Supporting Information

A new class of epitaxial porphyrin metal-organic framework thin films with extremely high photocarrier generation efficiency: promising materials for all-solid-state solar cell

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Figure S1. ¹H NMR spectrum of **2** at 25 °C in CDCl₃. Peaks marked with * are due to residual CHCl₃.



Figure S2. ¹H NMR spectrum of **3** at 25 °C in $CDCl_3$ /pyridine- d_5 . Peaks marked with * are due to residual CHCl₃.



Figure S3. ¹H NMR spectrum of **5** at 25 °C in CDCl₃. Peaks marked with * are due to residual CHCl₃.



Figure S4. ¹H NMR spectrum of **6** at 25 °C in $CDCl_3$ /pyridine- d_5 . Peaks marked with * are due to residual CHCl₃.



Figure S5. Out of plane XRD data of (a) Zn(II)porphyrin Zn-SURMOF 2 and (b) DPA-Zn(II)porphyrin Zn-SURMOF 2 grown on FTO glass (in blue), quartz glass (in red) and MUD SAM/Au substrates (in black) prepared by liquid-phase epitaxy process.

The peak intensity ration of (001) and (002) for the porphyrin SURMOF 2 grown on MUD SAM/Au is different from those fabricated on quartz glass and FTO glass due to the smoother surface of MUD SAM/Au than that of quartz glass and FTO glass.



Figure S6. Comparison of in plane, out of plane and simulated XRD data of Zn(II)porphyrin Zn-SURMOF 2 fabricated onto Si substrate by liquid-phase epitaxy process.

The XRD patterns of Zn(II)porphyrin Zn-SURMOF 2 in Figure S6 and DPA-Zn(II)porphyrin Zn-SURMOF 2 in Figure S7 are in excellent agreement with the simulated XRD patterns, suggesting the presence of a SURMOF-2 structure, which was reported in our previous work (J. X. Liu, et al., *Sci. Rep.*, 2012, **2**, 1-5.) with P4-geometry, i.e. $a=b\neq c$. The out-of-plane and in-plane XRD measure the order of the MOF thin materials in the direction perpendicular and parallel to the substrate, respectively, which gives the lattice parameters a and b, therefore (100) and (001) have the same 20 position in PXRD of in-plane and out-of plane.



Figure S7. Comparison of in plane, out of plane and simulated XRD data of DPA-Zn(II)porphyrin Zn-SURMOF 2 fabricated onto Si substrate by liquid-phase epitaxy process.



Figure S8. Simulated structure of Zn(II)porphyrin Zn-SURMOF 2 with lattice parameters a=b=2.347 nm, c=6.5 Å.



Figure S9. Infrared spectra of bulk Zn(II)porphyrin (in black) and Zn(II)porphyrin Zn-SURMOF 2 thin film grown on MUD/Au substrate (in red). The detailed band assignments are listed in Table S1.



Figure S10. Infrared spectra of bulk DPA-Zn(II)porphyrin (in black) and DPA-Zn(II)porphyrin Zn-SURMOF 2 thin film grown on MUD/Au substrate (in red). The detailed band assignments are listed in Table S2.



Figure S11. Steady-state emission spectra of Zn(II)porphyrin Zn-SURMOF 2 grown on FTO substates with (in red) and without (in black) top PEDOT:PSS layer. The samples were excited at wavelength of 390 nm.



Figure S12. Steady-state emission spectra of DPA-Zn(II)porphyrin Zn-SURMOF 2 grown on FTO substates with (in red) and without (in black) top PEDOT:PSS layer. The samples were excited at wavelength of 390 nm.



Figure S13. Transient absorption spectra averaged at 0–0.2 μ s of (a) Zn(II)porphyrin Zn-SURMOF 2 and (b) Zn(II)porphyrin Zn-SURMOF 2 grown on a quartz glass. The photon density of 355-nm excitation laser was 4.6 × 10¹⁵ photons pulse⁻¹ cm⁻². Two-dimensional transient absorption spectral data recorded for (c) Zn(II)porphyrin Zn-SURMOF 2 and (d) Zn(II)porphyrin Zn-SURMOF 2 grown on a quartz glass.



Figure S14. Two-dimensional transient absorption spectral data recorded for compound **2** in toluene (a)(d) under air, (b)(e) with Ar bubbling before measurements, and (c)(f) with O₂ bubbling before measurements. (a)–(c) and (d)–(f) were different in the monitoring wavelength ranges. Transient absorption spectra averaged at (g) 0–0.5 and (h) 1–1.5 μ s, respectively, recorded for compound **2** in toluene under air (black), with Ar bubbling before measurements (red), and with O₂ bubbling before measurements (blue). The photon density of 355-nm excitation laser was 4.6 × 10¹⁵ photons pulse⁻¹ cm⁻². The effect of O₂ on quenching of the transient species indicated that the triplet state was observed. We can recognize from these data that the triplet state has no typical absorption over 550 nm.



Figure S15. (a) Normalized FP-TRMC (black) and transient absorption profiles at 540 nm (green) and 570 nm (blue) of Zn(II)porphyrin Zn-SURMOF 2 grown on a quartz glass. (b) Normalized FP-TRMC (red) and transient absorption profiles at 595 nm (green) and 630 nm (blue) of DPA-Zn(II)porphyrin Zn-SURMOF 2 grown on a quartz glass. The difference of the kinetics in (b) is most likely due to the fundamental absorption over a broad wavelength range. The contribution of the triplet state of DPA-Zn(II)porphyrin to the transient absorption was found to be small, considering the experimental data shown in Figure S16.



Figure S16. Calculated band structure and Total density of states (DOS) of Zn(II)porphyrin Zn-SURMOF 2. The band gap E_g of Zn(II)porphyrin Zn-SURMOF 2 is 1.93 eV.



Figure S17. The band structures and total density of states (DOS) of DPA-Zn(II)porphyrin Zn-SURMOF 2 (upper) and DPA-Zn(II)porphyrin Zn-SURMOF 2 (bottom), respectively. The band gap E_g of Zn(II)porphyrin Zn-SURMOF 2 is 1.48 eV



Figure S18. SEM cross-section images of Zn(II)porphyrin Zn-SURMOF with top PEDOT:PSS thin film electrodes.



Figure S19. UV-Vis spectra of Zn(II)porphyrin Zn-SURMOF 2 grown on FTO substates with (in red) and without (in black) top PEDOT:PSS layer.



Figure S20. UV-Vis spectra of DPA-Zn(II)porphyrin Zn-SURMOF 2 grown on FTO substrates with (in red) and without (in black) top PEDOT:PSS layer.



Figure S21. The energy-level diagram of Zn(II)porphyrin and DPA-Zn(II)porphyrin Zn-SURMOF 2 based photovoltaic devices. The band gaps of Zn(II)porphyrin and DPA-Zn(II)porphyrin Zn-SURMOF 2 are calculated from the lower-limits optical band gaps.



Figure S22. Out of plane XRD data of (a) Zn(II)porphyrin Zn-SURMOF 2 and (b) DPA-Zn(II)porphyrin Zn-SURMOF 2 grown on FTO substrates. Pristine samples are in black, samples exposured in air for about two weeks are in red and samples after photovoltaic test are in blue.

The XRD data of the fabricated two dimensional porphyrin-based metal-organic framework thin films on FTO substrate have virtually no change after exposure in atmosphere conditions for about two weeks and photovoltaic test.



Figure S23. Photocurrent response of DPA-Zn(II)porphyrin Zn-SURMOF 2 (in blue), Zn(II)porphyrin Zn-SURMOF 2 (in red) and bare FTO substrate (in black) under illumination at 530 nm.



Figure S24. N1s XPS data of Zn(II)porphyrin (down) and DPA-Zn(II)porphyrin linkers. The peaks at 397.3 eV and 397.0 eV are attributed to the =N- of the Zn(II)metalloporphyrin unit, the peak at 399.0 eV is assigned to =N- of diphenylamine (DPA) groups.

Tables

Table S	51 . Vibrat	ional frequ	uencies of	Zn(II)porphyrin	as obtained	d spectra	from bulk	c and
MOF th	າin films ຼ	grown on N	MUD/Au s	ubstrate togethe	r with the a	ssignmen	ts.	

Band no.	Wavenumber (cm ⁻¹)		Assignment
	SURMOF	bulk	
1		1682	v C=O in free COOH
2	1592	1601	$v_{as} COO^{-}$; CC (aromatic ring)
3	1546	1558	COO-
4	1403	1416	$v_{s} COO^{-}$; Phenyl
5	1337	1337	def Porphyrin
6	1071		δ CH _{Porphyrin}
8	1000	990	i.p. Ph

Table S2. Vibrational frequencies of DPA-Zn(II)porphyrin as obtained spectra from bulk andMOF thin films grown on MUD/Au substrate together with the assignments.

Band no.	Wavenumber (cm ⁻¹)		Assignment		
	SURMOF	bulk			
1		1685	v C=O in free COOH		
2	1590	1599	$v_{as} \text{ COO}^{-}$; CC (aromatic ring)		
3	1546	1558	COO-		
4	1491	1487	Pyrrolic		
4	1403	1416	$v_{\rm s}$ COO ⁻ ; Phenyl		
5	1340	1340	def Porphyrin		
8	1000	996	i.p. Ph		

Explanation of band assignments:

v: stretching mode

 v_{sym} : symmetric stretching mode

 ν_{as} : asymmetric stretching mode

Table S3. Calculated effective electron and hole masses $(m_e^* \text{ and } m_h^*)$ in the unit of electron rest mass (m_0) for Zn(II)porphyrin Zn-SURMOF 2 and DPA-Zn(II)porphyrin Zn-SURMOF 2 with different directions.

	n	$n_{e}^{*}(m_{0})$	$m_{h}^{*}(m_{0})$		
Direction	Zn(II)porphyrin	DPA-Zn(II)porphyrin	Zn(II)porphyrin	DPA-Zn(II)porphyrin	
	Zn-SURMOF 2	Zn-SURMOF 2	Zn-SURMOF 2	Zn-SURMOF 2	
[100]//	3.19	2.21	1.99	0.63	
[010]//	3.19	2.13	1.99	0.86	
[001]⊥	43.7	26.85	35.07	27.39	

//: layers parallel to the substrate;

 \perp : layers perpendicular to the substrate.

Table S4. Lattice constants and volumes of Zn(II)porphyrin Zn-SURMOF 2 and DPA-Zn(II)porphyrin Zn-SURMOF 2 calculated by PBE-D3 scheme.

	a (Å)	<i>b</i> (Å)	<i>c</i> (Å)	$V(Å^3)$
Zn(II)porphyrin Zn-SURMOF 2	23.51	23.51	6.5	3596.71
DPA-Zn(II)porphyrin Zn-SURMOF 2	23.47	23.47	10.34	5700.96