2$, 75 wt. % in isopropanol], bis (*tri*-Fluor methane) sulfonamide lithium salt (LiTFSI), hex chloroplatinic acid hexahydrate ($H_2PtCl_6 \cdot 6H_2O$, 37.50% Pt basis), 2-methylimidazole (98.0%) and MK2 dye were purchased from Sigma-Aldrich, while Anhydrous acetonitrile (CH_3CN, 99.80%) , tert-butyl alcohol were from Alfa Aesar and Ru dye, cis-di (thiocyanato) bis (2, 2-bipyridyl-4, 4-dicarboxylate) ruthenium (II) (N719) from Dyesol. Titanium dioxide paste (average particle size: 18, 30 nm and 400 nm) and FTO conductive glass (2 mm thickness, square resistance 10–15 Ω sq^{-1}) from OPV Tech Co. Zn $(NO_3)_2.6H_2O$ (~99.99%), were obtained and ethylene glycol (EG) from Sinopharm Chemical Reagent Beijing Co., Ltd. All used reagents were of analytical purity and used as received. De-ionized (DI) water was obtained from an ultra-pure purifier (Ulu pure, China, resistivity ≥ 18.2 MΩ).

2 Fabrication of Mesoporous TiO_2 photoanode

The iodine electrolyte-based DSSCs were prepared as follows; TiO_2 photoanodes was prepared by using fluorine-doped SnO_2 (FTO) conducting glass substrates, FTO washed with a detergent solution, rinsed with deionized (DI) water and finally ethanol in an ultrasonic bath for 30 min. A thin blocking layer of TiO_2 was prepared on a clean FTO glass via spray pyrolysis of a 10% (v/v) solution of titanium isopropoxide bis-acetylacetonate in ethanol at 450°C. A commercial TiO_2 Paste (18 nm-sized) was printed onto the treated FTO-titanium isopropoxide to form the transparent layer (4×4 mm). The printing process was repeated for five times followed by annealing at 120 °C for 10 min. A scattering layer was printed on top of the transparent layer. The screen-printed TiO_2 films with 0.16 cm^2 active area were sintered at 500 °C for 30 min in programmable system followed by treated in 20 mM $TiCl_4$ (aq) bath at 70 °C for 30 min, after cooled to room temperature, the nanocrystalline TiO_2 electrode the electrode was washed with distilled water and ethanol and fired again at 500°C in air for 30 min. Once cooled, the electrodes were bathed into a 0.3 mM solution of N-719 dye in absolute ethanol for 18 h in dark at room temperature.

In case of cobalt electrolyte-based DSSCs, TiO_2 photoanode was fabricated also by the same technique in iodine DSSCs except for TiO_2 paste (20 nm) was used in transparent layer with little thickness, the obtained TiO_2 films were immersed on 0.3 mM MK-2 dye solution (1:1 acetonitrile and tert-butanol) and keep in dark at room temperature for about 5 h.

The symmetrical dummy cells for both iodine and cobalt electrolyte based DSSCs were prepared by two identical CEs, and the redox electrolytes are similar to that used in assembling complete DSSCs.



Scheme S1: Schematics for the prepare of ZIF-8/PEDOT: PSS CEs.

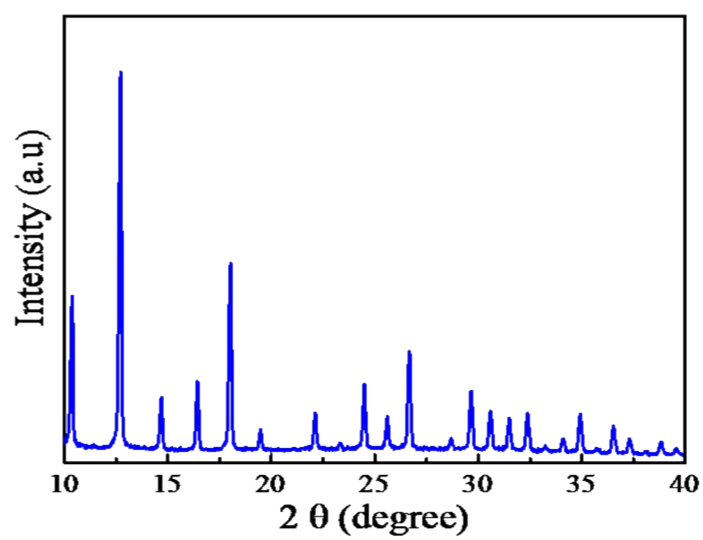


Fig. S1: XRD of the as prepared ZIF-8

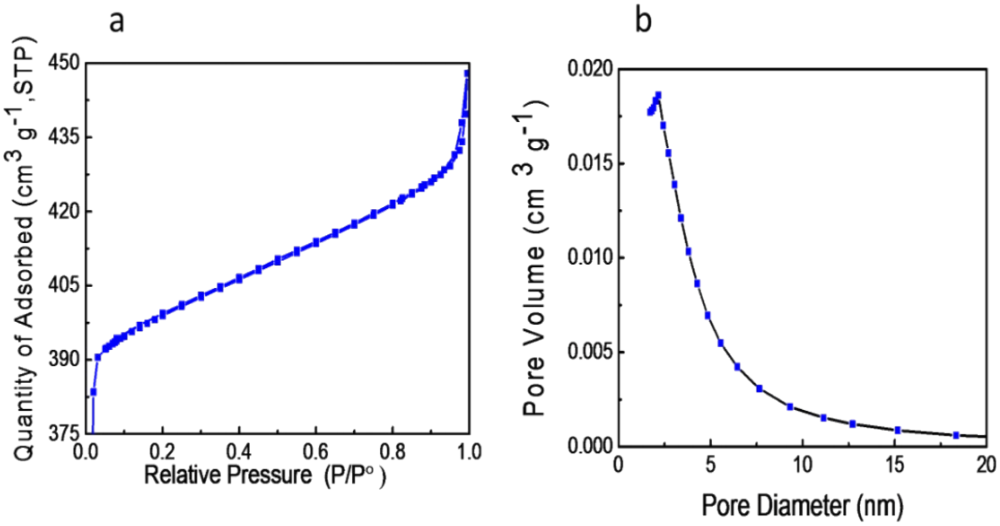


Fig. S2: (a) Nitrogen adsorption-desorption isotherms for ZIF-8 and (b) pore volume distribution.

Table S1. BET obtained parameters for ZIF-8.

BET surface area	BJH Desorption cumulative volume of pores	BJH Desorption average pore diameter (4V/A)
1592.27 $m^2 . g^{-1}$	0.11 $cm^3 . g^{-1}$	56.95 A°

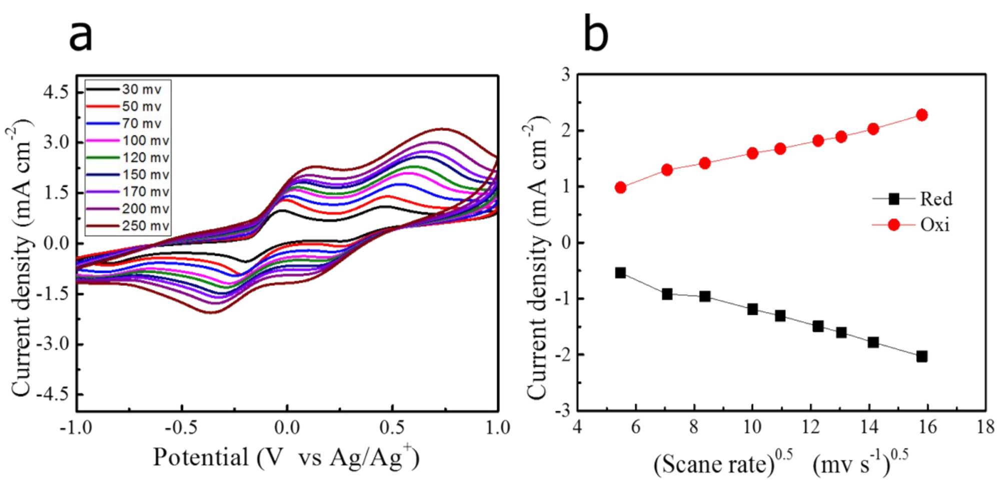


Fig. S3: (a) CV curves of (3%)ZIF-8/PEDOT: PSS CE at different scan rate and (b) the relationship between peak current density and the square root of scan rates of (3%) ZIF-8/PEDOT: PSS CE.

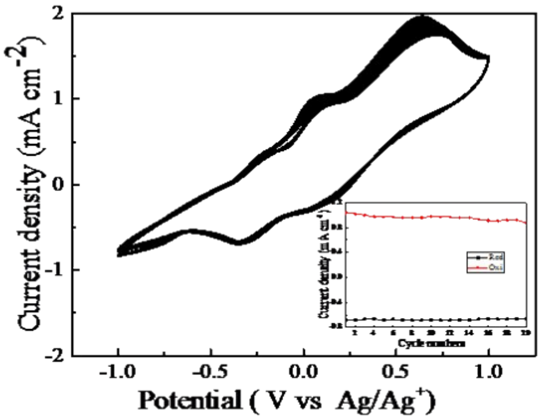


Fig.S4: 20 times consecutive CVs of the (3%) ZIF-8/ PEDOT: PSS complex CE with a scan rate of 50 mVs^{-1} in iodine-based electrolyte.

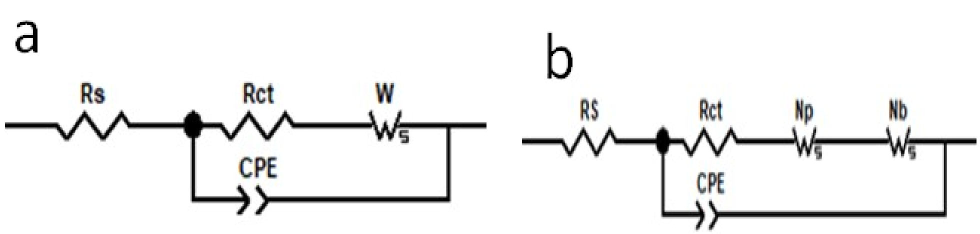


Fig. S5: (a) Equivalent circuit of Pt symmetric cell and (b) equivalent circuit of as prepared ZIF-8/ PEDOT: PSS based symmetric cells.

Table S2. Electrochemical parameters of symmetric dummy cells with iodine-based electrolyte

CEs	J_{PC} (mA m^{-2})	E_{pp} (mV)	$J_{ox}/\|J_{Red}\|$	Log J_o (mAcm^{-2})	R_{ct} Tafel	τ (μs)	D_n cm^{-2} s^{-1}
Pristine PEDOT: PSS	-0.55	611	1.55	0.53	3.71	37.92	3.69×10^{-6}
1% ZIF-8/ PEDOT: PSS	-0.67	504	1.54	0. 71	2.45	35.64	8.23×10^{-6}
3% ZIF-8/ PEDOT: PSS	-0.92	203	1.41	1.04	0.68	28.31	8.45×10^{-6}
5% ZIF-8/ PEDOT: PSS	-0.68	335	1.62	0.66	2.72	28.31	8.02×10^{-6}
Pt	-0.96	258	1.61	1.19	0.81	14.19	6.27×10^{-6}

with different CEs

Table S3. Photovoltaic performances of DSSCs with I^-/I_3^- redox couple electrolyte different CEs under AM1.5G illumination

CEs	DSSCs (number)	Voc mV	Jsc (mA/cm^2)	FF (%)	Eff (%)
Pt	Cell (1)	712	14.36	71.12	7.27
	Cell (2)	712	13.58	74.30	7.20
	Cell (3)	713	13.70	74.16	7.24
	Average	**712.3**	**13.88**	**73.19**	**7.24**
	SD (±)	0.00	0.42	01.79	0.03
PEDOT: PSS	Cell (1)	706	12.18	44.17	3.79
	Cell (2)	702	12.06	47.79	4.05
	Cell (3)	703	12.05	49.27	4.18
	Average	**704**	**12.10**	**47.08**	**4.00**
	SD (±)	0.002	0.07	2.622	0.19
(1%) ZIF-8/PEDOT: PSS	Cell (1)	756	12.17	50.72	4.67
	Cell (2)	753	12.14	51.84	4.74
	Cell (3)	751	12.13	52.88	4.82
	Average	**753**	**12.15**	**51.81**	**4.74**
	SD (±)	0.002	0.025	1.082	0.076
(3%) ZIF-8/PEDOT: PSS	Cell (1)	780	13.78	60.02	6.46
	Cell (2)	782	13.80	60.30	6.51
	Cell (3)	782	13.63	60.92	6.49
	Average	**781**	**13.74**	**60.40**	**6.49**
	SD (±)	0.000	0.094	0.462	0.025
(5%) ZIF-8/PEDOT: PSS	Cell (1)	734	13.30	57.20	5.61
	Cell (2)	733	13.14	59.63	5.74
	Cell (3)	730	13.15	60.33	5.79
	Average	**732**	**13.19**	**59.05**	**5.71**
	SD (±)	0.004	0.083	1.643	0.09

SD: standard deviation

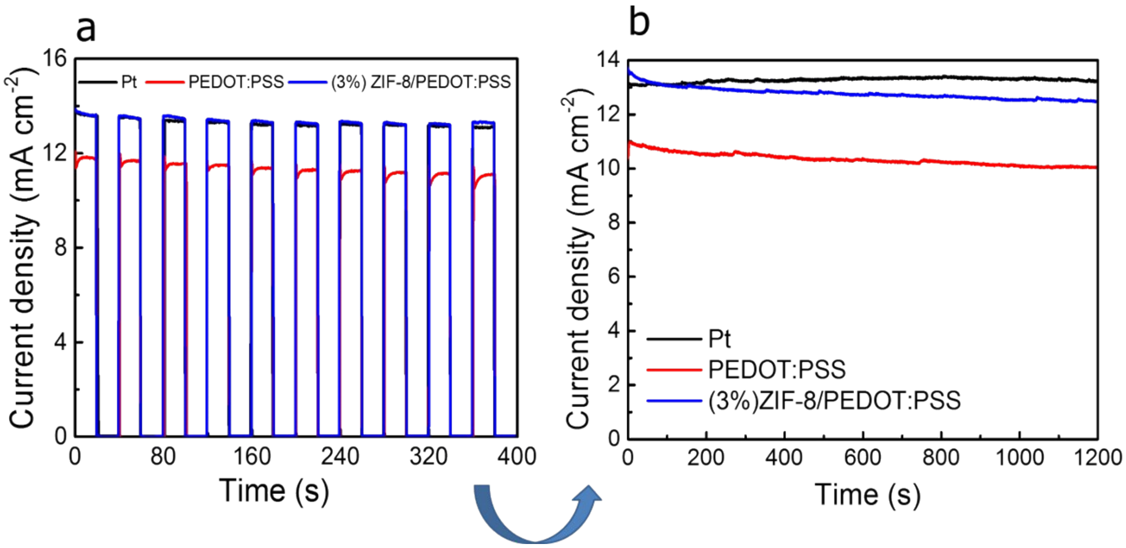


Fig. S6. Start-stop switches (a) of the DSSCs by alternately irradiating (100 mW.cm^{-2}) and darkening (0 mW.cm^{-2}) at an interval of 20 s and at 0 V, (b) the photocurrent stabilities of the DSSCs under continuous irradiation of 100 mW.cm^{-2}.

Cobalt electrolyte supplementary data

Table S4. Photovoltaic performances of DSSCs Co^{3+}/Co^{2+} electrolyte with different CEs under AM1.5G illumination.

CEs	DSSCs	Voc mV	Jsc (mA/cm^2)	FF (%)	Eff (%)
Pt	Cell (1)	823	13.09	72.03	7.76
	Cell (2)	818	12.8	69.9	7.32
	Cell (3)	806	12.86	73.3	7.60
	Average	**816**	**12.92**	**71.74**	**7.56**
	SD (±)	0.008	0.16	1.72	0.22
PEDOT: PSS	Cell (1)	855	10.14	65.57	5.69
	Cell (2)	853	10.30	65.80	5.78
	Cell (3)	850	10.43	65.73	5.83
	Average	**853**	**10.30**	**65.70**	**5.77**
	SD (±)	0.002	0.15	0.17	0.07
(1%) ZIF-8/PEDOT: PSS	Cell (1)	852	11.36	70.03	6.78
	Cell (2)	853	11.66	69.57	6.92
	Cell (3)	853	11.36	70.41	6.81
	Average	**852**	**11.46**	**70.00**	**6.84**
	SD (±)	0.000	0.17	0.42	0.07
(3%) ZIF-8/PEDOT: PSS	Cell (1)	859	9.54	66.78	5.48
	Cell (2)	856	8.49	64.86	4.72
	Cell (3)	858	8.53	65.48	4.79
	Average	**858**	**8.85**	**65.71**	**5.00**
	SD (±)	0.000	0.59	0.98	0.42
(5%) ZIF-8/PEDOT: PSS	Cell (1)	855	8.43	68.75	4.95
	Cell (2)	856	8.56	69.18	5.07
	Cell (3)	856	8.56	69.18	5.07
	Average	**856**	**8.52**	**69.04**	**5.03**
	SD (±)	0.000	0.08	0.25	0.07

Table S5. Electrochemical parameters of symmetric dummy cells with cobalt based electrolyte with different CEs

CEs	J_{PC} (mA m^{-2})	E_{pp} (mV)	$J_{ox}/\|J_{Red}\|$	Log J_o (mAcm-2)	R_s (Ω)	R_{ct} (Ω)	τ (µs)
Pt	-0.26	175	1.29	0.35	8.52	4.72	31.78
PEDOT: PSS	-0.22	238	1.75	0. 69	12.99	28.18	23.55
(1%) ZIF-8/PEDOT: PSS	-0.47	176	1.27	1.04	12.01	11.55	2.70
(3%) ZIF-8/PEDOT: PSS	-0.43	189	1.20	0.66	13.69	12.34	3.03
(5%) ZIF-8/PEDOT: PSS	-0.38	250	1.28	1.19	14.57	21.96	3.65

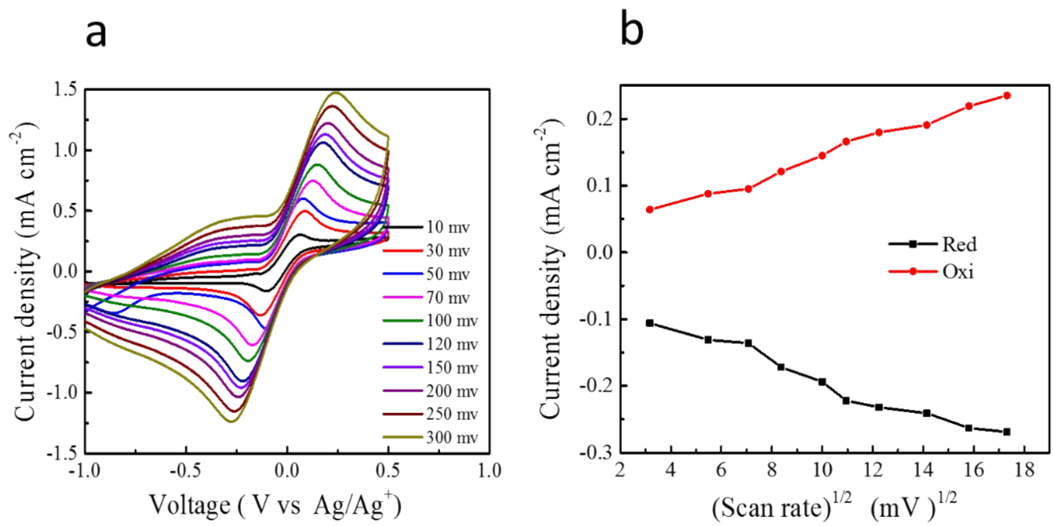


Fig. S7: 20 times consecutive CVs of the (1%) ZIF-8/ PEDOT: PSS complex CE with a scan rate of 50 mVs^{-1} in cobalt-based electrolyte.

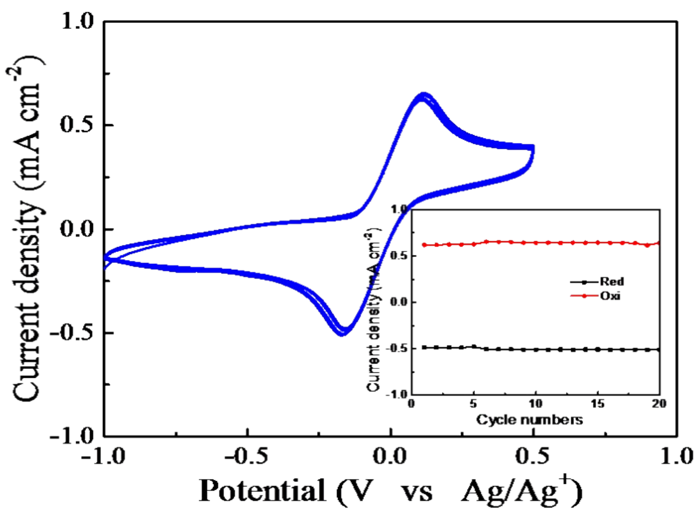


Fig. S8 A 20 consecutive CVs of the (1%) ZIF-8/ PEDOT: PSS complex CE with a scan rate of 50 mV s^{-1} in cobalt-based electrolyte.

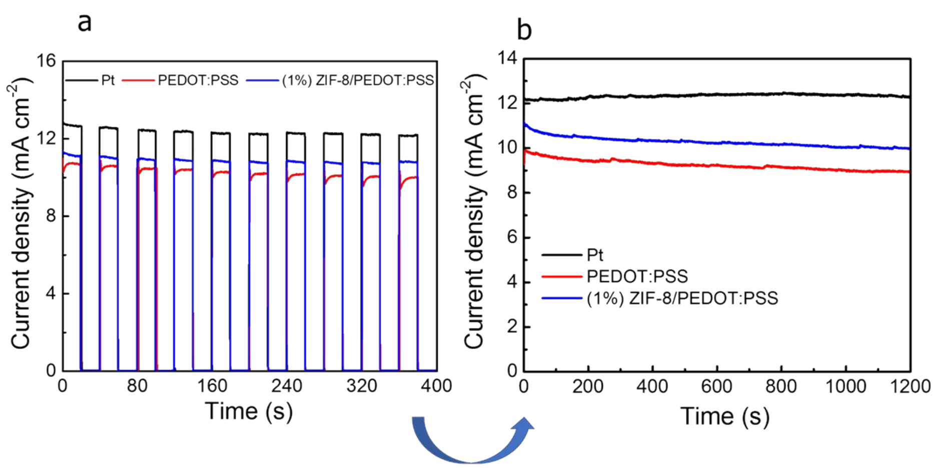


Fig. S9 Start-stop switches (a) of the DSSCs by alternately irradiating (100 $mW.cm^{-2}$) and darkening (0 $mW.cm^{-2}$) at an interval of 20 s and at 0 V, (b) the photocurrent stabilities of the DSSCs under continuous irradiation of 100 $mW.cm^{-2}$.