## **Electronic Supplementary Information (ESI)**

# Tailoring the porosity of MOF-derived N-doped carbon electrocatalysts for highly efficient solar energy conversion

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	Areal Ratio (%)		
	С–С	С-О	С=0
ZIF-8-C	79.12	11.37	9.51
ZIF-8-dopa-C	76.24	11.32	12.44
		Areal Ratio (%)	
	Pyridinic N	Areal Ratio (%) Pyrrolic N	Graphitic N
ZIF-8-C	<b>Pyridinic N</b> 47.73	Areal Ratio (%) Pyrrolic N 38.21	<b>Graphitic N</b> 14.06

**Table S1.** Summary of fitting results for XPS (a) carbon 1s and (b) nitrogen 1 s spectra of ZIF-8-C and ZIF-8-dopa-C.

(a) Carbon 1s

Temperature	$R_{\rm s}$ ( $\Omega \ {\rm cm}^2$ )	$R_{ m ct}$ ( $\Omega \  m cm^2$ )	$R_{ m dif}$ ( $\Omega \  m cm^2$ )
283 K	5.961	2.479	1.076
293 K	5.924	1.672	0.9594
303 K	5.861	1.153	0.8575
313 K	5.830	0.8061	0.7811
323 K	5.776	0.5361	0.7301

**Table S2.** Summary of fitting results for EIS spectra of the symmetric cells employing (a)platinum, (b) ZIF-8-C, and (c) ZIF-8-dopa-C electrodes.

### (a) Platinum

#### (b) ZIF-8-C

Temnerature	R <sub>s</sub>	R <sub>ct</sub>	$R_{ m dif}$
Temperature	$(\Omega \ \mathrm{cm}^2)$	$(\Omega \text{ cm}^2)$	$(\Omega \ \mathrm{cm}^2)$
283 K	7.432	70.60	10.75
293 K	7.119	43.77	9.303
303 K	6.503	28.75	7.647
313 K	6.562	19.95	5.898
323 K	6.511	12.66	4.964

#### (c) ZIF-8-dopa-C

Temperature	R <sub>s</sub> (Ω cm <sup>2</sup> )	$R_{ m ct}$ ( $\Omega  m cm^2$ )	$R_{ m dif}$ ( $\Omega \  m cm^2$ )
283 K	4.326	2.252	1.475
293 K	4.258	1.441	1.367
303 K	4.340	0.9747	1.276
313 K	4.218	0.6978	1.186
323 K	4.107	0.4857	1.113

Counter Electrode Material	Fill Factor (%)	Efficiency (%)	Reference
Carbon Black	68.5	9.10	(1)
Carbon Black	65.6	7.20	(2)
Carbon Black	71.3	8.35	(3)
Carbon Black + Graphite	71.2	6.67	(4)
Carbon Nanofiber	70	7.00	(5)
Single-Walled Carbon Nanotube	74	7.81	(6)
Single-Walled Carbon Nanotube	58.7	8.31	(7)
Multi-Walled Carbon Nanotube	64	7.67	(8)
Multi-Walled Carbon Nanotube	71	7.63	(6)
Reduced Graphene Oxide	72	7.19	(9)
N- and P-doped Graphene	72	8.57	(10)
Graphite Nanoball	67	7.88	(11)
Ordered Mesoporous Carbon	65	7.50	(12)
Carbonized ZIF-8	68	7.32	(13)
ZIF-8-dopa-C	72.8	9.03	our work

**Table S3.** Fill factors and power conversion efficiencies of DSCs employing carbon-based CEs reported in previous publications and from our experiment. The comparison on the performances is limited to the N719 dye- and  $I_3^{-}/I^{-}$  redox electrolyte-based cells for proper evaluations.

	V <sub>oc</sub> (V)	J <sub>sc</sub> (mA/cm <sup>2</sup> )	FF (%)	η (%)
Platinum	0.807	12.76	68.7	7.07
ZIF-8-C	0.701	12.01	57.5	4.84
ZIF-8-dopa-C	0.749	12.17	67.2	6.12

**Table S4.** Summary of J-V characteristics for DSCs employing  $[Co(bpy)_3]^{3+/2+}$  redox electrolyte and platinum, ZIF-8-C, and ZIF-8-dopa-C CEs.



Fig. S1. (a-d) TEM images of ZIF-8-C obtained at diverse magnifications.



Fig. S2. (a-d) TEM images of ZIF-8-dopa-C obtained at diverse magnifications.



Fig. S3. TGA curve of polydopamine shell prepared by removal of ZIF-8 from ZIF-8-dopa.



**Fig. S4.** (a) XPS C 1s spectra of ZIF-8-C and ZIF-8-dopa-C and (b,c) their fitted results; (b) ZIF-8-C and (c) ZIF-8-dopa-C.



Fig. S5. XPS N 1s spectra of (a) ZIF-8-C and (b) ZIF-8-dopa-C and their fitted results.



**Fig. S6.** Peak current densities vs. (scan rate)<sup>1/2</sup> plots of Pt, ZIF-8-C, and ZIF-8-dopa-C obtained from the  $I_3^{-}/I^{-}$  peak of the CV data measured at various scan rates (30, 60, 90, 120, 150 mV/s).



Fig. S7. Equivalent circuit for EIS analyses of symmetric cells.



**Fig. S8.** Enlarged Nyquist plots of the symmetric cells employing (a) Pt, (b) ZIF-8-C, and (c) ZIF-8-dopa-C CEs near the high-frequency region.



**Fig. S9.** CV diagrams showing the specific capacitance vs. potential plots for (a) ZIF-8-C and (b) ZIF-8-dopa-C measured at diverse scan rates using 1.0 M NaCl electrolyte.



**Fig. S10.** CV diagrams showing the specific capacitance vs. potential plots for (a) ZIF-8-C and (b) ZIF-8-dopa-C measured at diverse scan rates using 1.0 M NaClO<sub>4</sub> electrolyte.



Fig. S11. Raman spectra of (a) ZIF-8-C and (b) ZIF-8-dopa-C.



**Fig. S12.** *J*–*V* curves of DSCs employing  $[Co(bpy)_3]^{3+/2+}$  redox electrolyte and platinum, ZIF-8-C, and ZIF-8-dopa-C CEs measured under standard 1 sun illumination (AM 1.5G condition).

#### Notes and references

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