Supporting Information for

Three-Dimensional Porphyrin-Based Covalent Organic Frameworks with stp Topology for Efficient Electrocatalytic Oxygen Evolution Reaction

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1. Materials and methods

All the chemicals are commercially available, and used without further purification. All solvents were dried and distilled according to conventional methods. All products were isolated and handled under nitrogen using either glovebox or Schlenk line techniques.

Power X-ray diffraction (PXRD): PXRD patterns were collected on an X-ray diffraction (XRD) system (DX-27mini, China) using Cu Kα radiation.

Fourier transform infrared (FT-IR): IR spectra were measured on an IR spectrometer (Nicolet 6700) between the ranges of 4000 to 400 cm^{-1}.

Solid-state nuclear magnetic resonance (ssNMR): Solid-state nuclear magnetic resonance (NMR) data were performed on a Bruker AVANCE III 600 spectrometer with cross-polarization magic-angle-spinning (CP/MAS) at a resonance frequency of 150.9 MHz. ^{13}C CP/MAS NMR spectra were recorded using a 4 mm MAS probe and a spinning rate of 12kHz. A contact time of 4 ms and a recycle delay of 2 s were used for the ^{13}C CP/MAS NMR measurement. The chemical shifts of ^{13}C were externally referenced to tetramethylsilane (TMS).

Elemental analyses: Elemental analyses were performed on an Elementar vario MICRO UNICUBE series CHN elemental analyzer.

Scanning electron microscope (SEM): SEM images were collected using a GeminiSEM 500 system.

High-resolution transmission electron microscope (HR-TEM): HR-TEM images were collected using a Tecnai G2 F30 S-Twin (FEI Company, point resolution of 0.20 nm, line resolution of 0.102 nm, and information resolution of 0.14 nm) with an accelerating voltage of 300 kV.

Thermogravimetric analysis (TGA): TGA measurements were performed using a TA Q800 under flowing N_2 with 10 K min^{-1} ramp rate. Samples were heated in a Platinum pan (800 °C, 10 °C min^{-1}) under a N_2 flux (60 mL min^{-1}).

Sorption isotherm for N_2: Micrometrics ASAP2040 system were used to measure the specific surface area and pore structure using nitrogen as the adsorbate at 77 K, after outgassing the samples overnight at 120 °C.

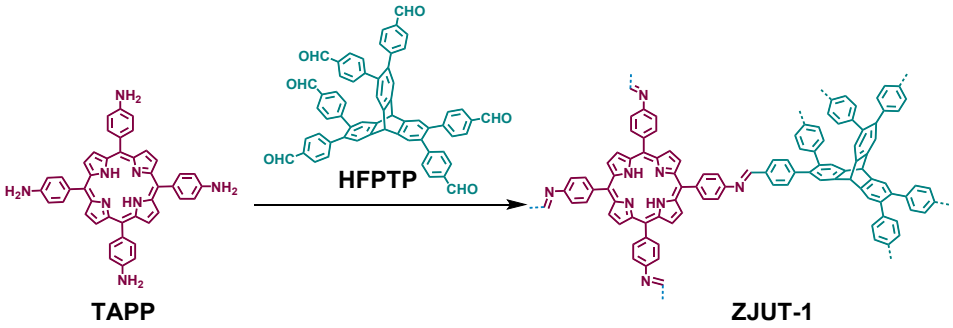
X-ray photoelectron spectroscopy(XPS)：X-ray photoelectron spectroscopy data were collected using a Kratos AXIS Ultra DLD.

Crystal structure modeling: Structural modeling of COFs was generated using the Materials Studio[1] program employing the building (Crystal) module, the lattice model was geometrically optimized using force-filed based method (Forcite molecular dynamics module) and SCC-DFTB (DFTB + module). The Pawley fitting (Reflex module) was performed to optimize the lattice parameters iteratively until the Rwp value converges and the overlay of the observed with refined profiles shows good agreement. Powder indexing and Rietveld refinement were performed using EXPO2014[2] various topology structures were illustrated by VESTA software[3].

2. Synthesis and characterization of ZJUT-1

2.1 Synthesis of ZJUT-1

Monomers of 2,3,6,7,14,15-hexa(4-formylphenyl)triptycene (HFPTP) and 5,10,15,20-Tetra(4-aminophenyl)porphyrin (TAPP) were synthesized according the Published methods[4,5].



Scheme S1. Synthesis of ZJUT-1.

ZJUT-1: HFPTP (17.6 mg, 0.02 mmol) and **TAPP** (20.2 mg, 0.03 mmol) were added into a 10-mL glass ampoule with mesitylene (0.9 mL) and N, N-dimethylacetamide (0.3 mL). The solution was ultrasound for 5 minutes to obtain dark purple turbid solution. 6 M acetic acid (0.2 mL) was added into the glass ampoule as catalyst. The glass ampoule was flash frozen at 77 K using the liquid nitrogen bath, degassed by freeze-pump-thaw three times and vacuumed to *ca.* 100 Pa, then sealed. The glass ampoule was placed in an oven at 120 ℃ for 5 days. The fuchsia solid was isolated by centrifugation and washed with N, N-dimethylacetamide (2×10 mL) and acetone (2×10 mL). The resulting precipitate was filtered then exhaustively washed with tetrahydrofuran and acetone by Soxhlet extraction for 48 hours. The sample was then transferred to vacuum chamber and evacuated to 20 mTorr at 80 ℃ for 24 h, yielding fuchsia powder **ZJUT-1** (Yield: 29.2 mg, 81.9%). Elemental analysis of **ZJUT-1** with a molecular formula of $(C_{128}H_{77}N_{12})n$ (% Calc/Found: C 86.22/86.79, H 4.35/4.13, N 9.43/9.08).

2.2 Characterization of ZJUT-1

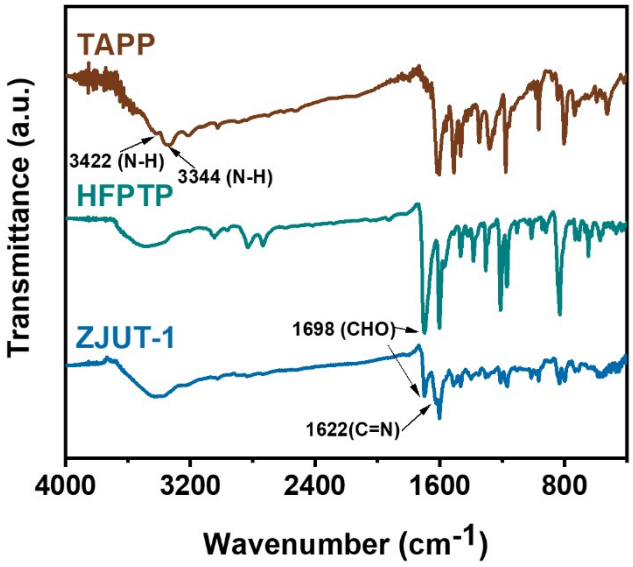


Figure S1. FT-IR spectra of TAPP, HFPTP, and ZJUT-1.

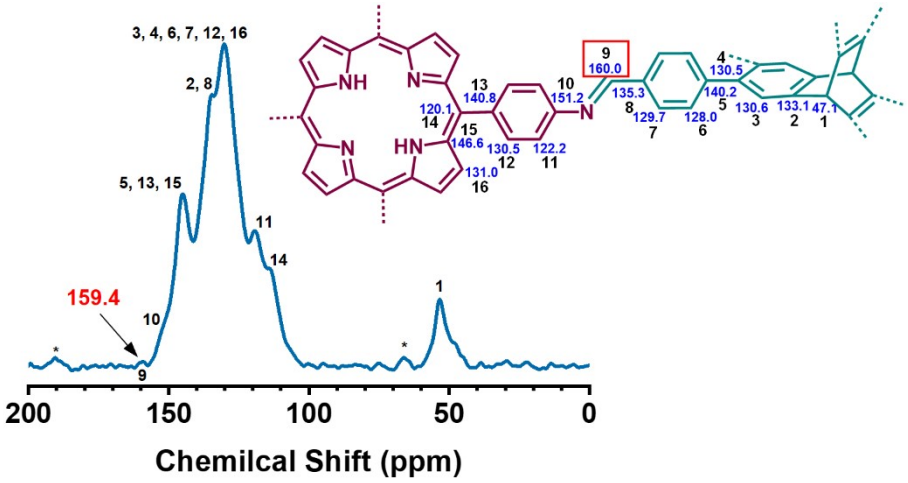


Figure S2. ^{13}C CP/MAS NMR spectrum of ZJUT-1. Asterisks (*) indicate peaks may arising from solvent molecules or spinning side bands.

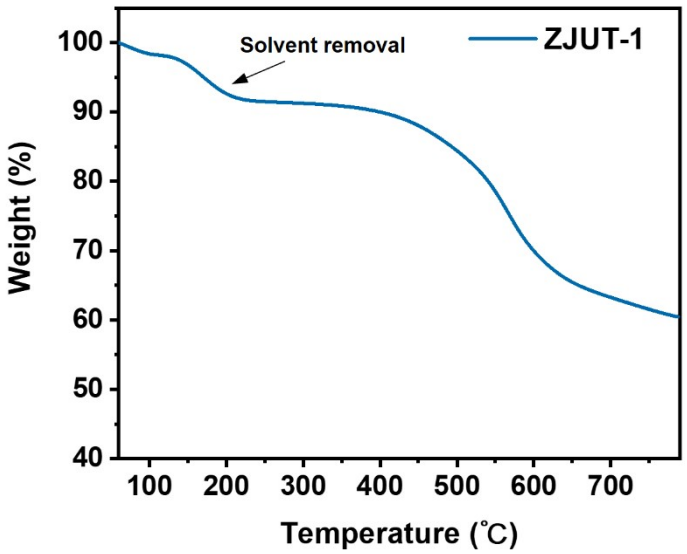


Figure S3. TGA curve of ZJUT-1.

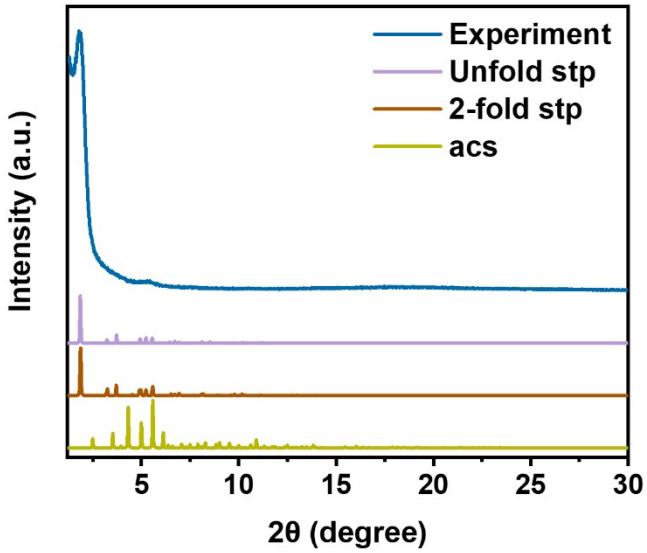


Figure S4. Simulated PXRD patterns for possible topologies (**stp** or **acs**) and different folds interpenetrated COF structures built from HFPTP and TAPP.

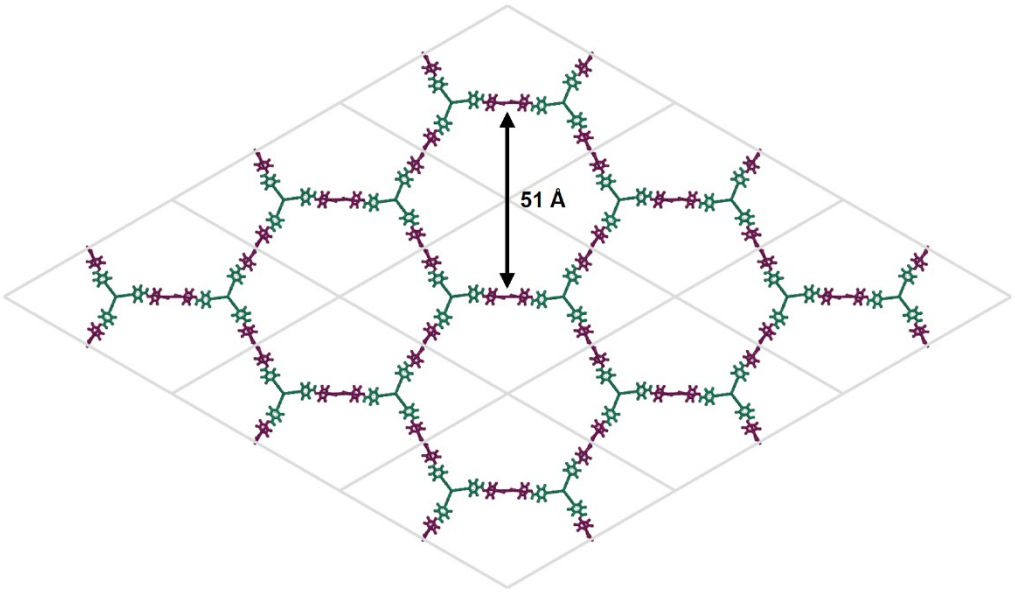


Figure S5. Structural model for unfold interpenetrated COF structure with **stp** topology built from HFPTP and TAPP.

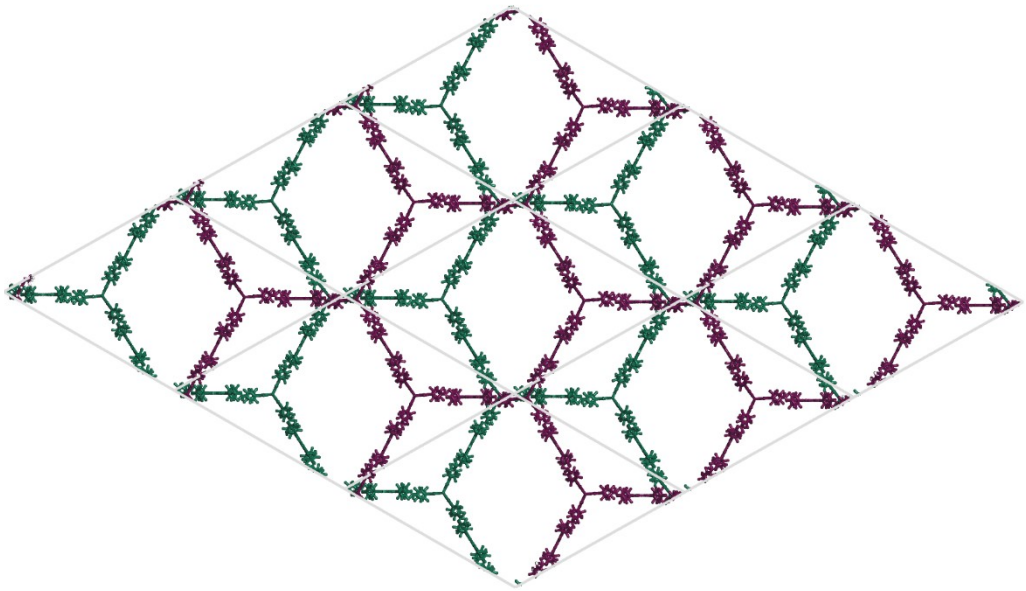


Figure S6. Structural model for 2-fold interpenetrated COF structure with **stp** topology built from HFPTP and TAPP.

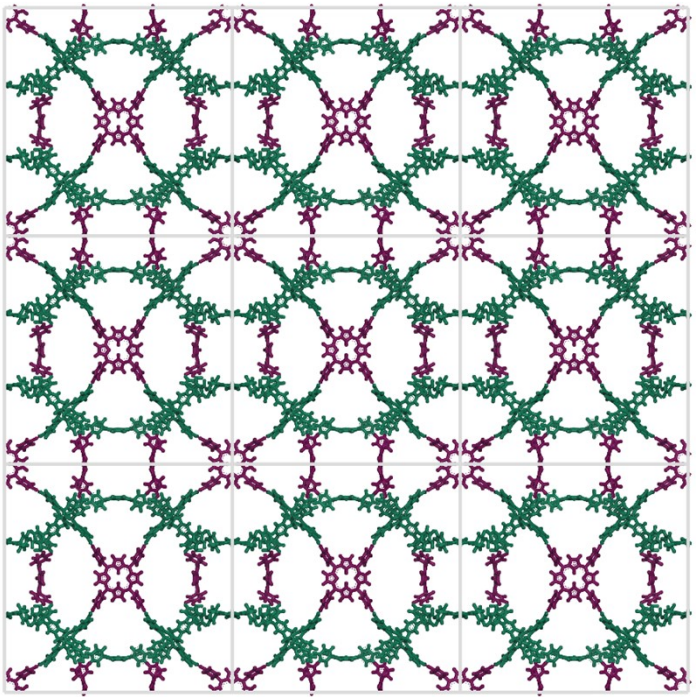


Figure S7. Structural model for acs topology built from HFPTP and TAPP.

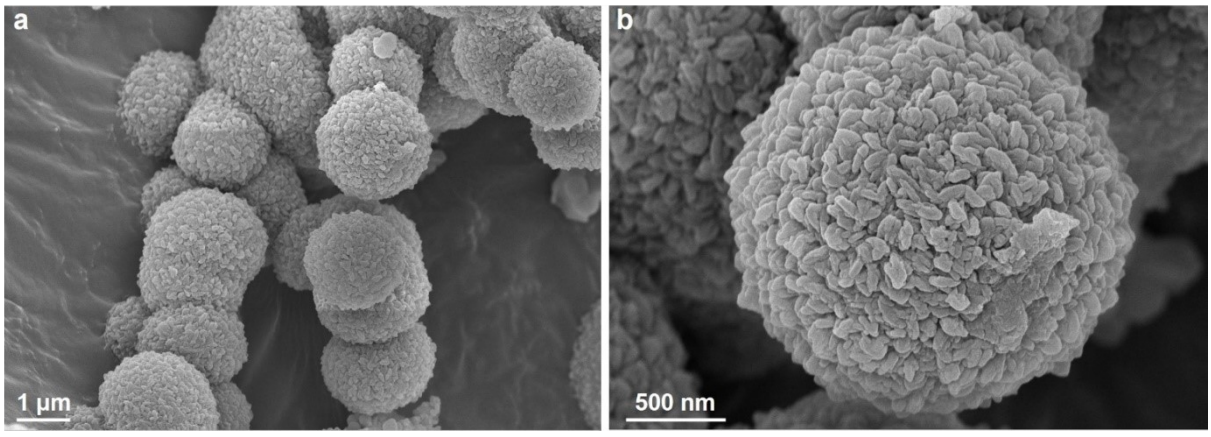


Figure S8. SEM images of ZJUT-1.

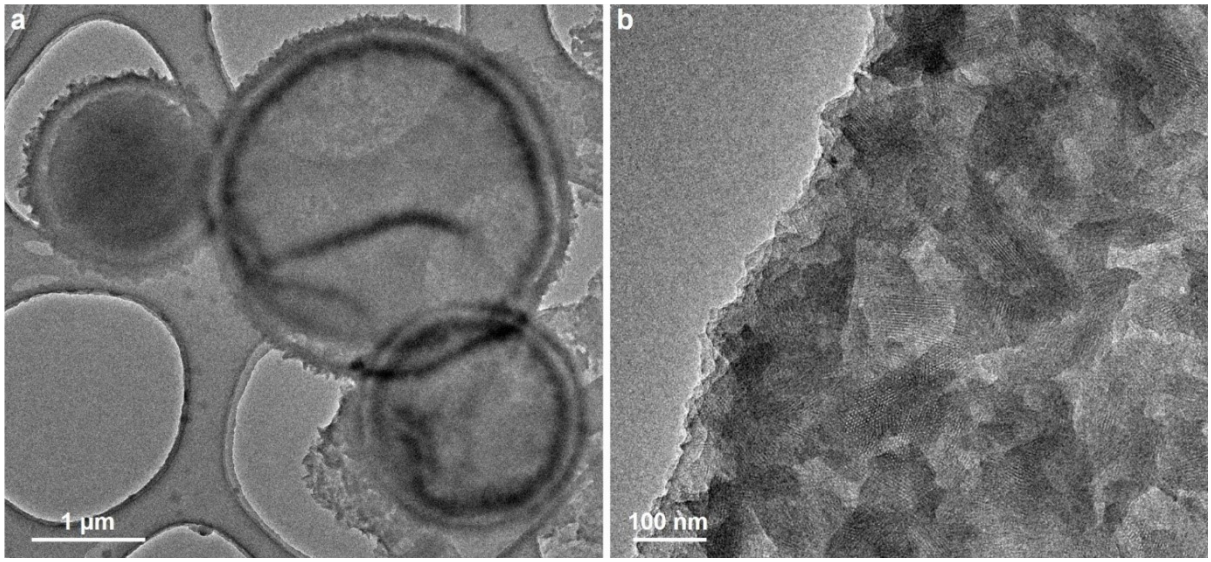


Figure S9. TEM images of ZJUT-1.

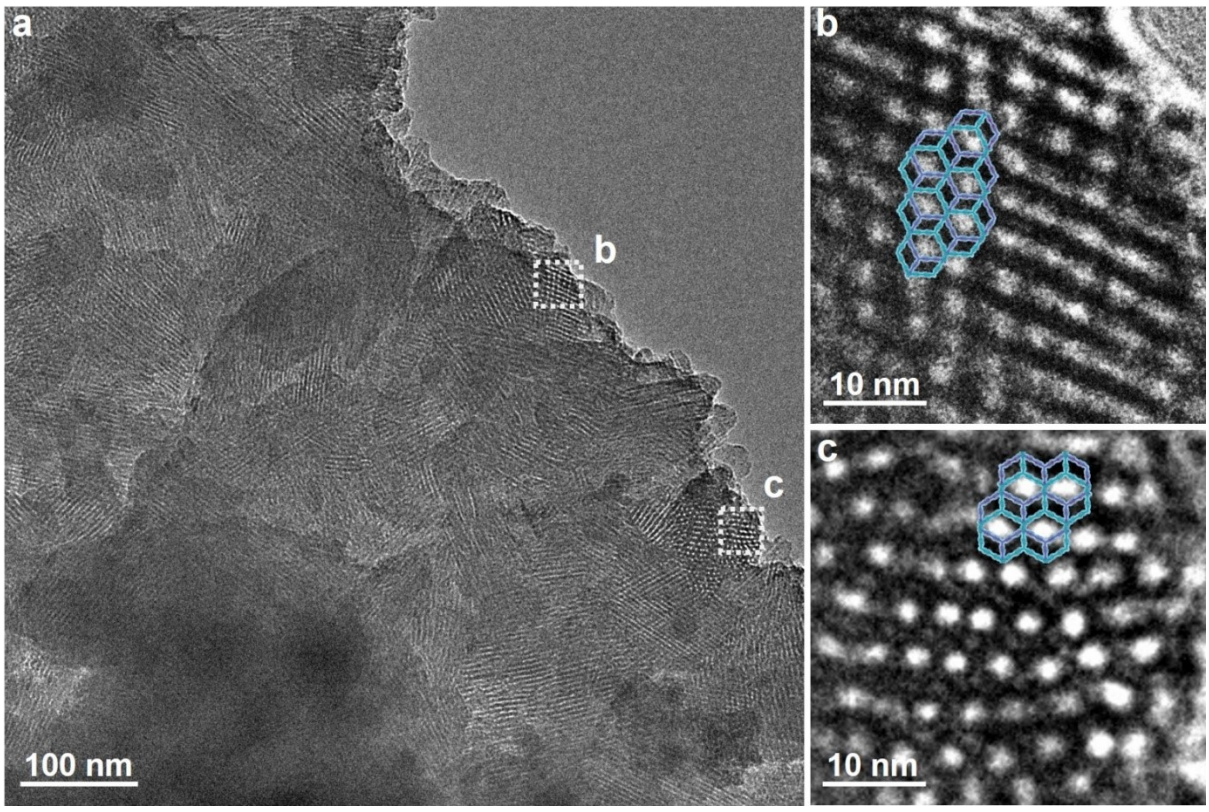
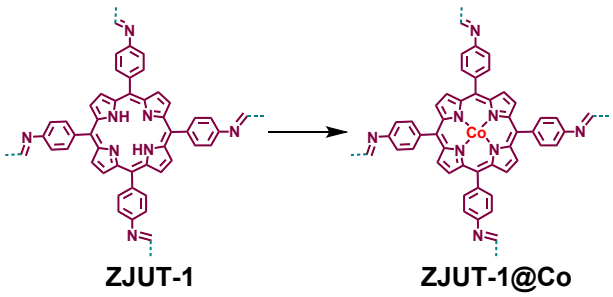


Figure S10. (a) A typical TEM image of ZJUT-1; (b, c) The HR-TEM images of the selected areas (white frames) in a with the simulated models of ZJUT-1.

3. Synthesis and characterization of ZJUT-1@Co

3.1 Synthesis of ZJUT-1@Co



Scheme S2. Synthesis of ZJUT-1@Co.

ZJUT-1@Co: ZJUT-1 (60.0 mg) and Cobalt(II) acetate tetrahydrate (119.6 mg, 0.48 mmol) were added into a 10-mL glass ampoule with N,N-dimethylacetamide (2.0 mL). The glass ampoule was flash frozen at 77 K using the liquid nitrogen bath, degassed by freeze-pump-thaw three times and vacuumed to *ca.* 100 Pa, then sealed. The glass ampoule was placed in an oven at 120 ℃ for 24 h. The dark red solid was isolated by centrifugation and washed with H_2O (3×10 mL), then immersed in 80 ℃ N,N-dimethylacetamide and exchanged solvent several times. The resulting precipitate was filtered then exhaustively washed with tetrahydrofuran and acetone by Soxhlet extraction for 48 hours. The sample was then transferred to vacuum chamber and evacuated to 20 mTorr at 80 ℃ for 24 h, yielding dark red powder **ZJUT-1@Co** (Yield: 53.4 mg, 84.8%).

3.2 Characterization of ZJUT-1@Co

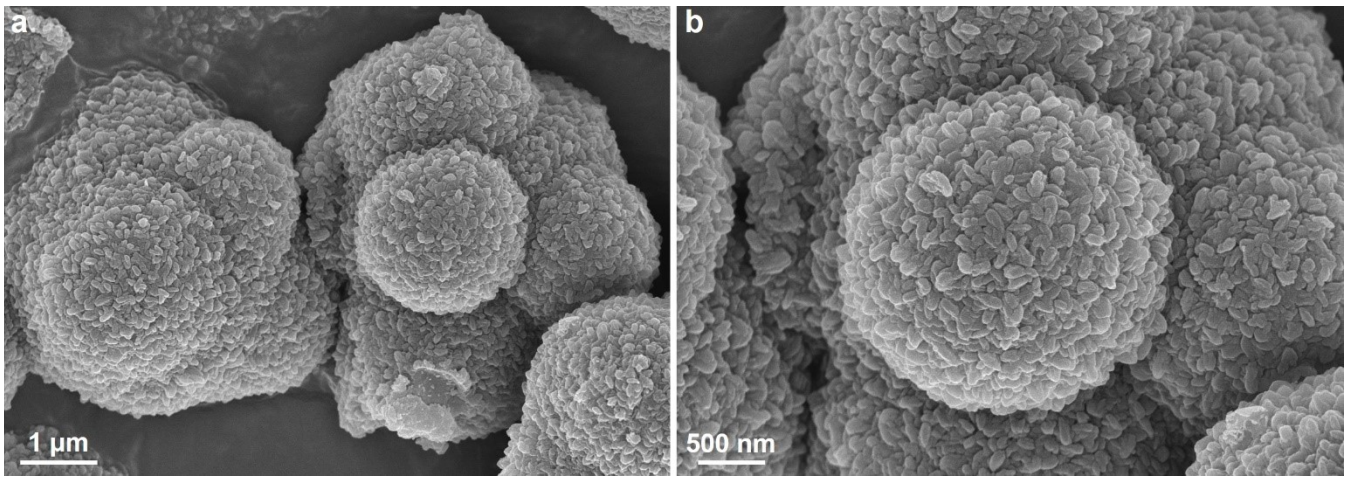


Figure S11. SEM images of ZJUT-1@Co.

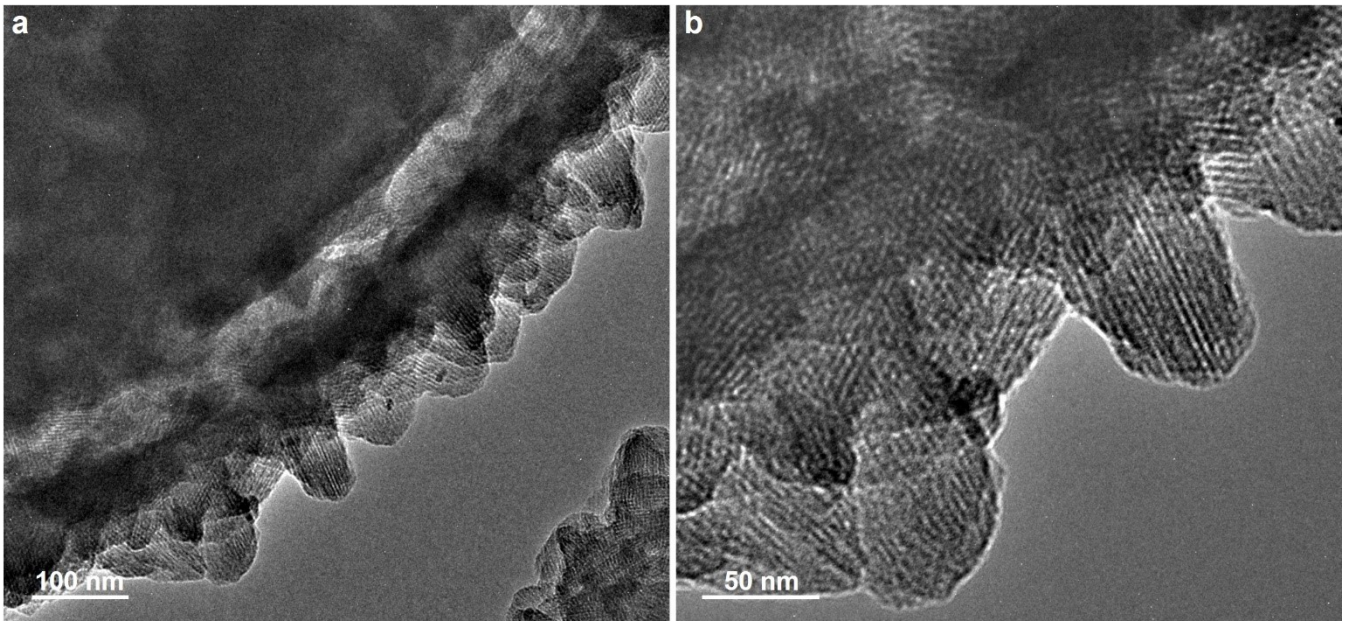


Figure S12. TEM images of ZJUT-1@Co.

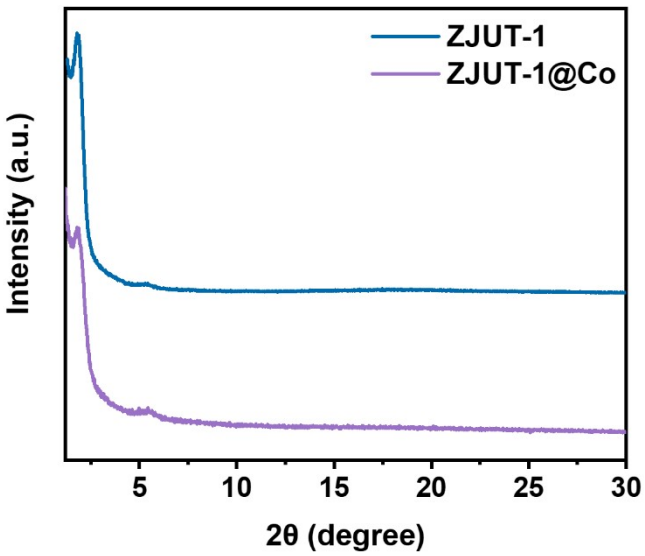


Figure S13. PXRD patterns of ZJUT-1 and ZJUT-1@Co. The crystallinity characters of the synthesized ZJUT-1@Co are well preserved compared to the ZJUT-1.

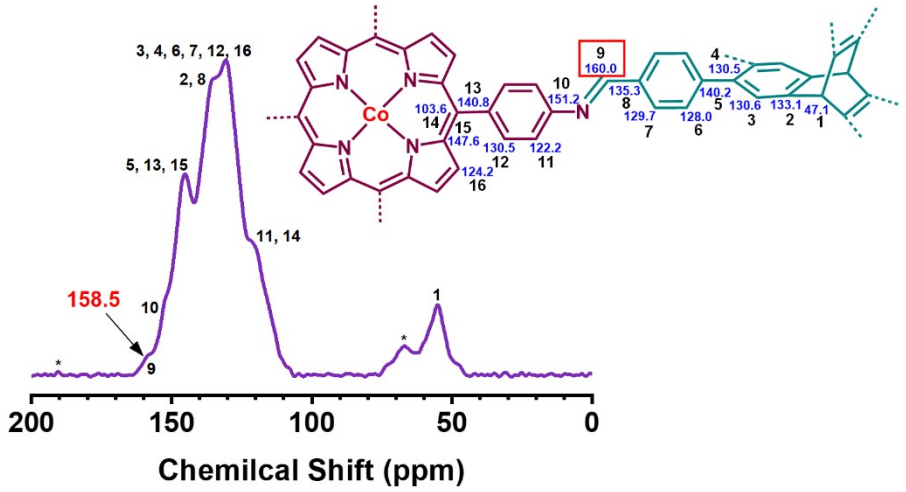


Figure S14. ^{13}C CP/MAS NMR spectrum of ZJUT-1@Co. Asterisks (*) indicate peaks may arising from solvent molecules or spinning side bands.

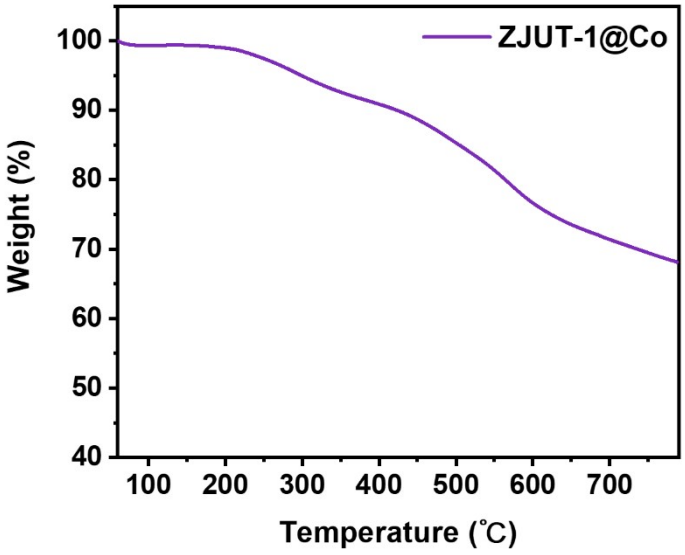


Figure S15. TGA curve of ZJUT-1@Co.

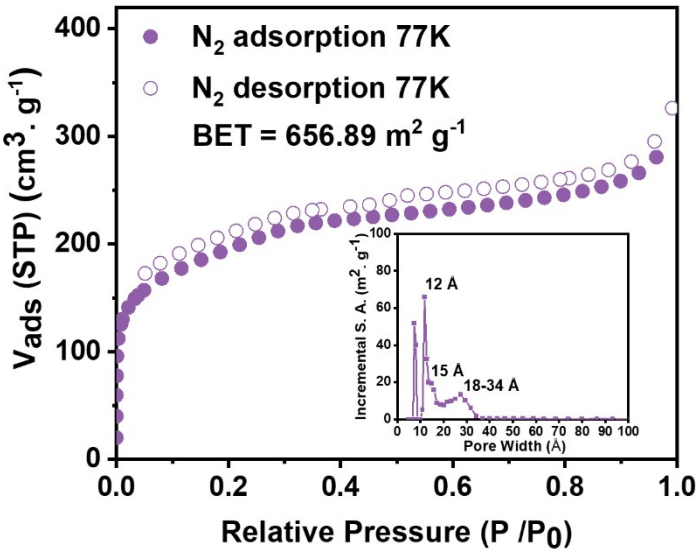


Figure S16. N_2 adsorption-desorption isotherms measured at 77 K and pore-size distribution of ZJUT-1@Co.

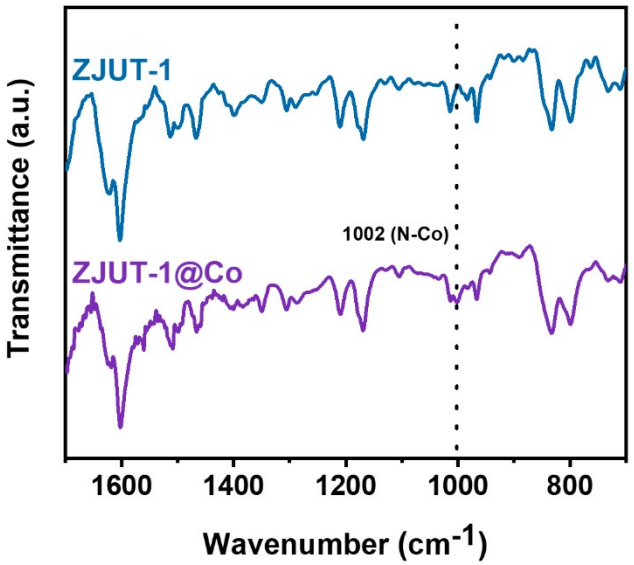


Figure S17. FT-IR spectra of ZJUT-1 and ZJUT-1@Co in the ranges of 700 to 1700 cm^{-1}.

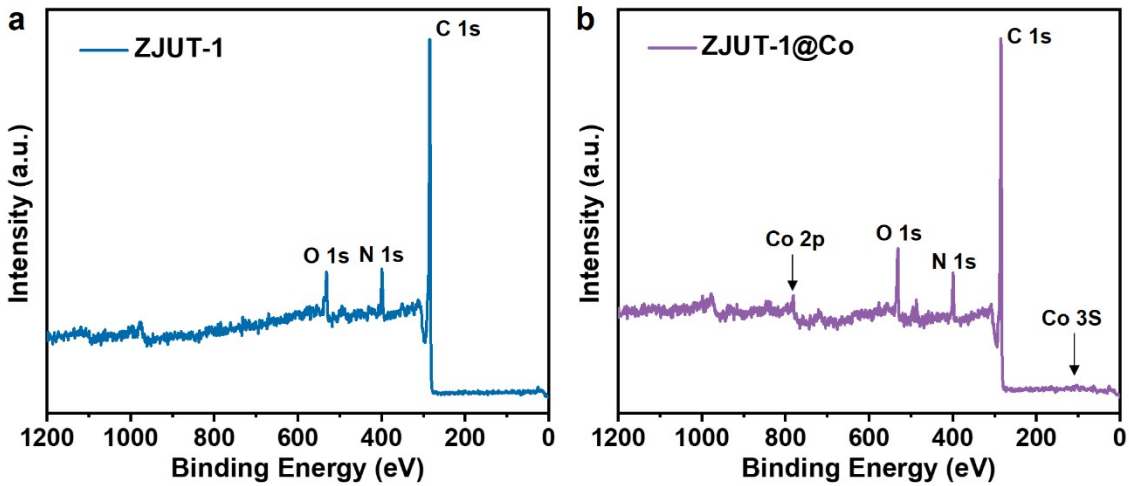


Figure S18. XPS spectra of (a) ZJUT-1 and (b) ZJUT-1@Co.

4. Unit cell parameters and fractional atomic coordinates for ZJUT-1

Table S1. Unit cell parameters and fractional atomic coordinates for ZJUT-1 calculated based on the 2-fold interpenetrated **stp** topology.

Space group		*P1*	
Calculated unit cell		a = 54.4694 Å, b = 55.2247 Å c = 21.3866 Å α = 90.2243°, β = 89.9411°, γ = 120.7033°.	
Atoms	X	Y	Z
C1	0.71895	0.91279	0.80007
C2	0.69062	0.8973	0.78193
C3	0.68201	0.89247	0.71877
C4	0.6533	0.87731	0.69946
C5	0.64509	0.87291	0.63727
C6	0.7071	0.92469	0.62852
C7	0.72876	0.93581	0.58357
C8	0.74812	0.92632	0.57963
C9	0.74541	0.90535	0.62091
C10	0.72377	0.89421	0.66563
C11	0.70456	0.9039	0.66992
N12	0.77076	0.93869	0.5347
C13	0.79046	0.93217	0.53204
C14	0.81578	0.96428	0.44194
C15	0.83919	0.97689	0.4014
C16	0.86088	0.97038	0.40592
C17	0.85898	0.95134	0.45147
C18	0.8356	0.93871	0.49166
C19	0.81399	0.94514	0.48724
C20	0.91293	0.99906	0.39852
C21	0.93811	1.01345	0.36495
C22	0.88671	0.98484	0.36692
C23	0.54194	0.81679	0.79937
C24	0.57026	0.83245	0.7814
C25	0.57886	0.83748	0.71829
C26	0.60759	0.85276	0.69924
C27	0.61584	0.85734	0.63713
C28	0.55414	0.80552	0.62691
C29	0.53255	0.79438	0.58168
C30	0.5129	0.80352	0.57833
C31	0.51522	0.82415	0.62056
C32	0.5368	0.83532	0.66559
C33	0.55632	0.82599	0.66924
N34	0.49033	0.79103	0.53312
C35	0.47032	0.79712	0.53058
C36	0.44563	0.76485	0.43988
C37	0.42217	0.75156	0.39945
C38	0.39982	0.75712	0.40436
C39	0.4012	0.77602	0.45007
C40	0.42464	0.78935	0.49018
C41	0.44685	0.78376	0.48549
C42	0.34777	0.72703	0.39716
C43	0.32259	0.71173	0.36363
C44	0.37393	0.74178	0.3655
C45	0.54197	0.81622	0.86335
C46	0.57031	0.8314	0.88166
C47	0.5789	0.83571	0.94493
C48	0.60758	0.8519	0.9644
C49	0.6158	0.85641	0.02654

C50	0.5386	0.79329	-0.00395
C51	0.5157	0.78096	0.03776
C52	0.51007	0.79775	0.07735
C53	0.52792	0.82718	0.07541
C54	0.55082	0.83955	0.03353
C55	0.55619	0.82266	0.99337
N56	0.48531	0.78442	0.11654
C57	0.47853	0.79788	0.15615
C58	0.43216	0.75461	0.18162
C59	0.4069	0.74093	0.21617
C60	0.40141	0.75544	0.26282
C61	0.42138	0.78398	0.27376
C62	0.44662	0.79771	0.23894
C63	0.45218	0.78306	0.19298
C64	0.34874	0.72542	0.26538
C65	0.32291	0.71132	0.29747
C66	0.37455	0.7407	0.29889
C67	0.71894	0.9132	0.86407
C68	0.69059	0.8981	0.88221
C69	0.682	0.89368	0.94543
C70	0.65331	0.87749	0.96462
C71	0.64504	0.87288	0.02669
C72	0.72251	0.93593	-0.00271
C73	0.74543	0.94809	0.03911
C74	0.75086	0.93114	0.07826
C75	0.7328	0.90174	0.07577
C76	0.70989	0.88955	0.03379
C77	0.70471	0.90658	0.99405
N78	0.77564	0.94425	0.11756
C79	0.78201	0.93057	0.15713
C80	0.82894	0.97323	0.18315
C81	0.85421	0.98638	0.21789
C82	0.8591	0.97152	0.2644
C83	0.83853	0.94319	0.27512
C84	0.81329	0.92999	0.24013
C85	0.80834	0.94497	0.19424
C86	0.91185	0.99987	0.26669
C87	0.93774	1.01336	0.29875
C88	0.88604	0.98558	0.30032
N89	0.13122	0.86389	0.7368
N90	0.13182	0.8636	0.92516
N91	0.67303	0.88822	0.83205
N92	0.58785	0.84149	0.8316
C93	0.08778	0.90712	0.80137
C94	0.10189	0.89348	0.78242
C95	0.10602	0.8895	0.71906
C96	0.11973	0.87507	0.69902
C97	0.12341	0.87095	0.63664
C98	0.0734	0.88273	0.62956
C99	0.06264	0.89344	0.5852
C100	0.07329	0.92242	0.58171
C101	0.09504	0.94069	0.62298
C102	0.10585	0.93	0.66717
C103	0.09503	0.90094	0.67087
N104	0.06138	0.93271	0.53674
C105	0.06877	0.959	0.5334
C106	0.03661	0.95094	0.44223
C107	0.02372	0.96082	0.40118
C108	0.03004	0.98878	0.40534
C109	0.04934	1.00666	0.45092

C110	0.0623	0.99683	0.49163
C111	0.05589	0.96895	0.48776
C112	0.00008	1.00998	0.39794
C113	-0.01528	1.01929	0.36437
C114	0.0148	0.9989	0.36635
C115	0.17583	0.82116	0.79626
C116	0.16117	0.83446	0.77898
C117	0.1563	0.83835	0.71606
C118	0.14219	0.85257	0.6977
C119	0.13764	0.85643	0.63579
C120	0.18793	0.84505	0.62432
C121	0.1983	0.83428	0.57887
C122	0.18775	0.8053	0.57505
C123	0.16644	0.78712	0.617
C124	0.15602	0.79786	0.66227
C125	0.1668	0.82691	0.66645
N126	0.19965	0.79492	0.52991
C127	0.19243	0.76865	0.52712
C128	0.22508	0.77606	0.43722
C129	0.23806	0.76577	0.39725
C130	0.23142	0.73773	0.40202
C131	0.21174	0.72019	0.44713
C132	0.19871	0.73042	0.48677
C133	0.20538	0.75836	0.48224
C134	0.26092	0.71596	0.39596
C135	0.27602	0.70609	0.36299
C136	0.24646	0.72708	0.36373
C137	0.17653	0.82157	0.86026
C138	0.16245	0.83528	0.87929
C139	0.15861	0.83957	0.94279
C140	0.14363	0.85275	0.96294
C141	0.13951	0.8565	0.02527
C142	0.20058	0.84066	-0.0067
C143	0.21222	0.82971	0.03473
C144	0.1945	0.80738	0.07414
C145	0.16484	0.79625	0.07226
C146	0.15315	0.80717	0.03064
C147	0.17097	0.82936	0.9907
N148	0.20713	0.79567	0.11329
C149	0.19287	0.77552	0.15287
C150	0.23563	0.77204	0.17885
C151	0.24872	0.76043	0.21378
C152	0.23349	0.74059	0.26046
C153	0.20479	0.73219	0.27103
C154	0.19164	0.74374	0.23584
C155	0.20704	0.76382	0.18986
C156	0.2627	0.71798	0.26419
C157	0.27647	0.7065	0.29683
C158	0.24768	0.72853	0.29711
C159	0.08744	0.90648	0.8653
C160	0.10124	0.89234	0.88258
C161	0.10518	0.8876	0.94549
C162	0.12009	0.87422	0.96414
C163	0.12434	0.87014	0.02604
C164	0.06315	0.88483	-0.0007
C165	0.0513	0.89564	0.04076
C166	0.0689	0.91917	0.07767
C167	0.0987	0.93165	0.07336
C168	0.1106	0.92086	0.03172
C169	0.09284	0.89746	0.9943

N170	0.05593	0.93058	0.11691
C171	0.07002	0.95132	0.15556
C172	0.02662	0.9536	0.18197
C173	0.01309	0.96481	0.21701
C174	0.02807	0.98497	0.26363
C175	0.05696	0.99408	0.27403
C176	0.07055	0.98295	0.23868
C177	0.05541	0.96258	0.19274
C178	-0.00177	1.00687	0.26623
C179	-0.01577	1.01832	0.29824
C180	0.01353	0.99688	0.29977
N181	0.12642	0.36221	0.73441
N182	0.12642	0.3618	0.92265
N183	0.11025	0.88431	0.83198
N184	0.1529	0.84323	0.82965
C185	0.08503	0.27478	0.79459
C186	0.09792	0.30274	0.77709
C187	0.10169	0.31137	0.71416
C188	0.11549	0.33974	0.69553
C189	0.11931	0.34797	0.63353
C190	0.10962	0.2872	0.6237
C191	0.0993	0.26601	0.57818
C192	0.07001	0.24668	0.57325
C193	0.05104	0.24886	0.6142
C194	0.06133	0.27006	0.65958
C195	0.0907	0.28928	0.66476
N196	0.06017	0.22446	0.52797
C197	0.03361	0.20475	0.52319
C198	0.04341	0.18086	0.4354
C199	0.03433	0.15766	0.39566
C200	0.00608	0.13514	0.39837
C201	-0.01299	0.13612	0.44084
C202	-0.00395	0.15935	0.4803
C203	0.02428	0.18169	0.47807
C204	-0.01268	0.08432	0.39387
C205	-0.02101	0.05951	0.3614
C206	-0.00304	0.10952	0.36096
C207	0.16829	0.44938	0.79797
C208	0.15513	0.42148	0.77934
C209	0.15125	0.41312	0.71604
C210	0.1373	0.38482	0.69636
C211	0.13339	0.37681	0.63406
C212	0.14367	0.43749	0.62583
C213	0.15418	0.45876	0.58083
C214	0.18347	0.47821	0.57696
C215	0.20224	0.47605	0.61849
C216	0.19177	0.45477	0.6633
C217	0.1624	0.43543	0.66743
N218	0.19358	0.50042	0.53194
C219	0.22013	0.5203	0.52887
C220	0.21185	0.54415	0.43882
C221	0.22184	0.56722	0.39859
C222	0.25015	0.58958	0.40316
C223	0.26827	0.58862	0.44826
C224	0.25833	0.56556	0.48815
C225	0.23011	0.54334	0.48386
C226	0.27146	0.64078	0.3966
C227	0.28115	0.66554	0.36333
C228	0.26048	0.61505	0.36464
C229	0.16776	0.44921	0.86198

C230	0.15412	0.4212	0.87962
C231	0.14963	0.41258	0.94268
C232	0.13671	0.38426	0.96149
C233	0.13278	0.37599	0.02344
C234	0.14706	0.45176	-0.00484
C235	0.15771	0.47431	0.03716
C236	0.18074	0.48029	0.0761
C237	0.19286	0.46312	0.07327
C238	0.18222	0.44054	0.0311
C239	0.15936	0.43485	0.99158
N240	0.19222	0.50471	0.11548
C241	0.21302	0.51188	0.15461
C242	0.21536	0.55711	0.1805
C243	0.22674	0.58201	0.21521
C244	0.24719	0.58796	0.2617
C245	0.25643	0.56881	0.27235
C246	0.24512	0.54391	0.23736
C247	0.22443	0.53789	0.19155
C248	0.26943	0.6398	0.26478
C249	0.28076	0.66523	0.29717
C250	0.259	0.61441	0.29802
C251	0.08557	0.27467	0.85859
C252	0.09892	0.30259	0.87733
C253	0.10324	0.31094	0.94069
C254	0.11597	0.33917	0.9606
C255	0.11962	0.34714	0.02287
C256	0.10647	0.27208	-0.008
C257	0.09604	0.24941	0.03323
C258	0.07266	0.24281	0.0716
C259	0.05997	0.25945	0.06897
C260	0.0704	0.28216	0.02759
C261	0.09363	0.28849	0.98868
N262	0.06161	0.21843	0.11056
C263	0.04051	0.21066	0.14908
C264	0.04009	0.16652	0.17567
C265	0.02971	0.14199	0.21091
C266	0.00911	0.13557	0.25728
C267	-0.0014	0.15378	0.2671
C268	0.00891	0.17831	0.23156
C269	0.02983	0.18487	0.18602
C270	-0.01051	0.08418	0.26206
C271	-0.02061	0.05924	0.29521
C272	-0.00144	0.10963	0.29443
N273	0.63043	0.86498	0.7378
N274	0.63045	0.86472	0.92611
N275	0.10653	0.31998	0.82757
N276	0.14633	0.40402	0.82915
C277	0.28648	0.05784	0.36373
C278	0.31482	0.07333	0.38187
C279	0.32342	0.07816	0.44503
C280	0.35214	0.09332	0.46434
C281	0.36035	0.09772	0.52653
C282	0.29834	0.04593	0.53528
C283	0.27667	0.03482	0.58023
C284	0.25732	0.04431	0.58417
C285	0.26002	0.06528	0.54289
C286	0.28167	0.07642	0.49817
C287	0.30088	0.06672	0.49388
N288	0.23468	0.03194	0.6291
C289	0.21498	0.03845	0.63176

C290	0.18966	0.00635	0.72186
C291	0.16625	-0.00626	0.7624
C292	0.14456	0.00025	0.75788
C293	0.14646	0.01928	0.71233
C294	0.16983	0.03192	0.67214
C295	0.19144	0.02549	0.67655
C296	0.0925	-0.02843	0.76528
C297	0.06732	-0.04282	0.79885
C298	0.11872	-0.01421	0.79688
C299	0.4635	0.15384	0.36443
C300	0.43518	0.13818	0.3824
C301	0.42658	0.13315	0.44551
C302	0.39785	0.11787	0.46456
C303	0.38959	0.11329	0.52667
C304	0.4513	0.16511	0.53689
C305	0.47288	0.17625	0.58211
C306	0.49253	0.16711	0.58547
C307	0.49022	0.14648	0.54323
C308	0.46864	0.13531	0.49821
C309	0.44911	0.14463	0.49455
N310	0.5151	0.1796	0.63068
C311	0.53512	0.17351	0.63322
C312	0.55981	0.20577	0.72392
C313	0.58327	0.21907	0.76435
C314	0.60561	0.21351	0.75944
C315	0.60424	0.19461	0.71372
C316	0.5808	0.18128	0.67362
C317	0.55859	0.18687	0.67831
C318	0.65767	0.2436	0.76664
C319	0.68285	0.2589	0.80017
C320	0.63151	0.22884	0.7983
C321	0.46347	0.15441	0.30045
C322	0.43512	0.13923	0.28213
C323	0.42654	0.13492	0.21887
C324	0.39786	0.11873	0.1994
C325	0.38964	0.11422	1.13725
C326	0.46684	0.17734	1.16775
C327	0.48974	0.18967	1.12604
C328	0.49537	0.17288	1.08644
C329	0.47752	0.14345	1.08839
C330	0.45461	0.13108	1.13027
C331	0.44925	0.14797	0.17043
N332	0.52013	0.18621	1.04726
C333	0.52691	0.17275	1.00765
C334	0.57328	0.21602	0.98218
C335	0.59854	0.2297	0.94762
C336	0.60403	0.21519	0.90098
C337	0.58405	0.18665	0.89004
C338	0.55882	0.17292	0.92486
C339	0.55326	0.18757	0.97082
C340	0.65669	0.2452	0.89842
C341	0.68253	0.25931	0.86633
C342	0.63088	0.22993	0.86491
C343	0.2865	0.05743	0.29973
C344	0.31485	0.07252	0.28158
C345	0.32343	0.07694	0.21837
C346	0.35213	0.09314	0.19918
C347	0.36039	0.09775	1.13711
C348	0.28293	0.0347	1.16651
C349	0.26001	0.02254	1.12469

C350	0.25457	0.03948	1.08554
C351	0.27264	0.06889	1.08803
C352	0.29555	0.08108	1.13001
C353	0.30073	0.06405	0.16974
N354	0.2298	0.02638	1.04624
C355	0.22343	0.04006	1.00666
C356	0.1765	-0.0026	0.98065
C357	0.15123	-0.01576	0.94591
C358	0.14634	-0.00089	0.8994
C359	0.16691	0.02744	0.88868
C360	0.19214	0.04064	0.92367
C361	0.1971	0.02566	0.96956
C362	0.09359	-0.02924	0.89711
C363	0.0677	-0.04273	0.86505
C364	0.1194	-0.01496	0.86348
N365	0.87422	0.10673	0.427
N366	0.87362	0.10702	0.23864
N367	0.3324	0.08241	0.33175
N368	0.41759	0.12914	0.33219
C369	0.91766	0.06351	0.36242
C370	0.90355	0.07715	0.38138
C371	0.89942	0.08113	0.44474
C372	0.88571	0.09556	0.46478
C373	0.88203	0.09968	0.52716
C374	0.93204	0.0879	0.53424
C375	0.94279	0.07719	0.5786
C376	0.93214	0.04821	0.58209
C377	0.9104	0.02994	0.54082
C378	0.89959	0.04063	0.49662
C379	0.91041	0.06969	0.49293
N380	0.94406	0.03791	0.62706
C381	0.93667	0.01162	0.6304
C382	0.96883	0.01969	0.72157
C383	0.98172	0.00981	0.76262
C384	0.9754	-0.01815	0.75846
C385	0.9561	-0.03603	0.71288
C386	0.94314	-0.0262	0.67217
C387	0.94955	0.00168	0.67604
C388	1.00536	-0.03935	0.76586
C389	1.02072	-0.04866	0.79943
C390	0.99064	-0.02827	0.79745
C391	0.82961	0.14947	0.36753
C392	0.84426	0.13617	0.38482
C393	0.84913	0.13228	0.44774
C394	0.86325	0.11806	0.4661
C395	0.86779	0.1142	0.52801
C396	0.81751	0.12558	0.53947
C397	0.80714	0.13635	0.58493
C398	0.81769	0.16533	0.58875
C399	0.839	0.1835	0.54679
C400	0.84941	0.17277	0.50153
C401	0.83864	0.14372	0.49735
N402	0.80579	0.1757	0.63388
C403	0.813	0.20198	0.63668
C404	0.78036	0.19457	0.72657
C405	0.76738	0.20486	0.76655
C406	0.77402	0.23289	0.76178
C407	0.7937	0.25044	0.71667
C408	0.80673	0.24021	0.67703
C409	0.80006	0.21227	0.68156

C410	0.74451	0.25466	0.76783
C411	0.72942	0.26453	0.80081
C412	0.75897	0.24355	0.80007
C413	0.8289	0.14906	0.30353
C414	0.84298	0.13535	0.2845
C415	0.84683	0.13106	0.22101
C416	0.86181	0.11788	0.20086
C417	0.86593	0.11413	1.13853
C418	0.80486	0.12997	1.1705
C419	0.79322	0.14092	1.12907
C420	0.81094	0.16325	1.08966
C421	0.8406	0.17438	1.09154
C422	0.85228	0.16346	1.13316
C423	0.83446	0.14127	0.1731
N424	0.79831	0.17496	1.0505
C425	0.81257	0.19511	1.01093
C426	0.76981	0.19859	0.98495
C427	0.75672	0.2102	0.95002
C428	0.77195	0.23004	0.90333
C429	0.80065	0.23844	0.89277
C430	0.81379	0.22688	0.92796
C431	0.79839	0.20681	0.97394
C432	0.74273	0.25265	0.89961
C433	0.72897	0.26413	0.86697
C434	0.75776	0.24209	0.86668
C435	0.91799	0.06415	0.2985
C436	0.9042	0.07829	0.28121
C437	0.90026	0.08303	0.21831
C438	0.88535	0.09641	0.19965
C439	0.8811	0.10049	1.13775
C440	0.94228	0.0858	1.16449
C441	0.95414	0.07499	1.12304
C442	0.93653	0.05145	1.08613
C443	0.90673	0.03897	1.09044
C444	0.89484	0.04977	1.13208
C445	0.91259	0.07317	0.16949
N446	0.94951	0.04005	1.04689
C447	0.93542	0.01931	1.00824
C448	0.97882	0.01703	0.98183
C449	0.99235	0.00581	0.94679
C450	0.97736	-0.01434	0.90017
C451	0.94848	-0.02346	0.88976
C452	0.93489	-0.01232	0.92511
C453	0.95003	0.00805	0.97106
C454	1.0072	-0.03624	0.89757
C455	1.02121	-0.04769	0.86556
C456	0.9919	-0.02625	0.86403
N457	0.87902	0.60842	0.42939
N458	0.87901	0.60883	0.24115
N459	0.89519	0.08632	0.33182
N460	0.85254	0.1274	0.33415
C461	0.9204	0.69585	0.36921
C462	0.90751	0.66788	0.38671
C463	0.90375	0.65926	0.44964
C464	0.88994	0.63089	0.46826
C465	0.88612	0.62266	0.53027
C466	0.89581	0.68343	0.5401
C467	0.90613	0.70462	0.58562
C468	0.93542	0.72395	0.59055
C469	0.95439	0.72176	0.5496

C470	0.9441	0.70057	0.50422
C471	0.91474	0.68135	0.49903
N472	0.94527	0.74617	0.63583
C473	0.97183	0.76587	0.64061
C474	0.96202	0.78977	0.7284
C475	0.9711	0.81297	0.76814
C476	0.99935	0.83548	0.76543
C477	1.01843	0.83451	0.72296
C478	1.00939	0.81128	0.6835
C479	0.98115	0.78894	0.68573
C480	1.01812	0.88631	0.76993
C481	1.02645	0.91112	0.8024
C482	1.00848	0.86111	0.80284
C483	0.83714	0.52125	0.36583
C484	0.85031	0.54915	0.38446
C485	0.85419	0.55751	0.44776
C486	0.86814	0.58581	0.46743
C487	0.87205	0.59382	0.52973
C488	0.86176	0.53313	0.53796
C489	0.85125	0.51187	0.58297
C490	0.82196	0.49241	0.58684
C491	0.8032	0.49458	0.54531
C492	0.81367	0.51585	0.5005
C493	0.84303	0.5352	0.49637
N494	0.81186	0.47021	0.63186
C495	0.78531	0.45033	0.63493
C496	0.79359	0.42648	0.72498
C497	0.78359	0.40341	0.76521
C498	0.75529	0.38104	0.76064
C499	0.73717	0.38201	0.71554
C500	0.74711	0.40507	0.67565
C501	0.77532	0.42729	0.67994
C502	0.73398	0.32985	0.7672
C503	0.72429	0.30509	0.80047
C504	0.74496	0.35558	0.79916
C505	0.83768	0.52142	0.30182
C506	0.85131	0.54943	0.28418
C507	0.8558	0.55804	0.22112
C508	0.86872	0.58637	0.20231
C509	0.87266	0.59463	1.14036
C510	0.85838	0.51887	1.16863
C511	0.84773	0.49632	1.12664
C512	0.8247	0.49034	1.0877
C513	0.81258	0.50751	1.09053
C514	0.82321	0.53008	1.1327
C515	0.84608	0.53578	0.17222
N516	0.81321	0.46592	1.04832
C517	0.79242	0.45875	1.00919
C518	0.79007	0.41352	0.9833
C519	0.7787	0.38861	0.94859
C520	0.75825	0.38267	0.9021
C521	0.74901	0.40182	0.89145
C522	0.76032	0.42672	0.92644
C523	0.781	0.43274	0.97225
C524	0.73601	0.33083	0.89902
C525	0.72468	0.3054	0.86663
C526	0.74644	0.35622	0.86577
C527	0.91987	0.69595	0.30521
C528	0.90652	0.66804	0.28647
C529	0.90219	0.65969	0.22311

C530	0.88947	0.63146	0.2032
C531	0.88582	0.62348	1.14093
C532	0.89896	0.69854	1.1718
C533	0.9094	0.72121	1.13057
C534	0.93277	0.72782	1.0922
C535	0.94547	0.71117	1.09483
C536	0.93504	0.68847	1.1362
C537	0.91181	0.68214	0.17511
N538	0.94382	0.7522	1.05323
C539	0.96492	0.75997	1.01472
C540	0.96535	0.80411	0.98813
C541	0.97572	0.82864	0.95289
C542	0.99632	0.83506	0.90652
C543	1.00684	0.81685	0.8967
C544	0.99653	0.79232	0.93224
C545	0.9756	0.78576	0.97777
C546	1.01594	0.88644	0.90174
C547	1.02605	0.91139	0.86859
C548	1.00688	0.861	0.86937
N549	0.37501	0.10565	0.426
N550	0.37498	0.1059	0.23769
N551	0.8989	0.65065	0.33623
N552	0.8591	0.56661	0.33465
C553	-0.03265	0.03087	0.39195
C554	-0.03295	0.03001	0.26587
C555	0.03796	-0.06046	0.76932
C556	0.03826	-0.05961	0.8954
C557	0.29318	0.69449	0.39314
C558	0.29342	0.69429	0.2671
C559	0.71226	0.27614	0.77066
C560	0.71202	0.27633	0.8967

5. Fabrication of working electrodes and electrochemical characterization

5.1 Fabrication of working electrodes

The as-obtained **ZJUT-1@Co@CF**, **ZJUT-1@CF**, **RuO_2@CF** were directly used as the working electrode without further treatments.

Pre-treatment of CF: The carbon fiber (CF) was cut into slices (1 cm × 1 cm) and successively ultrasonicated in HNO_3 (40 wt%), acetone, ethanol, and deionized water for 30 min. Then, the CF was dried under vacuum at 60 ℃ overnight.

Electrodes preparation: The **ZJUT-1@CF**、**ZJUT-1@Co@CF** and **RuO_2@CF** electrodes were prepared as follows: **ZJUT-1**、**ZJUT-1@Co** and **RuO_2** (4 mg) catalyst were dispersed in a 1.0 mL mixed solution containing 900 μL of ethanol and 100 μL of 5 wt% Nafion solution, followed by sonication for 1 h to mixing. Then, the solution was loaded onto the surfaces of CF, and the overall loading amount of **ZJUT-1**、**ZJUT-1@Co** and **RuO_2** catalysts was approximately 4 mg/cm^2.

5.2 Electrochemical characterization

All electrochemical measurements were carried out with a *CHI761E* (CH Instruments, Inc.,Shanghai) electrochemical workstation 1 M KOH solution (pH = 14). The electrochemical characterizations were conducted in a standard three-electrode electrochemical cell employing a Platinum plates counter electrode and a Ag/AgCl electrode reference electrode, and the working electrodes were 1 cm ×1 cm **ZJUT-1@Co@CF** electrode、**ZJUT-1@CF** electrode and **RuO_2@CF** electrode, respectively. All potentials measured were calibrated to RHE according to the following equation $E_{RHE} = E_{Ag/AgCl} + 0.059\ pH + 0.243\ V$, and the current density was normalized to the effective geometrical surface area of CF. All the LSV measurements for HER were carried out at a scan rate of 5 mV/s with 85% *iR*-corrections. Tafel plots derived from HER polarization curves obtained were fitted to the equation $\eta = b\ logj + a$ (overpotential η, current density j, Tafel slope b, and Tafel constant a).

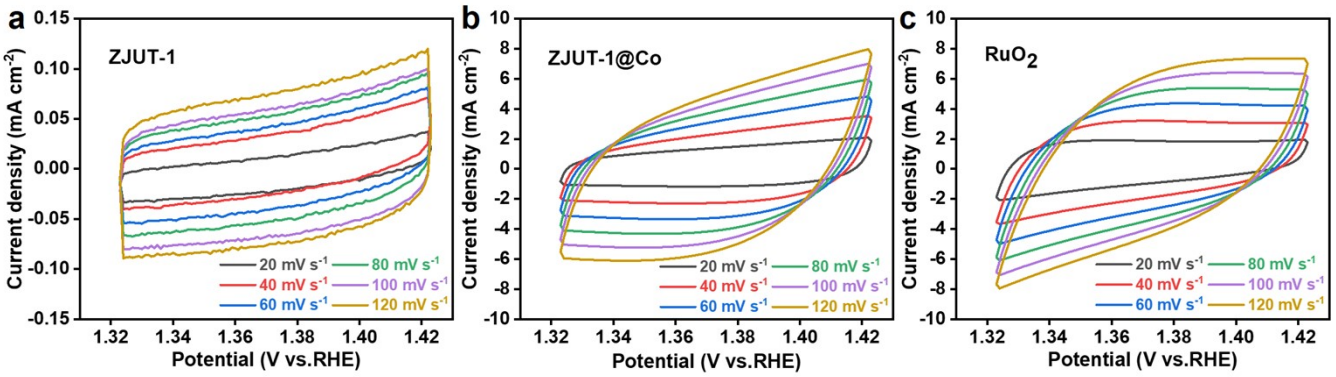


Figure S19. Cyclic voltammetry scans for as-prepared catalysts recorded at different rates ranging from 20 to 120 mV s^{-1} to calculate the electrochemical double-layer capacitances.

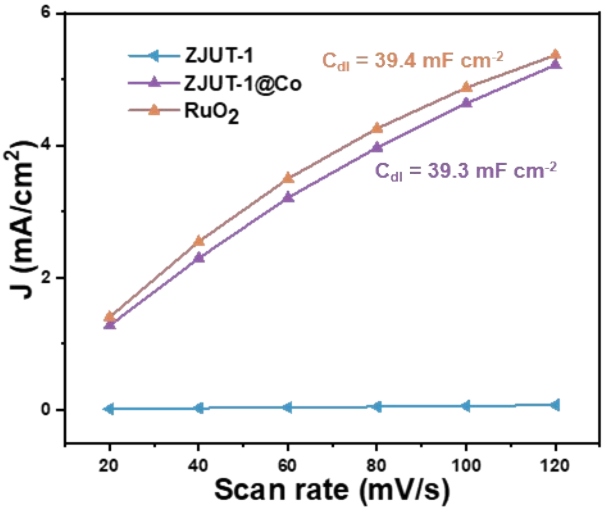


Figure S20. Capacitive currents versus scan rates on the basis of CV curves recorded at different scan rates.

Table S2. Comparative table for the OER performances with reported porphyrin-based catalysts.

Catalysts	Electrode	Electrolyte (KOH)	Loading (mg. cm^{-2})	η_{10} (mV)	Tafel (mV. dec^{-1})	Ref.
ZJUT-1@Co	**CF**	**1.0 M**	**4**	**295**	**63**	**This work**
Co-PDY/CF	CF	1.0 M	-	270	99	(6)
CoCOP	CFP	1.0 M	290	350	151	(7)
M-N_4/C	GC	1.0 M	0.25	407	60.3	(8)
$(CoP)_n$-MWCNTs	GC	1.0 M	0.14	410	60.8	(9)
CoTAPP-NA	GC	1.0 M	0.42	416	68	(10)
PCOF-1-Co	GC	1.0 M	0.643	473	89	(11)
PCOF-2-Co	GC	1.0 M	0.643	487	95	(11)

Table S3. Normalised current densities of RuO_2 and ZJUT-1@Co.

Catalysts[a]	Tafel slope (mV/dec)	η_{10} (mA cm^{-2})	J_0, geometrica (μA cm^{-2})[b]	C_{dl} (mF cm^{-2})	Relative surface area	J_0, normalized (μA cm^{-2})
RuO_2	81	1.582	1.408	39.4	1	1.40
ZJUT-1@Co	63	1.525	1.513	39.3	0.997	1.52

a) All the parameters were measured under the same conditions; b) Exchange current densities (J_0) were obtained from Tafel curves by using extrapolation methods.

6. Density functional theory calculations of OER performance

All the DFT calculations were performed by Vienna Ab initio Simulation Package (VASP)[12]. The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) was used to express the electron exchange-correlation and the projector augmented wave (PAW) was applied to describe the ionic cores[13,14]. The lattice parameters of ZJUT-1 and ZJUT-1@Co were 25.67 Å × 25.04 Å × 15 Å. Combining with the calculation accuracy and cost, the K-points were set to be 1 × 1 × 1 for geometry optimization and electronic structural calculations. The 400-eV plane wave energy cutoff was used in the calculations and the electronic energy and forces were converged to within 10^{-5} eV and 0.02 eV/Å, respectively. Furthermore, the VASP implicit solvent model was set to consider the effect of water[15].

The change in Gibbs free energy (ΔG) was calculated by computational hydrogen electrode (CHE) model[16]. In the CHE model, $H^+ + e^- \rightarrow 1/2\ H_2$ (g) was equilibrated at 0 V vs the reversible hydrogen electrode (RHE). Free energies (G) of each state can be obtained by the following equation,

$$G = E + ZPE + \int C_p dT - TS \qquad (1)$$

where E, ZPE are electronic energy and the zero-point energy, respectively. And $\int C_p dT$ and TS represent enthalpy change from 0 to T K contributed by molecular vibration, and entropy correction, which are obtained based on vibration analysis at 298.15 K. And related calculation results were treated by vaspkit[17].

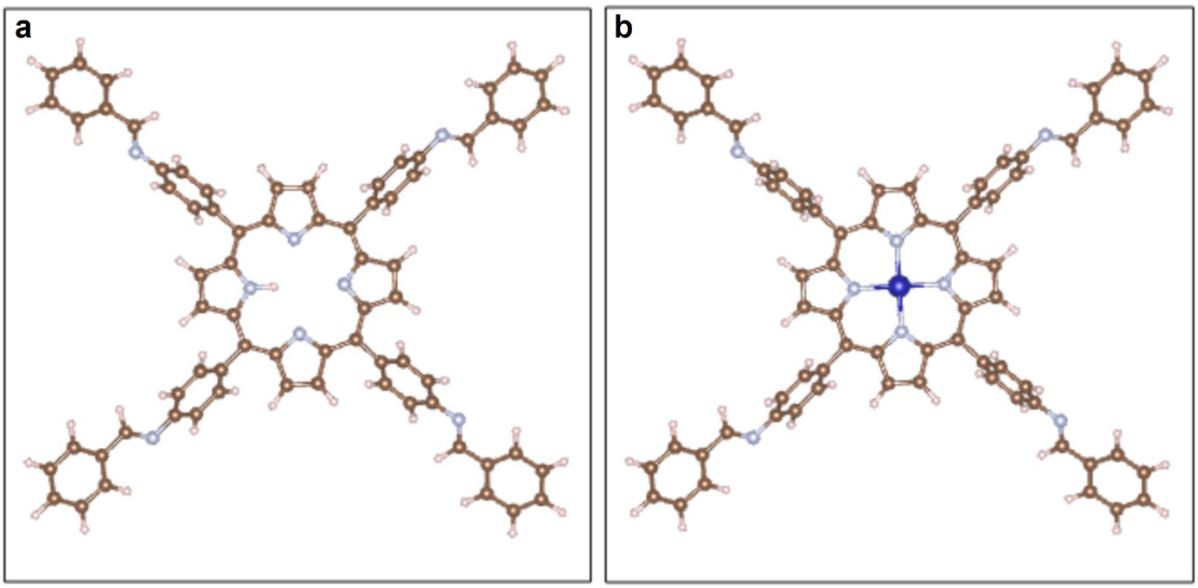
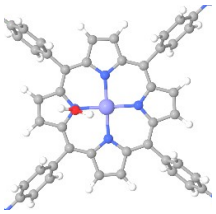
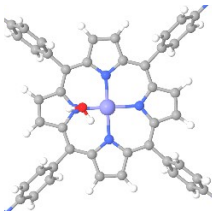
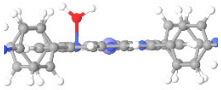
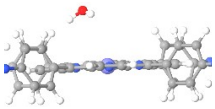
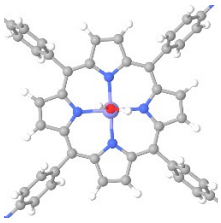
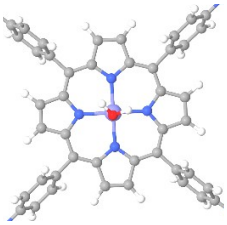
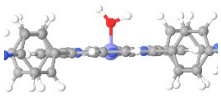
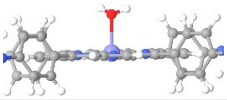


Figure S21. The optimized structures of (**a**) ZJUT-1 and (**b**) ZJUT-1@Co.

Table S4. The initial adsorption of H_2O molecules on N and Co sites of ZJUT-1@Co.

Adsorption sites	Adsorption before	Adsorption after	Distance (Å)	E_{ads} (eV)
N sites			3.57	-0.92
				
Co sites			2.25	-1.13
				

Theoretical calculations demonstrated that H_2O molecules are prone to be adsorbed on Co sites with a more stable adsorption energy (-1.13 eV) than that on N sites (-0.92 eV) in ZJUT-1@Co catalysts. Therefore, Co sites of ZJUT-1@Co catalysts were chosen as the active sites for calculation and selected to further explore their catalytic activity towards OER.

7. References

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