Supporting information for

2D Porphyrin Covalent Organic Frameworks with Tunable Catalytic Active Sites for Oxygen Reduction Reaction

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1. Supplementary materials

1.1 Materials

5,10,15,20-tetrakis(para-aminophenyl)porphyrin (TAPP) was purchased from Jilin Chinese Academy of Sciences Yanshen Technology Co., Ltd. $Pd(PPh_3)_4$, $CoCl_2·6H_2O$, $NiCl_2·6H_2O$, $Mn(OAc)_2$ and anhydrous THF were purchased from Energy Chemical. All the chemicals and solvents involved in this work were utilized with no further purification.

1.2 Instruments

The powder X-ray diffraction (PXRD) characterization was performed on D8 ADVANCE with Cu Kα radiation (λ = 1.5405 Å) with a 2θ range from 2° to 30° at room temperature. Fourier transform infrared (FT-IR) Spectra were recorded on

Bruker ALPHA FT-IR Spectrometer ranging from 500 to 4000 cm^{-1}. ^{1}H NMR spectra were acquired on Bruker Avance 400 MHz NMR spectrometers. Solid-state ^{13}C NMR spectrum was exploited on a Bruker Avance III 400 MHz instrument. Thermogravimetric analysis (TGA) was collected on TGA/SDTA851e in N_2 atmosphere at 10 °C min^{-1} from 30 °C to 1000 °C. Scanning electron microscopy (SEM) images were recorded on a SUB010 instrument. Transmission electron microscopy (TEM) analysis was conducted on Hitachi HT7700 electron microscope. The Brunauer-Emmett-Teller (BET) surface areas were tested on an ASAP 2020/TriStar 3000 (Micromeritics) at 77 K. Ultraviolet-visible (UV-Vis) spectra were performed on a Hitachi U-4100 spectrophotometer. X-ray photoelectron spectroscopy (XPS) spectra were obtained from PHI Versa probe II.

2. Supplementary experimental section

2.1 The synthesis of M-TAPP

TAPP (500 mg), $CoCl_2·6H_2O$ (1g), 60 mL of DMF, 30 mL of MeOH and 180 mL of $CHCl_3$ were added into a 500 mL flask. The reaction system was refluxed under N_2 for 24 h. The dark purple precipitation was filtered and washed with water and EtOH and dried under vacuum with the yield about 88%.

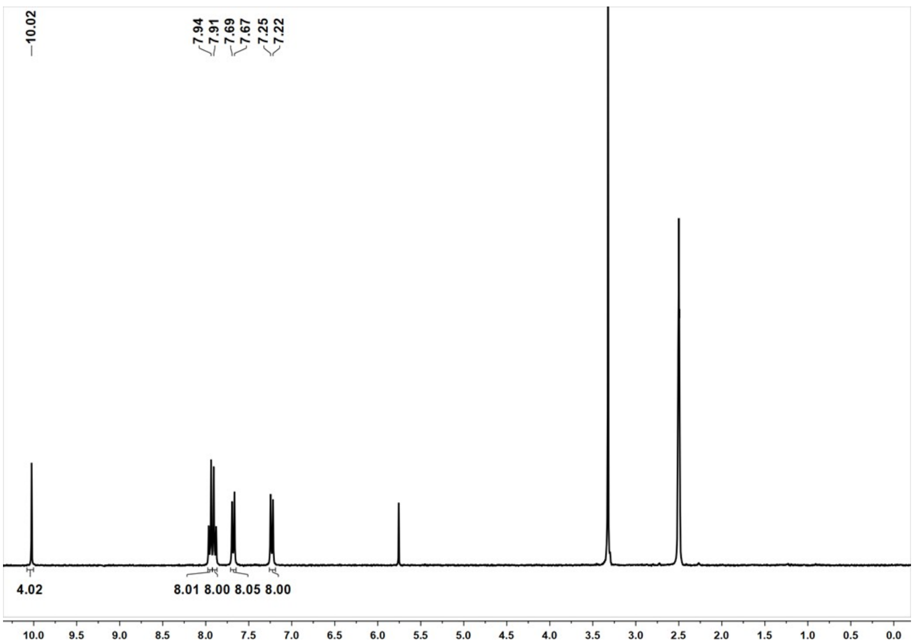
TAPP (500 mg), $NiCl_2·6H_2O$ (1g), 60 mL of DMF, 30 mL of MeOH and 180 mL of $CHCl_3$ were added into a 500 mL flask. The reaction system was refluxed under N_2 for 24 h. The dark pink precipitation was filtered and washed with water and dried under vacuum with the yield about 85%.

TAPP (500 mg), $Mn(OAc)_2$ (1g), 60 mL of DMF, 30 mL of MeOH and 180 mL of

$CHCl_3$ were added into a 500 mL flask. The reaction system was refluxed for 48 h. The dark green precipitation was filtered and washed with water and dried under vacuum with the yield about 83%.

2.2 The synthesis of 1,1,2,2-tetrakis(4-formyl-(1,1´-biphenyl))ethane (TPTE)

TPTE was synthesized according to the reported literature[1] and obtained a yellowish green solid with the yield about 70%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.02 (s, 4H), 7.94 (d, J = 8.3 Hz, 8H), 7.91 (d, J = 8.2 Hz, 8H), 7.68 (d, J = 8.2 Hz, 8H), 7.23 (d, J = 8.3 Hz, 8H).



2.3 The synthesis of M-TP-COFs

TAPP (0.02 mmol, 13.50 mg), PTPE (0.02 mmol, 14.98 mg), 0.5 mL of *o*-DCB, 0.5 mL of *n*-BuOH were added into a 10 mL glass tube and sonicated for 5 min to get well dispersed. After added 0.1 mL of HAC (6M), the tube was then put into the liquid N_2 and degassed for freeze-pump-thaw cycles. The glass tube was sealed and put into the oven, heated at 120 °C for 3 days. The mixture was filtered and washed for 6 times with THF and water. The purple precipitate was then suffered from a Soxhlet extraction with THF for 3 days and dried under vacuum. H-TP-COF with a yield about 90% was obtained.

Co-TAPP (0.02 mmol, 14.62 mg), PTPE (0.02 mmol, 14.98 mg), 0.5 mL of *o*-DCB, 0.5 mL of dioxane were added into a 10 mL glass tube and sonicated for 5 min to get well dispersed. After added 0.1 mL of HAC (6M), the tube was then put into the liquid N_2 and degassed for freeze-pump-thaw cycles. The glass tube was sealed and put into the oven, heated at 120 °C for 3 days. The mixture was filtered and washed for 6 times with THF and water. The dark purple precipitate was then suffered from a Soxhlet extraction with THF for 3 days and dried under vacuum. Co-TP-COF with a yield about 88% was obtained.

Ni-TAPP (0.02 mmol, 14.65 mg), PTPE (0.02 mmol, 14.98 mg), 0.5 mL of *o*-DCB, 0.5 mL of *n*-BuOH were added into a 10 mL glass tube and sonicated for 5 min to get well dispersed. After added 0.1 mL of HAC (6M), the tube was then put into the liquid N_2 and degassed for freeze-pump-thaw cycles. The glass tube was sealed and put into the oven, heated at 120 °C for 3 days. The mixture was filtered and washed for 6 times with THF and water. The dark pink precipitate was then suffered from a Soxhlet extraction with THF for 3 days and dried under vacuum. Ni-TP-COF with a yield about 85% was obtained.

Mn-TAPP (0.02 mmol, 14.63 mg), PTPE (0.02 mmol, 14.98 mg), 0.2 mL of *o*-DCB, 0.8 mL of *n*-BuOH were added into a 10 mL glass tube and sonicated for 5 min to get well dispersed. After added 0.1 mL of HAC (6M), the tube was then put into the liquid N_2 and degassed for freeze-pump-thaw cycles. The glass tube was sealed and put into the oven, heated at 120 °C for 3 days. The mixture was filtered and washed for 6 times with THF and water. The dark green precipitate was then suffered from a Soxhlet extraction with THF for 3 days and dried under vacuum. Mn-TP-COF with a yield about 86% was obtained.

2.4 Electrochemical measurements

Preparation of ink and working electrode: 3 mg of M-TP-COFs and 7 mg of acetylene black were dispersed in 1.25 mL of ethanol and sonicated for 30 minutes to get a well dispersed black ink. Then 36 μL of ink was loaded on the pre-polished rotating ring disk electrode (RDE, diameter 4 mm) as the working electrode. Finally, a layer of Nafion solution (0.5 wt%) was covered on the RDE and the working electrode was dried at room temperature. A commercial Pt/C catalyst (20 wt%) was prepared under the same conditions as a comparative sample.

Electrochemical test: 0.1 M KOH aqueous solutions were utilized as electrolyte. All electrochemical were tested on electrochemical workstation (Chenhua, China, CHI 760E) and RRDE-3A (ALS, Japan) devices were exploited to measure ORR performance. The Ag/AgCl (KCl-saturated) electrode was used as the reference electrode and the graphite rod electrode was used as the counter electrode. The cyclic voltammetry (CV) was performed at the scan rate of 50 mV s^{-1} and the linear scan voltammetry (LSV) was measured at the scan rate of 50 mV s^{-1}. Before the ORR test, the electrolyte was saturated with oxygen for 30 minutes. LSV test was done in N_2 saturated and O_2 saturated electrolyte, respectively. The platinum ring potential of the

RRDE was fixed at 0.7 V and RRDE measurements were performed at a rotation speed of 1600 rpm. The electric double layer capacitance was carried out with the scanning rate at 50, 80, 100, 150 and 200 mV s^{-1}.

The electron transfer number n and H_2O_2 yield was calculated by the following equations:

$$n = 4 * \frac{I_D}{I_D + I_R/N}$$

$$H_2O_2 = 200*\frac{I_R/N}{I_D + I_R/N} \quad (N = 42.4\%)$$

Herein, I_R and I_D are ring and disk current, respectively. N is the collection efficiency of ring electrode and measured to be 42.4%.

2.5 The density functional theory calculation of the ORR catalytic process

All DFT calculations were performed on the basis of ωB97XD[2]/BSI level by Gaussian 09 D.01 software package. The BSI denotes a mixed basis set, which uses 6-311G(D)[3] basis set for non-metal atoms, and LANL2TZ[4] basis set for the metal atoms. Geometry optimizations were performed until the total energy converged to within 1×10^{-6} Ha, and the forces on all atoms were less than 0.0017 a.u.. The single point energy (E) of the optimized structure was taken into calculating the adsorption energy. The ORR mechanism was investigated according to *Noskov* model. Each step energy was calculated by the following equations:

$* + O_2 = *O_2$

$*O_2 + H^+ + e^- = *OOH$

$*OOH + H^+ + e^- = *O + H_2O$

$*O + H^+ + e^- = *OH$

$*OH + e^- = * + OH^-$

where * denotes the M-TP-COF catalyst. The adsorption energy (E_{ad}) of the adsorbates O_2 with M-TP-COFs were calculated according to the following equation: $E_{ad} = E_{por+lig} - E_{por} - E_{lig}$, where $E_{por+lig}$ is the energy of the optimized binding complex, and E_{por} and E_{lig} refer to the energy of the M-TP-COF substrate and the adsorbate, respectively.

3. Supplementary figures and tables

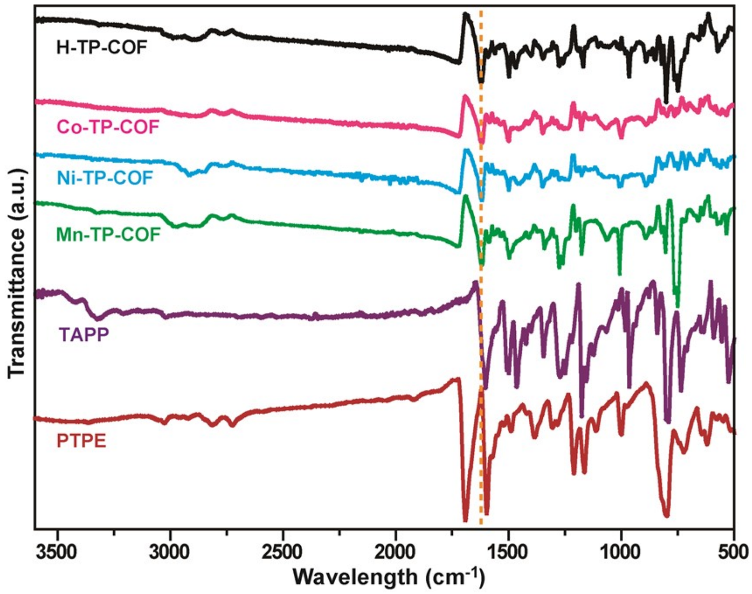


Fig. S1 FT-IR spectra of H-TP-COF (black line), Co-TP-COF (pink line), Ni-TP-COF (blue line), Mn-TP-COF (green line), TAPP (purple line) and PTPE (red line).

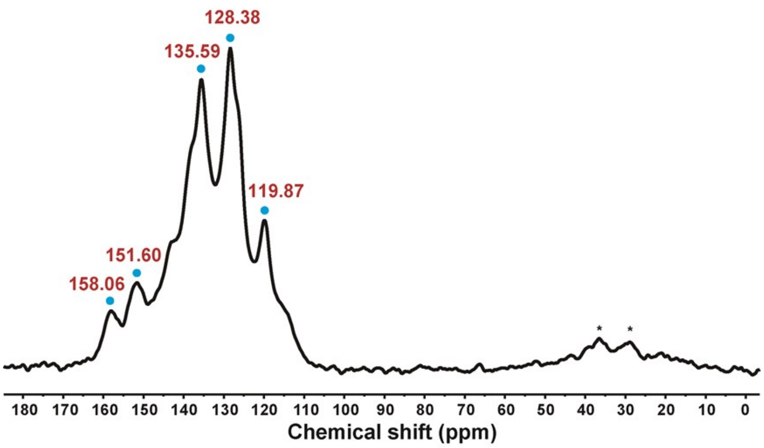


Fig. S2 The solid-state ^{13}C NMR spectrum of H-TP-COF.

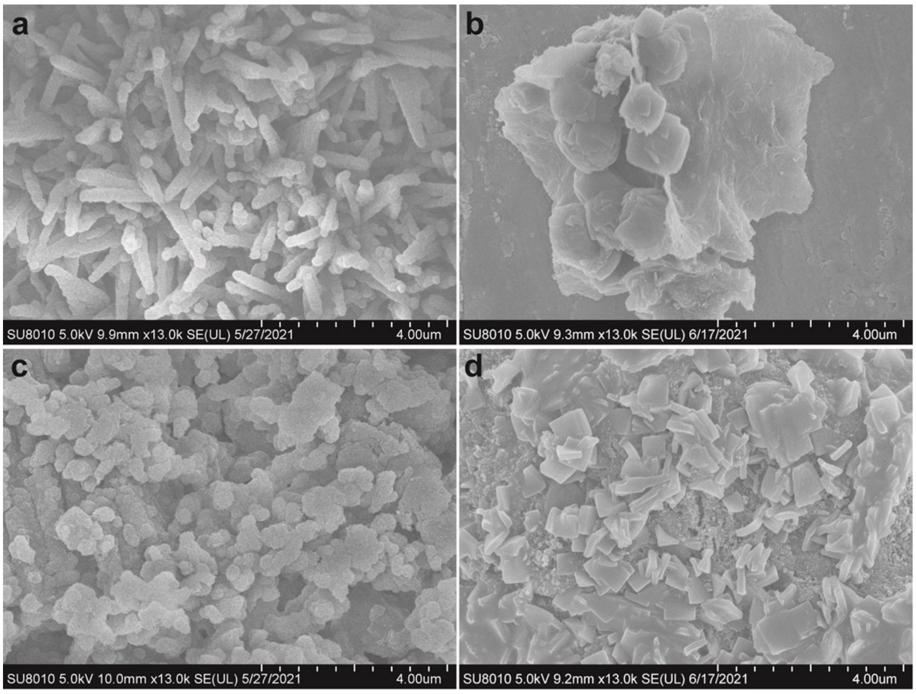


Fig. S3 SEM images of (a) H-TP-COF, (b) Co-TP-COF, (c) Ni-TP-COF and (d) Mn-TP-COF.

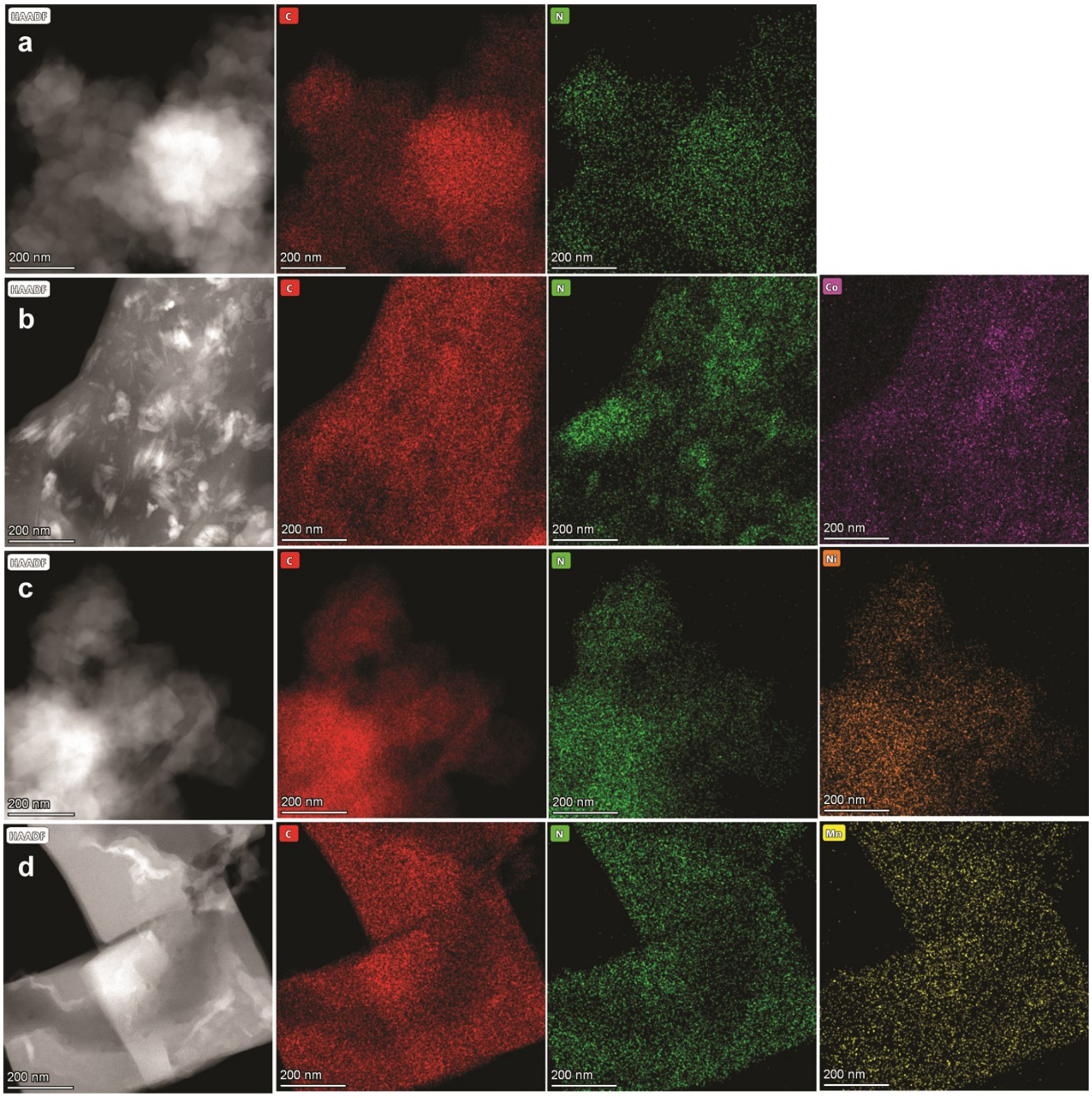


Fig. S4 HRTEM images and corresponding elemental mapping images of (a) H-TP-COF, (b) Co-TP-COF, (c) Ni-TP-COF and (d) Mn-TP-COF.

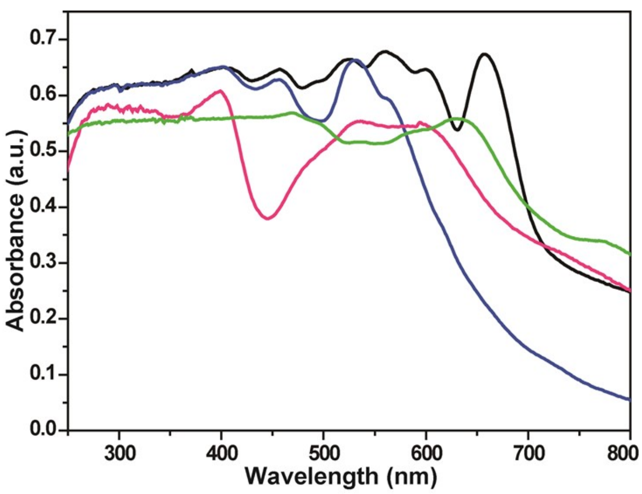


Fig. S5 UV-vis absorption spectra of H-TP-COF (black line), Co-TP-COF (pink line), Ni-TP-COF (blue line) and Mn-TP-COF (green line).

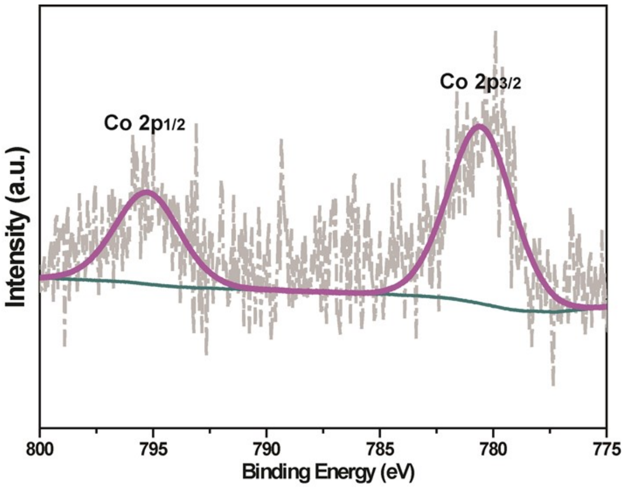


Fig. S6 XPS spectra of Co 2p in Co-TP-COF and the peaks are 795.26 eV and 780.57 eV.

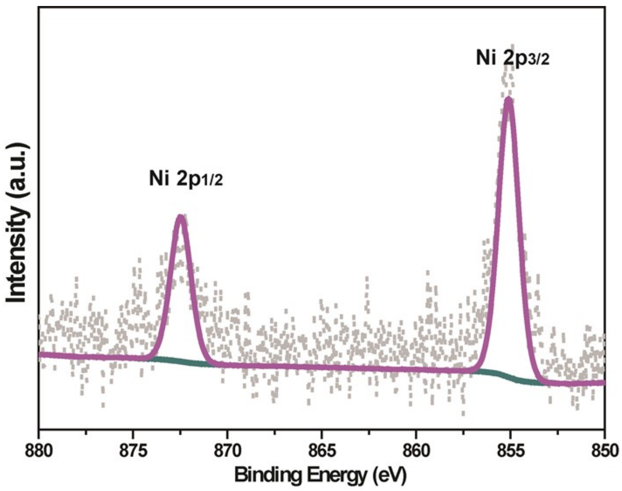


Fig. S7 XPS spectra of Ni 2p in Ni-TP-COF and the peaks are 872.43 eV and 855.15 eV.

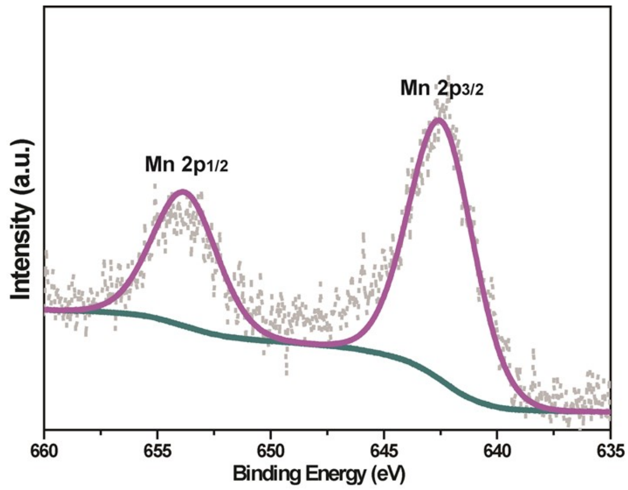


Fig. S8 XPS spectra of Mn 2p in Mn-TP-COF and the peaks are 653.79 eV and 642.47 eV.

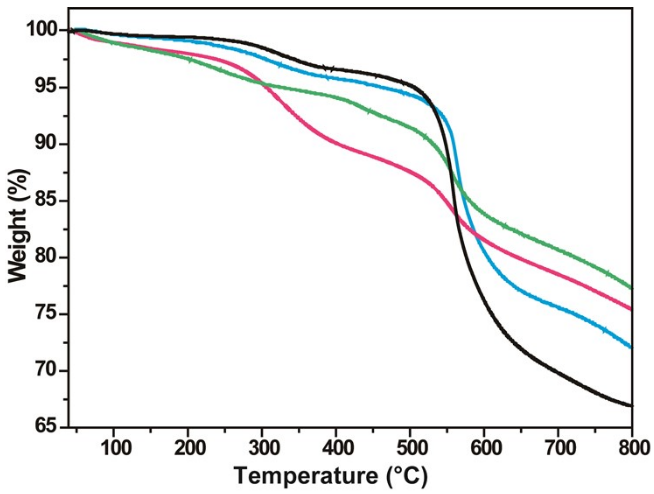


Fig. S9 TGA curves of H-TP-COF (black line), Co-TP-COF (pink line), Ni-TP-COF (blue line) and Mn-TP-COF (green line).

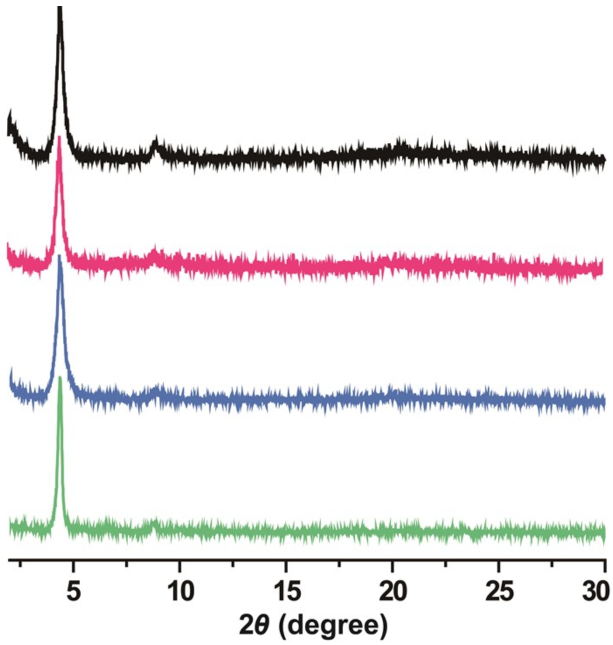


Fig. S10 PXRD patterns of H-TP-COF (black line), Co-TP-COF (pink line), Ni-TP-COF (blue line) and Mn-TP-COF (green line) after soaked in 0.1 M KOH for 24 h.

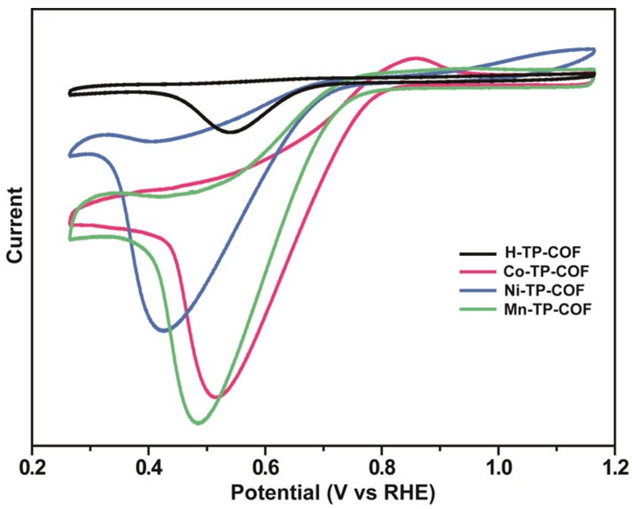


Fig. S11 CV curves of H-TP-COF, Co-TP-COF, Ni-TP-COF and Mn-TP-COF at a scan rate of 50 mV s^{-1} in O_2-saturated 0.1 M KOH solution.

COF-based electrocatalyst	pyrolysis or not	electrolyte	onset potential (V) vs RHE	half-wave potential (V) vs RHE	diffusion-limited current density (mA cm^{-2})	references
Co-TP-COF	no	KOH (0.1 M)	0.81	0.73	4.8	this work
Mn-TP-COF	no	KOH (0.1 M)	0.75	0.68	5	
Ni-TP-COF	no	KOH (0.1 M)	0.72	0.66	2.2	
H-TP-COF	no	KOH (0.1 M)	0.71	0.65	2.3	
COP-PSO_3-Co-rGO	no	KOH (0.1 M)	0.88	/	/	*Angew. Chem. Int. Ed.* 2018, 57, 12567
COP-P-SO_3Co	no	KOH (0.1 M)	0.68	/	/	
Pt@COF	no	$HClO_4$ (0.1 M)	1.05	0.89	5.52	*Chem. Mater.* 2020, 32, 9747
JUC-528	no	KOH (0.1 M)	/	0.7	/	*J. Am. Chem. Soc.* 2020, 142, 8104
1″-NP	yes	KOH (0.1 M)	/	0.81	5.5	*ACS Appl. Nano Mater.* 2020, 3, 5481
2″-NP	yes	KOH (0.1 M)	/	0.67	3.5	
3″-NP	yes	KOH (0.1 M)	/	0.68	3.4	
4″-NP	yes	KOH (0.1 M)	/	0.7	4.7	
Fe-ISAS/CN	yes	KOH (0.1 M)	/	0.861	5.47	*Chem. Sci.* 2020, 11, 786
CN	yes	KOH (0.1 M)	/	0.633	/	
C-Fe,Co-COF	yes	KOH (0.1 M)	0.89	0.81	6.1	*Chem. Eur. J.* 2019, 25, 3105
C-COF	yes	KOH (0.1 M)	0.86	0.73	4.6	
C-Fe-COF	yes	KOH (0.1 M)	0.73	0.55	3.2	
C-Co-COF	yes	KOH (0.1 M)	0.86	0.79	5.1	

Tab. S1 The ORR performance of M-TP-COFs and other reported COF-based electrocatalysts.

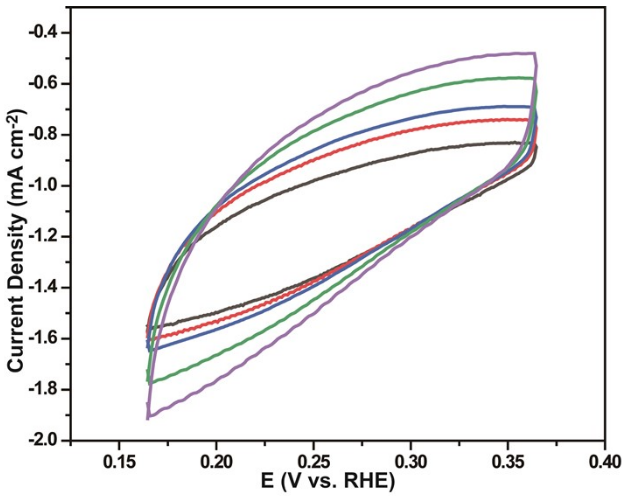


Fig. S12 CV curves of H-TP-COF at different scan rate (black line: 50 mV s^{-1}; red line: 80 mV s^{-1}; blue line: 100 mV s^{-1}; green line: 150 mV s^{-1}; purple line: 200 mV s^{-1}) in 0.1 M KOH solution.

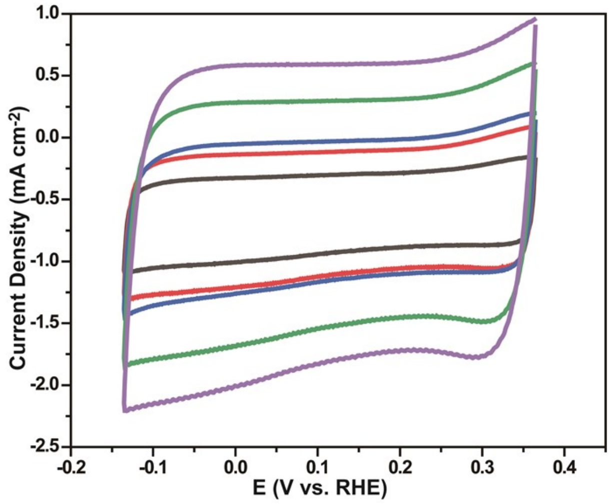


Fig. S13 CV curves of Co-TP-COF at different scan rate (black line: 50 mV s^{-1}; red line: 80 mV s^{-1}; blue line: 100 mV s^{-1}; green line: 150 mV s^{-1}; purple line: 200 mV s^{-1}) in 0.1 M KOH solution.

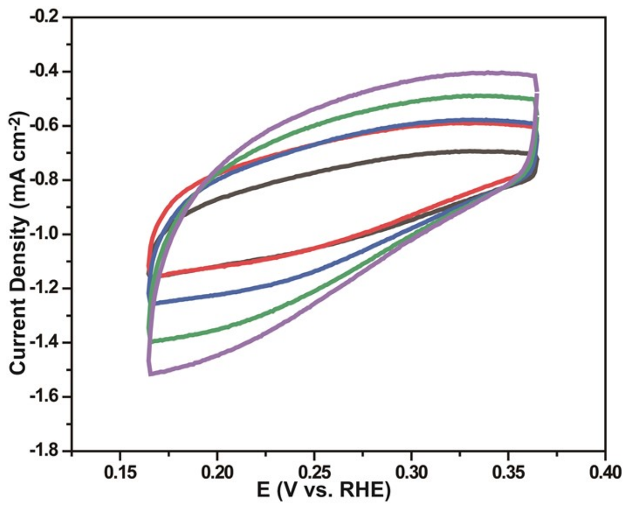


Fig. S14 CV curves of Ni-TP-COF at different scan rate (black line: 50 mV s^{-1}; red line: 80 mV s^{-1}; blue line: 100 mV s^{-1}; green line: 150 mV s^{-1}; purple line: 200 mV s^{-1}) in 0.1 M KOH solution.

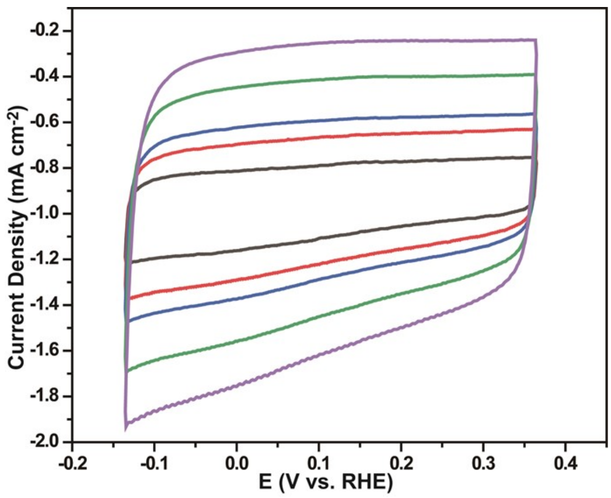


Fig. S15 CV curves of Mn-TP-COF at different scan rate (black line: 50 mV s^{-1}; red line: 80 mV s^{-1}; blue line: 100 mV s^{-1}; green line: 150 mV s^{-1}; purple line: 200 mV s^{-1}) in 0.1 M KOH solution.

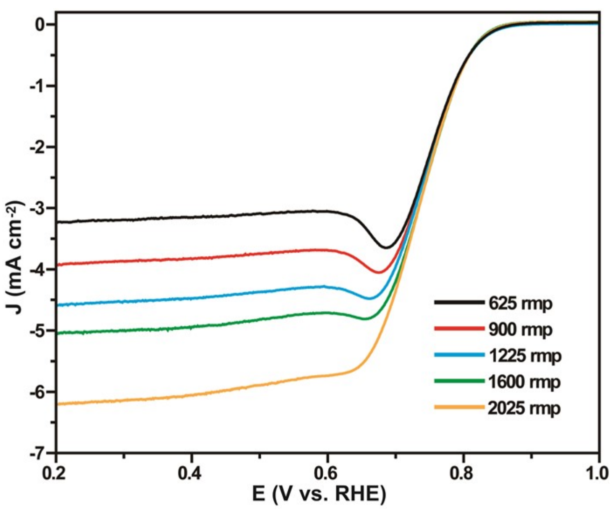


Fig. S16 LSV curves of Co-TP-COF at different rotation speed.

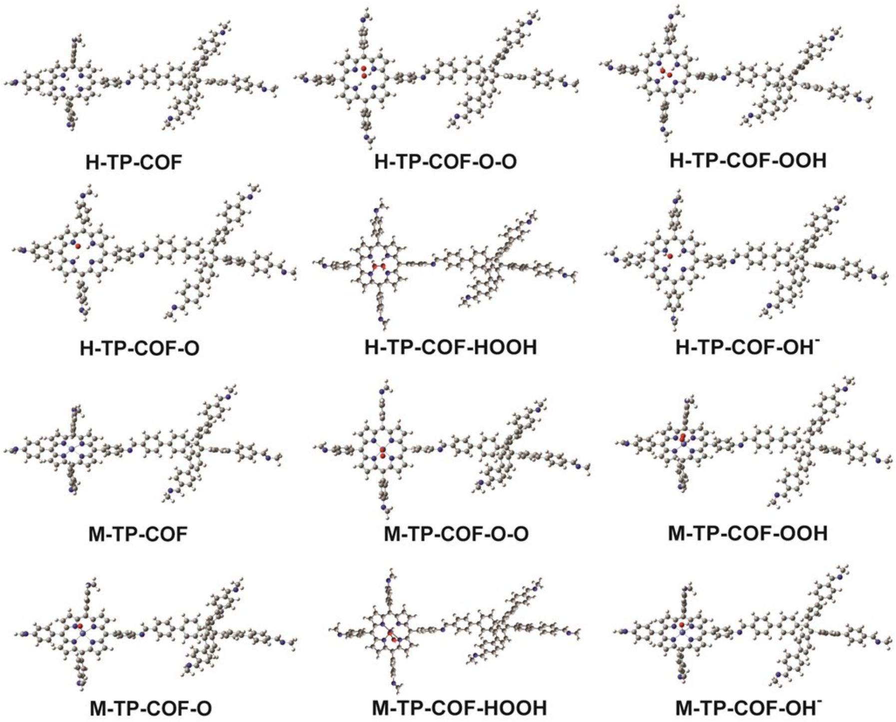


Fig. S17 Computational models of H-TP-COF and M-TP-COF (M = Co, Ni and Mn) used in DFT calculations.

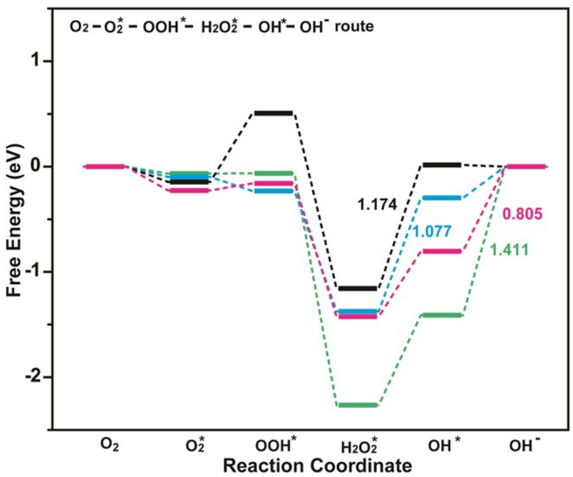


Fig. S18 Gibbs free energy curves of H-TP-COF (black line), Co-TP-COF (pink line), Ni-TP-COF (blue line) and Mn-TP-COF (green line) in the ORR process by O_2-O_2*-OOH*-H_2O_2*-OH*-OH^- route in alkaline medium.

Lattice parameters
a = 25.93 Å
b = 31.31 Å
c = 5.59 Å
α = β = γ = 90°

Atom	x	y	z
H1	0.047964	0.165679	0.480798
H2	0.172293	0.193071	0.054511
H3	0.107782	0.132522	0.078711
H4	0.579476	0.627367	0.865762
H5	0.524619	0.560828	0.850451
H6	0.594654	0.526284	0.159677
H7	0.648331	0.593511	0.170561
H8	0.626718	0.323279	0.820654
H9	0.684161	0.258242	0.792761
H10	0.73858	0.300844	0.085013
H11	0.681328	0.365672	0.113557
H12	0.766784	0.15748	0.237628
H13	0.831595	0.097486	0.212241
H14	0.762992	0.229117	0.228912
H15	0.803218	0.049845	0.545035
H16	-0.04796	-0.16568	0.480798
H17	-0.17229	-0.19307	0.054511
H18	-0.10778	-0.13252	0.078711
H19	-0.57948	-0.62737	0.865762
H20	-0.52462	-0.56083	0.850451
H21	-0.59465	-0.52628	0.159677
H22	-0.64833	-0.59351	0.170561
H23	-0.62672	-0.32328	0.820654
H24	-0.68416	-0.25824	0.792761
H25	-0.73858	-0.30084	0.085013
H26	-0.68133	-0.36567	0.113557
H27	-0.76678	-0.15748	0.237628
H28	-0.8316	-0.09749	0.212241
H29	-0.76299	-0.22912	0.228912
H30	-0.80322	-0.04985	0.545035
H31	-0.04796	0.165679	-0.4808
H32	-0.17229	0.193071	-0.05451
H33	-0.10778	0.132522	-0.07871
H34	-0.57948	0.627367	-0.86576
H35	-0.52462	0.560828	-0.85045

H36	-0.59465	0.526284	-0.15968
H37	-0.64833	0.593511	-0.17056
H38	-0.62672	0.323279	-0.82065
H39	-0.68416	0.258242	-0.79276
H40	-0.73858	0.300844	-0.08501
H41	-0.68133	0.365672	-0.11356
H42	-0.76678	0.15748	-0.23763
H43	-0.8316	0.097486	-0.21224
H44	-0.76299	0.229117	-0.22891
H45	-0.80322	0.049845	-0.54504
H46	0.047964	-0.16568	-0.4808
H47	0.172293	-0.19307	-0.05451
H48	0.107782	-0.13252	-0.07871
H49	0.579476	-0.62737	-0.86576
H50	0.524619	-0.56083	-0.85045
H51	0.594654	-0.52628	-0.15968
H52	0.648331	-0.59351	-0.17056
H53	0.626718	-0.32328	-0.82065
H54	0.684161	-0.25824	-0.79276
H55	0.73858	-0.30084	-0.08501
H56	0.681328	-0.36567	-0.11356
H57	0.766784	-0.15748	-0.23763
H58	0.831595	-0.09749	-0.21224
H59	0.762992	-0.22912	-0.22891
H60	0.803218	-0.04985	-0.54504
C1	0.026073	0.134271	0.489047
C2	0.110847	0.034434	0.479712
C3	0.170814	0.172054	0.22093
C4	0.135338	0.138648	0.234079
C5	0.617208	0.614057	0.519237
C6	0.582814	0.604836	0.706363
C7	0.552587	0.568119	0.698311
C8	0.556341	0.540034	0.50406
C9	0.59089	0.549098	0.317584
C10	0.620812	0.586025	0.324168
C11	0.650643	0.348003	0.467473
C12	0.651746	0.318255	0.655106
C13	0.683498	0.282345	0.640083
C14	0.713524	0.305707	0.250625
C15	0.681892	0.341483	0.265814
C16	0.28536	0.275853	0.562848
C17	0.833143	0.02369	0.519397
C18	0.958697	0.092058	0.518624

C19	0.795347	0.179913	0.58872
C20	0.795649	0.152555	0.389154
C21	0.831195	0.119305	0.375486
C22	0.866539	0.112534	0.561847
C23	0.906887	0.079204	0.538246
C24	0.748429	0.238395	0.414507
C25	-0.02607	-0.13427	0.489047
C26	-0.11085	-0.03443	0.479712
C27	-0.17081	-0.17205	0.22093
C28	-0.13534	-0.13865	0.234079
C29	-0.61721	-0.61406	0.519237
C30	-0.58281	-0.60484	0.706363
C31	-0.55259	-0.56812	0.698311
C32	-0.55634	-0.54003	0.50406
C33	-0.59089	-0.5491	0.317584
C34	-0.62081	-0.58603	0.324168
C35	-0.65064	-0.348	0.467473
C36	-0.65175	-0.31826	0.655106
C37	-0.6835	-0.28235	0.640083
C38	-0.71352	-0.30571	0.250625
C39	-0.68189	-0.34148	0.265814
C40	-0.28536	-0.27585	0.562848
C41	-0.83314	-0.02369	0.519397
C42	-0.9587	-0.09206	0.518624
C43	-0.79535	-0.17991	0.58872
C44	-0.79565	-0.15256	0.389154
C45	-0.8312	-0.11931	0.375486
C46	-0.86654	-0.11253	0.561847
C47	-0.90689	-0.0792	0.538246
C48	-0.74843	-0.2384	0.414507
C49	-0.02607	0.134271	-0.48905
C50	-0.11085	0.034434	-0.47971
C51	-0.17081	0.172054	-0.22093
C52	-0.13534	0.138648	-0.23408
C53	-0.61721	0.614057	-0.51924
C54	-0.58281	0.604836	-0.70636
C55	-0.55259	0.568119	-0.69831
C56	-0.55634	0.540034	-0.50406
C57	-0.59089	0.549098	-0.31758
C58	-0.62081	0.586025	-0.32417
C59	-0.65064	0.348003	-0.46747
C60	-0.65175	0.318255	-0.65511
C61	-0.6835	0.282345	-0.64008

C62	-0.71352	0.305707	-0.25063
C63	-0.68189	0.341483	-0.26581
C64	-0.28536	0.275853	-0.56285
C65	-0.83314	0.02369	-0.5194
C66	-0.9587	0.092058	-0.51862
C67	-0.79535	0.179913	-0.58872
C68	-0.79565	0.152555	-0.38915
C69	-0.8312	0.119305	-0.37549
C70	-0.86654	0.112534	-0.56185
C71	-0.90689	0.079204	-0.53825
C72	-0.74843	0.238395	-0.41451
C73	0.026073	-0.13427	-0.48905
C74	0.110847	-0.03443	-0.47971
C75	0.170814	-0.17205	-0.22093
C76	0.135338	-0.13865	-0.23408
C77	0.617208	-0.61406	-0.51924
C78	0.582814	-0.60484	-0.70636
C79	0.552587	-0.56812	-0.69831
C80	0.556341	-0.54003	-0.50406
C81	0.59089	-0.5491	-0.31758
C82	0.620812	-0.58603	-0.32417
C83	0.650643	-0.348	-0.46747
C84	0.651746	-0.31826	-0.65511
C85	0.683498	-0.28235	-0.64008
C86	0.713524	-0.30571	-0.25063
C87	0.681892	-0.34148	-0.26581
C88	0.28536	-0.27585	-0.56285
C89	0.833143	-0.02369	-0.5194
C90	0.958697	-0.09206	-0.51862
C91	0.795347	-0.17991	-0.58872
C92	0.795649	-0.15256	-0.38915
C93	0.831195	-0.11931	-0.37549
C94	0.866539	-0.11253	-0.56185
C95	0.906887	-0.0792	-0.53825
C96	0.748429	-0.2384	-0.41451
C97	0.526206	0.5	0.5
C98	-0.52621	-0.5	0.5
N1	0.761678	0.216089	0.600693
N2	-0.76168	-0.21609	0.600693
N3	-0.76168	0.216089	-0.60069
N4	0.761678	-0.21609	-0.60069
N5	0	0.065787	0.5
N6	0	-0.06579	0.5

N7	0.080107	0	0.5
N8	-0.08011	0	0.5

Tab. S2 Atomic coordinates for H-TP-COF with AA packing model.

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