Supplemental information

2D Microporous Covalent Organic Frameworks as Cobalt Nanoparticle Supports for Electrocatalytic Hydrogen Evolution Reaction

Jialong Song [1, 2 §], Li Liao [1 §], Zerong Zhang [1], Yusran Yusran [1], Rui Wang [1], Jing Fang [1], Yaozu Liu [1], Yu Hou [2], Yujie Wang [1, *] and Qianrong Fang [1, *]

[1]*State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, Jilin University, Changchun 130012, P. R. China*

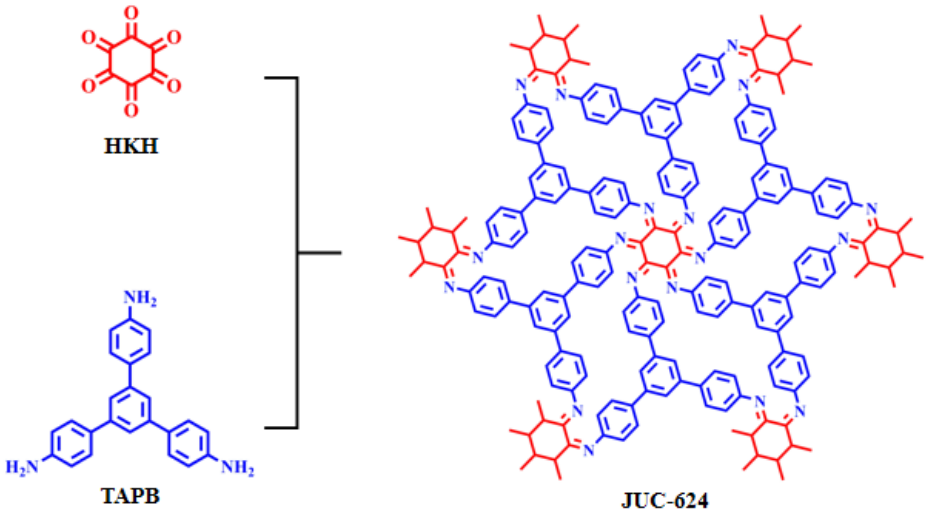
E-mail: qrfang@jlu.edu.cn or wyujie@jlu.edu.cn

[2]*School of Chemical Engineering and New Energy Materials, Zhuhai College of Science and Technology, Zhuhai 519041, P. R. China*。

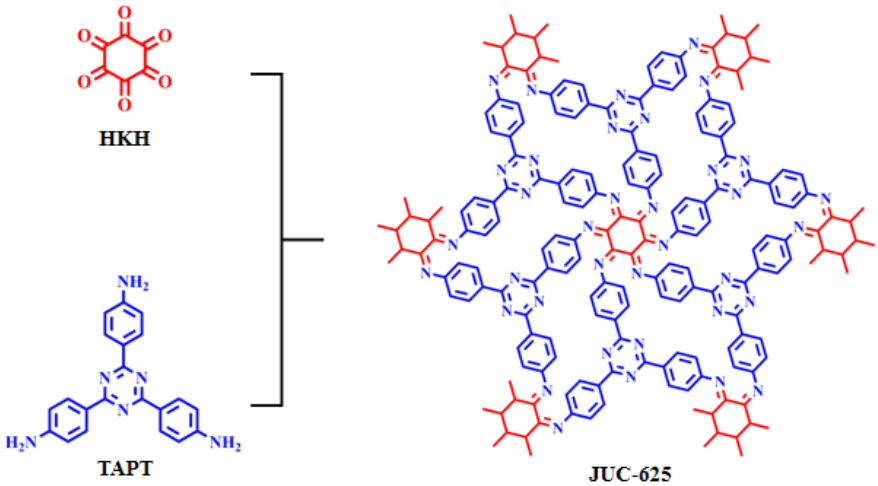
Table of contents

Section S1. Synthesis and characterization

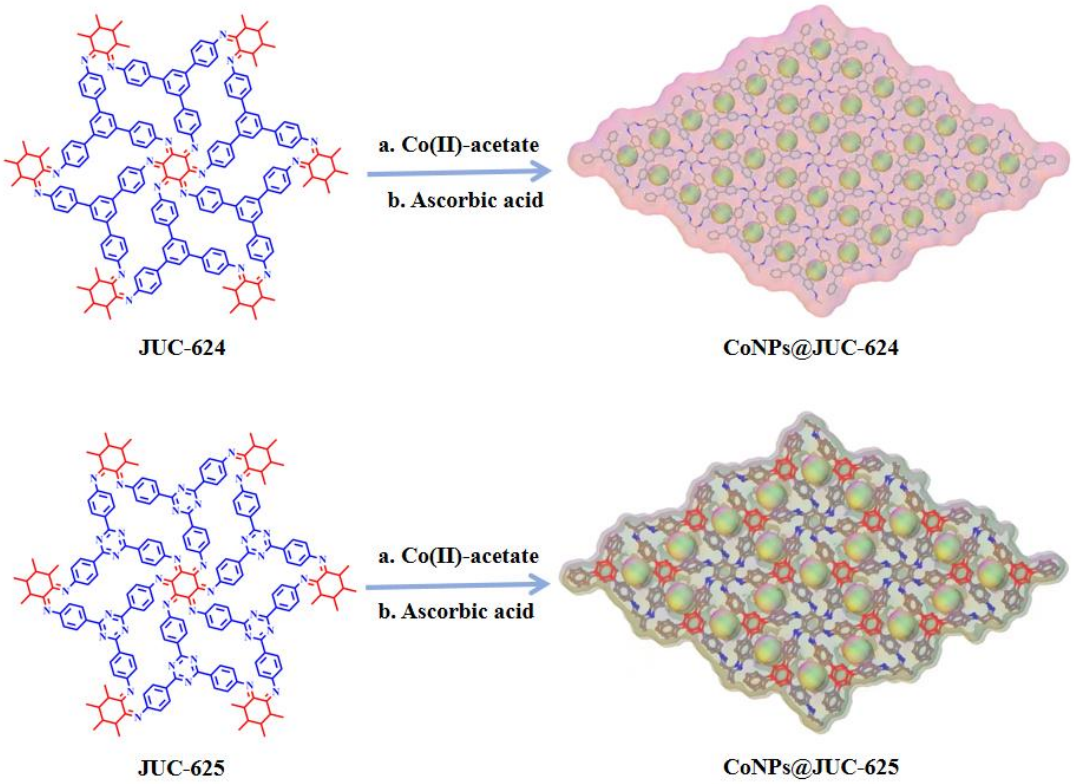
Scheme S1. Synthesis of JUC-624.



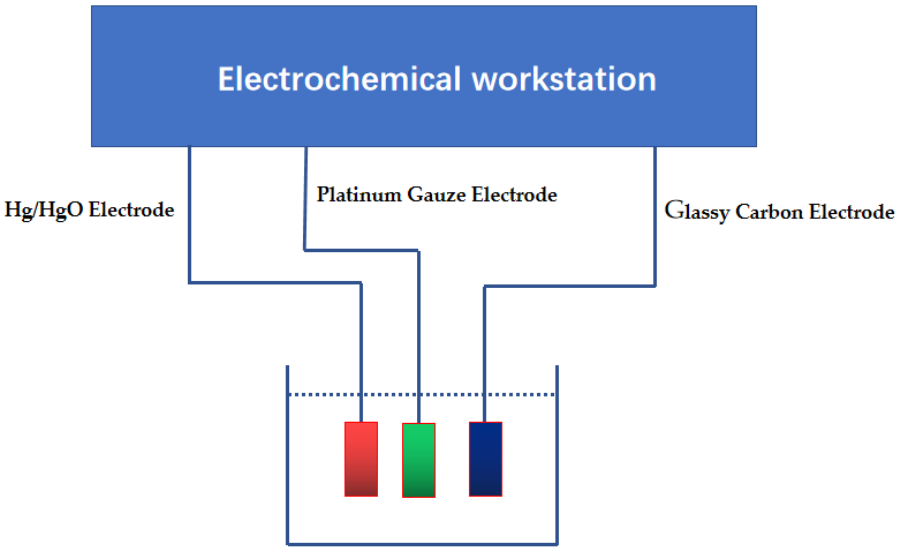
Scheme S2. Synthesis of JUC-625.



Scheme S3. Synthesis of CoNPs@JUC-624 and CoNPs@JUC-625.



Scheme S4. Electrochemical measurements.



Section S2. FT-IR spectra

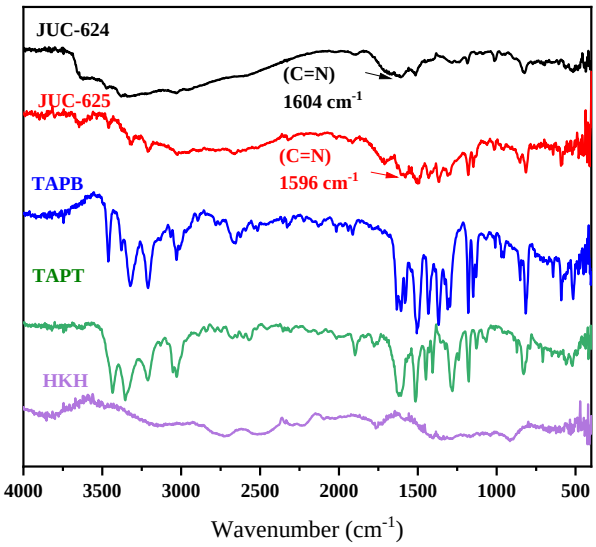


Figure S1. FT-IR spectra of JUC-624 (black), JUC-625 (red), TAPB (blue), TAPT (green), and HKH (purple).

Section S3. TGA curves

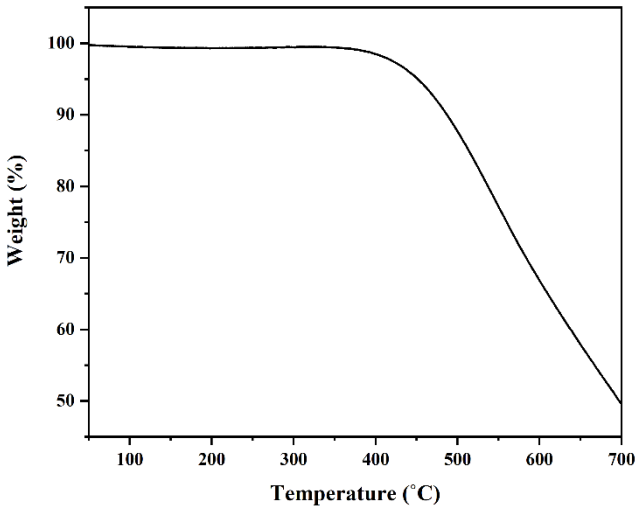


Figure S2. TGA curve of JUC-624.

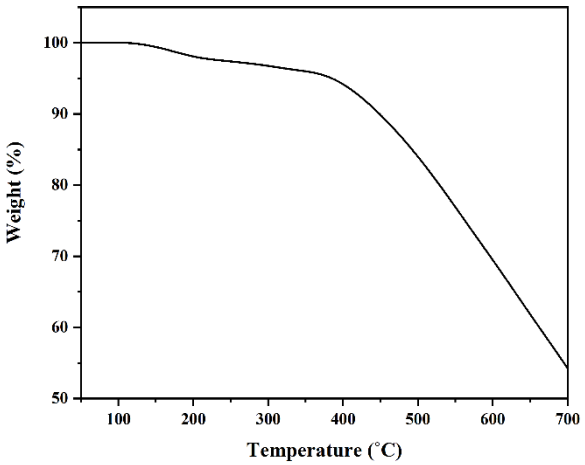


Figure S3. TGA curve of JUC-625.

Section S4. Nitrogen adsorption and pore size distribution

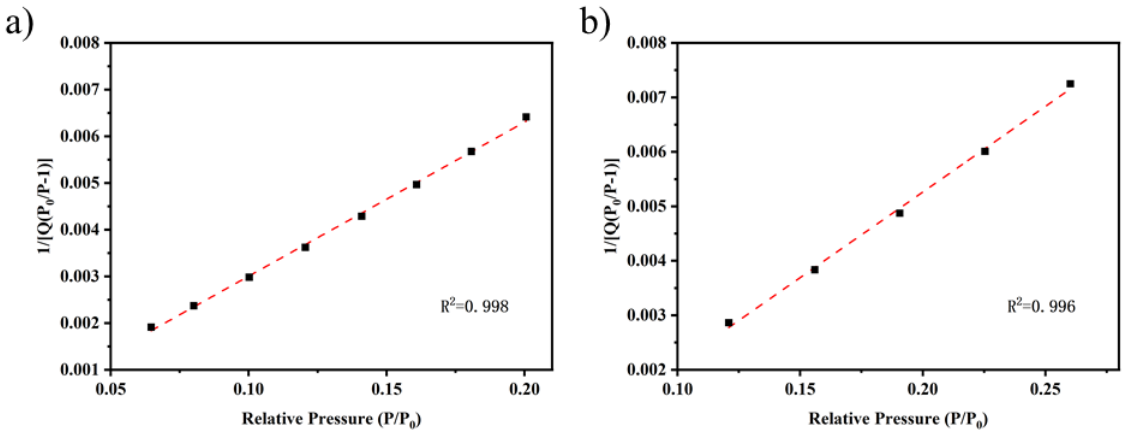


Figure S4. BET plots of JUC-624 (a) and JUC-625 (b) calculated from N_2 adsorption isotherm at 77 K.

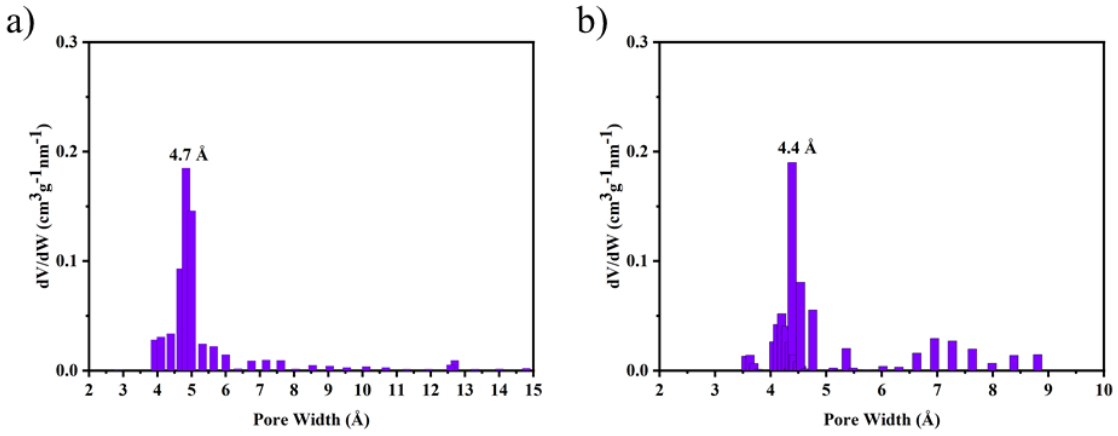


Figure S5. Pore-size distribution of JUC-624 (a) and JUC-625 (b) calculated by fitting on the NLDFT model to the adsorption data.

Section S5. SEM mapping for loading of cobalt

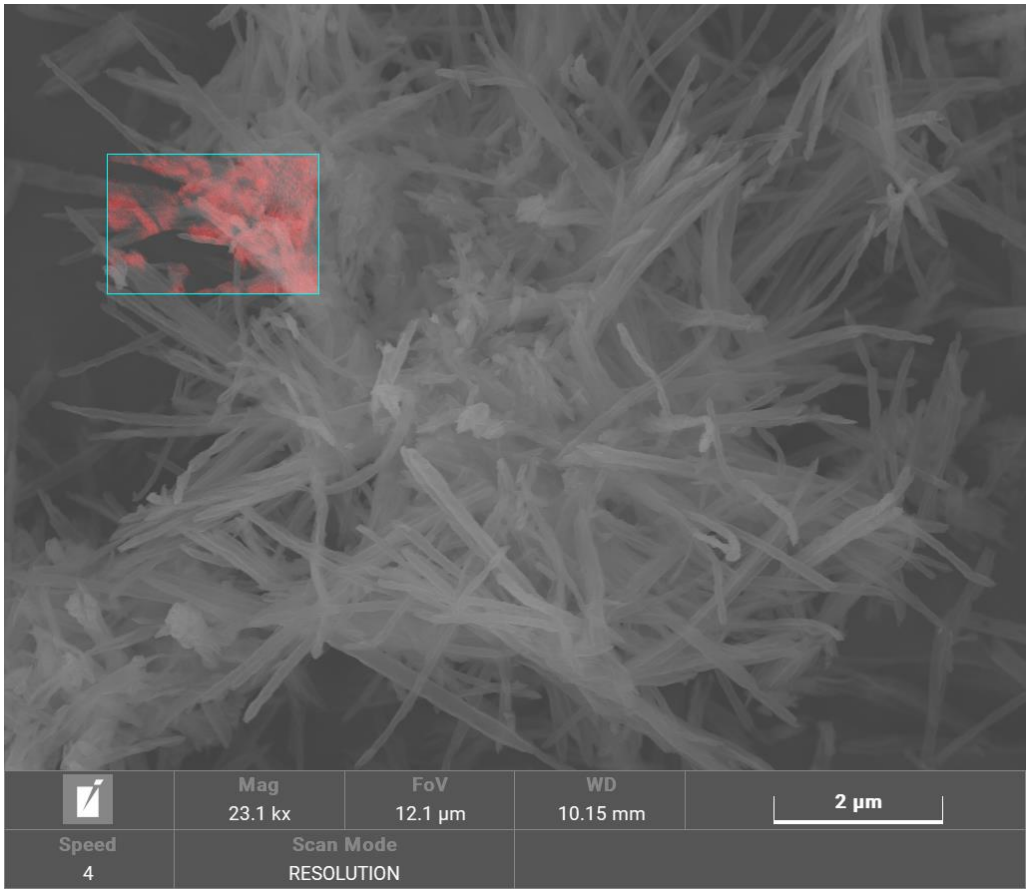


Figure S6. SEM-EDS mapping of Co(II)NPs@JUC-624.

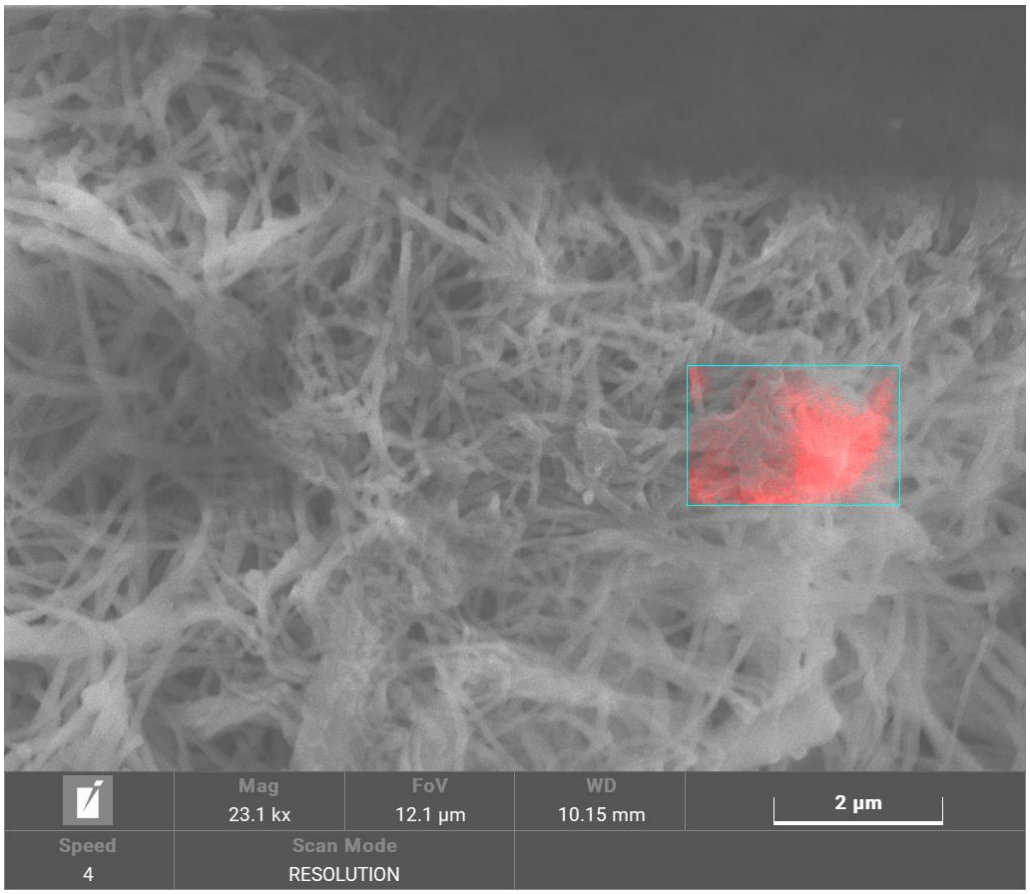


Figure S7. SEM-EDS mapping of Co(II)NPs@JUC-625.

Section S6. Electrochemical HER performance

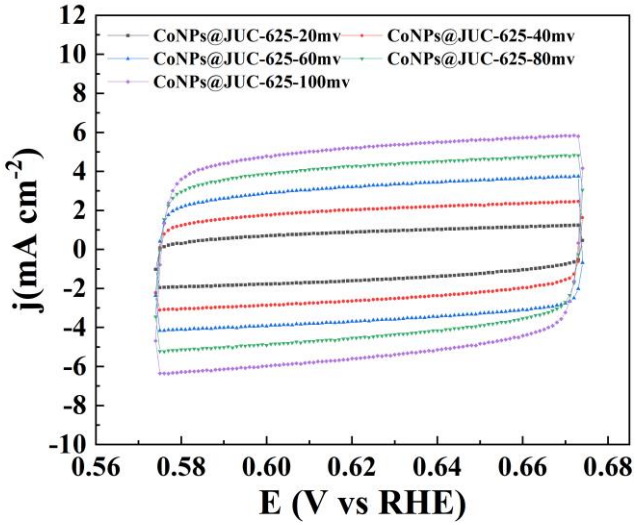


Figure S8. CV curves at different scan of CoNPs@JUC-625.

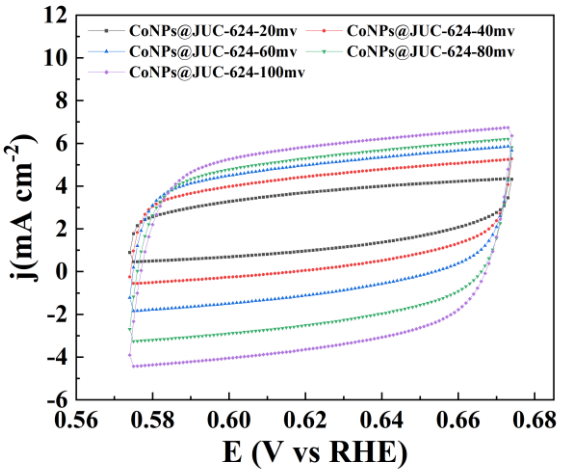


Figure S9. CV curves at different scan of CoNPs@JUC-624.

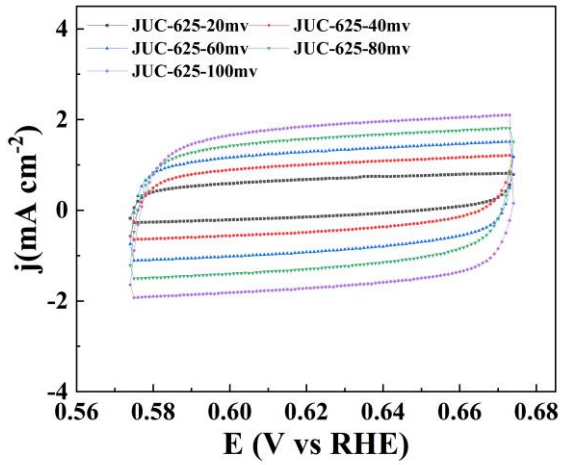


Figure S10. CV curves at different scan of JUC-625.

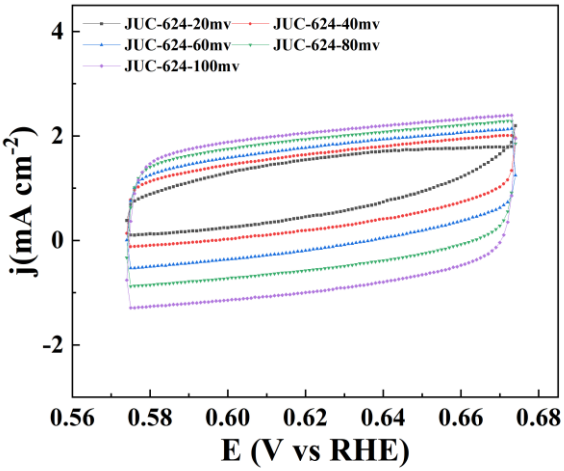


Figure S11. CV curves at different scan of JUC-624.

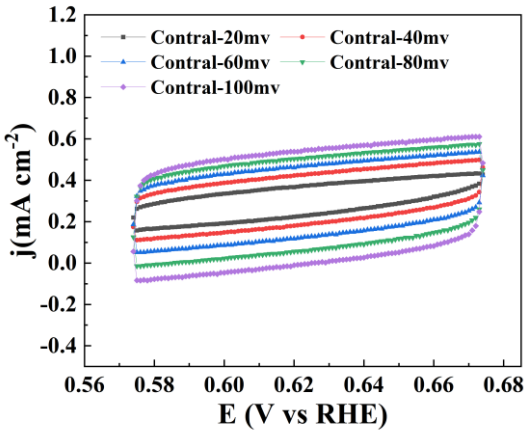


Figure S12. CV curves at different scan rates of GC.

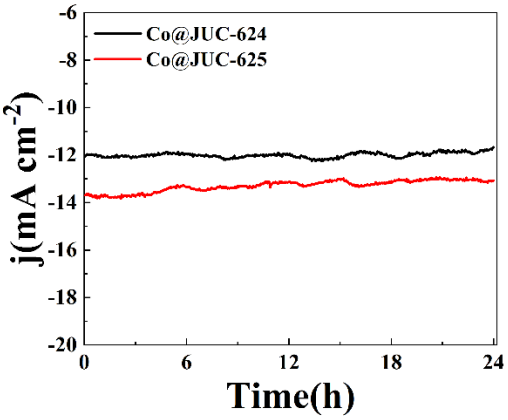


Figure S13. **i–t** curves of CoNPs@JUC-624 and CoNPs@JUC-625 for 24 h.

Table S1. Summary of COF-based materials as electrocatalysts for the HER in the literature.

COF-based electrocatalysts	Electrolyte	Loading [mg cm^{-2}]	$\eta_{J=10}$ [mV vs RHE]	b [mV dec^{-1}]	Ref.
CoNPs@JUC-624	1.0 M KOH	0.142	176	190	This work
CoNPs@JUC-625	1.0 M KOH	0.142	146	186	This work
TpPAM-COF	0.5 M H_2SO_4	–	250	106	1
COF/rGO-Ru	1.0 M KOH		42	46	2
Cu@2DCCOF1	–	–	541	130	3
Ru@COF	1.5 M H_2SO_4	0.305	212	75	4
C6-TRZ-TFP COF	0.5 m H_2SO_4	0.035	200	82	5

Section S7. PXRD patterns and structures

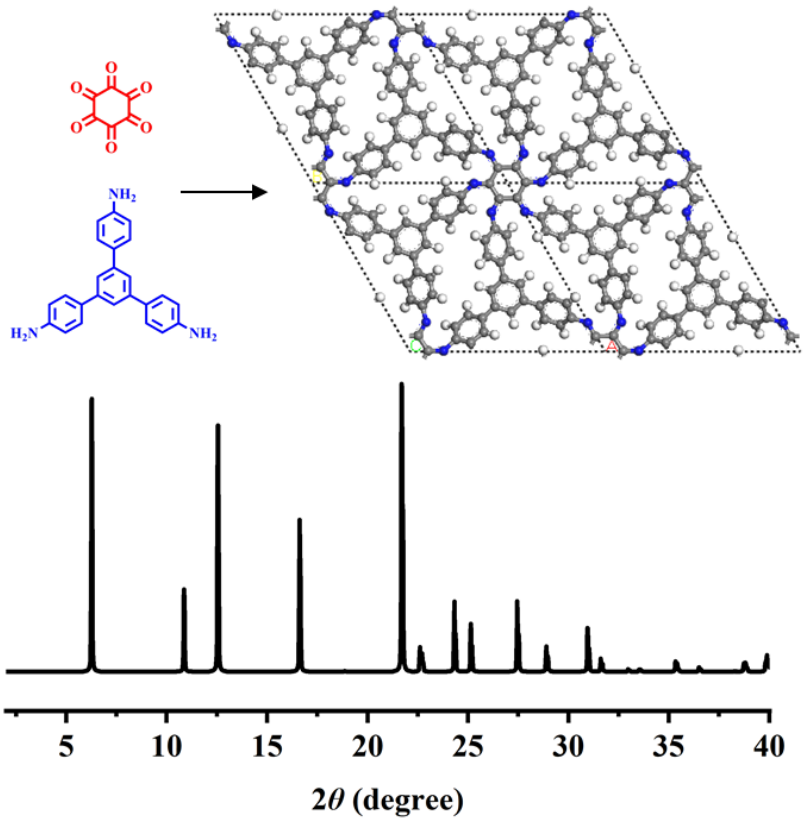


Figure S14. Calculated PXRD pattern of JUC-624 based on the AA-stacked **kgd** net.

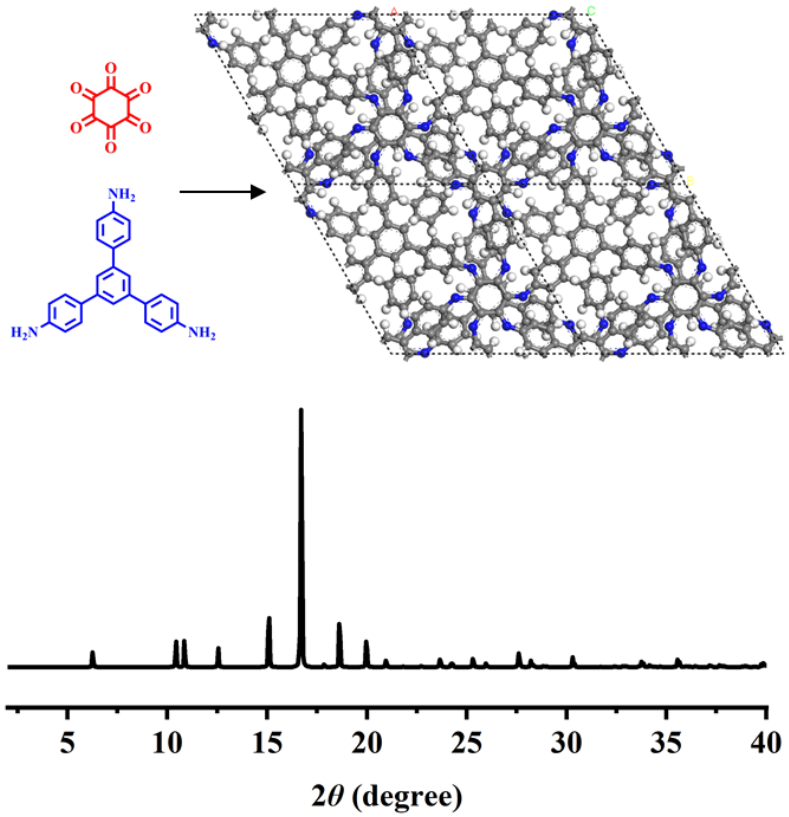


Figure S15. Calculated PXRD pattern of JUC-624 based on the AB-stacked **kgd** net.

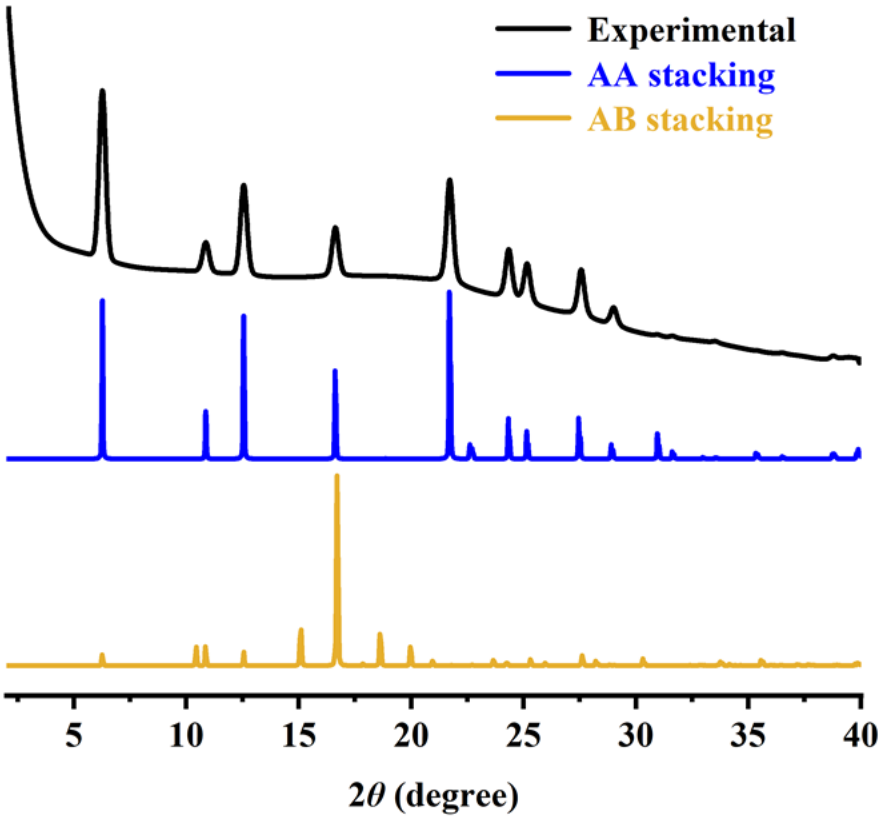


Figure S16. The comparison of PXRD patterns for JUC-624: calculated based on AA-stacked **kgd** net (blue), AB-stacked **kgd** net (yellow), and experimental (black).

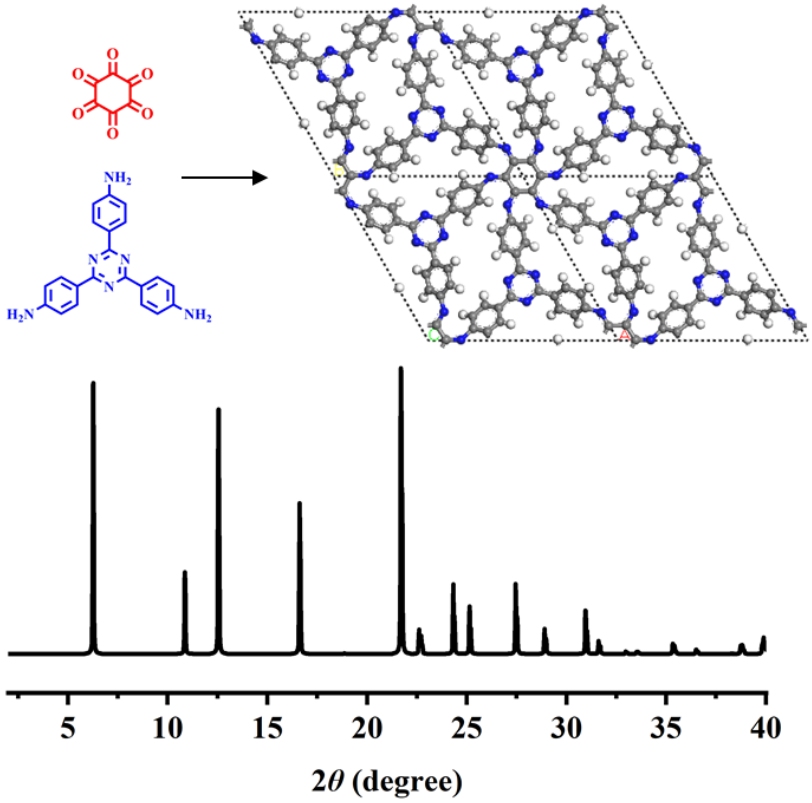


Figure S17. Calculated PXRD pattern of JUC-625 based on the AA-stacked **kgd** net.

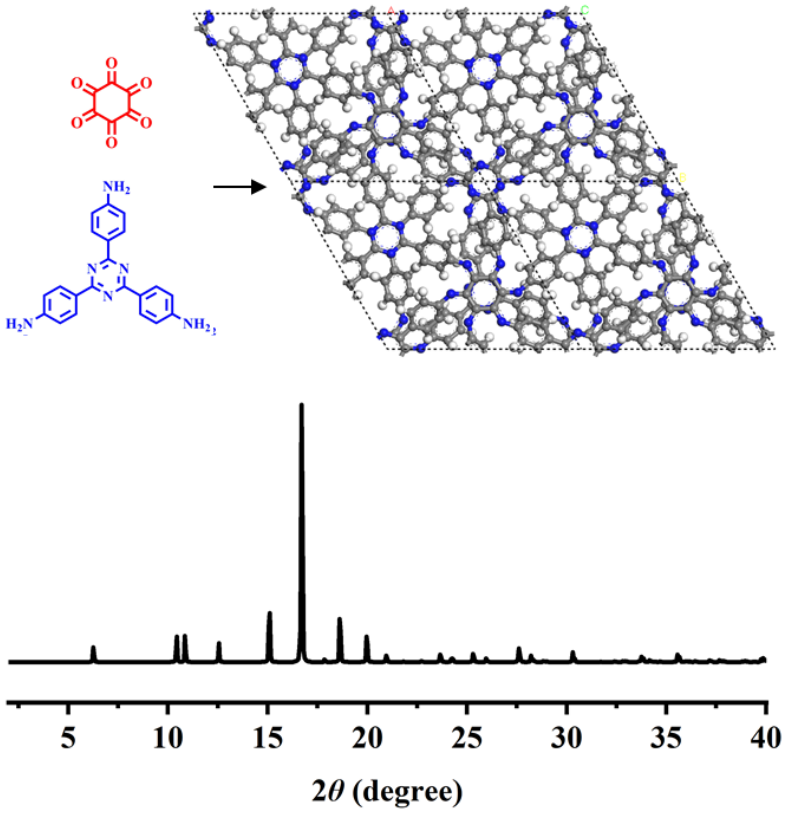


Figure S18. Calculated PXRD pattern of JUC-625 based on the AB-stacked **kgd** net.

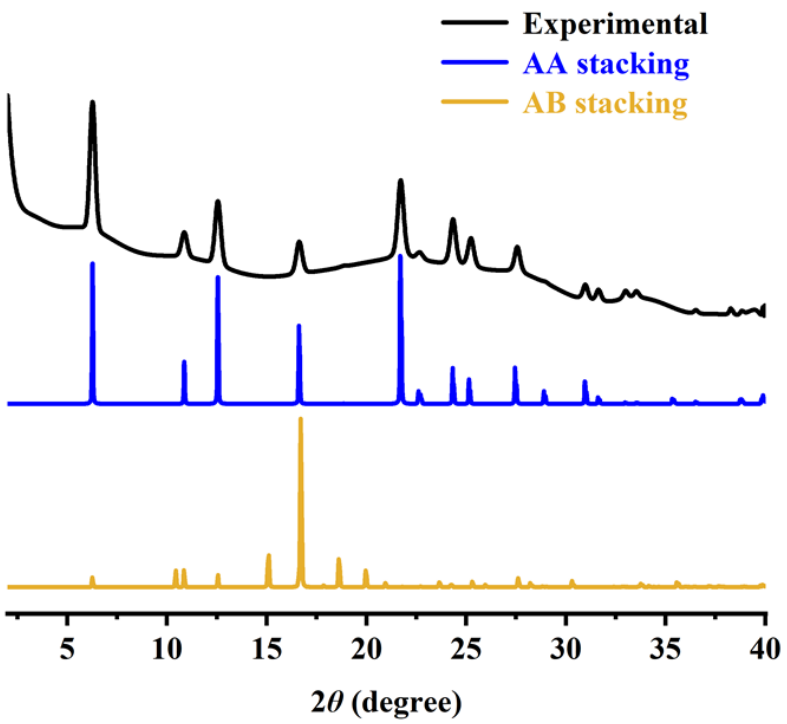


Figure S19. The comparison of PXRD patterns for JUC-625: calculated based on AA-stacked **kgd** net (blue), AB-stacked **kgd** net (yellow), and experimental (black).

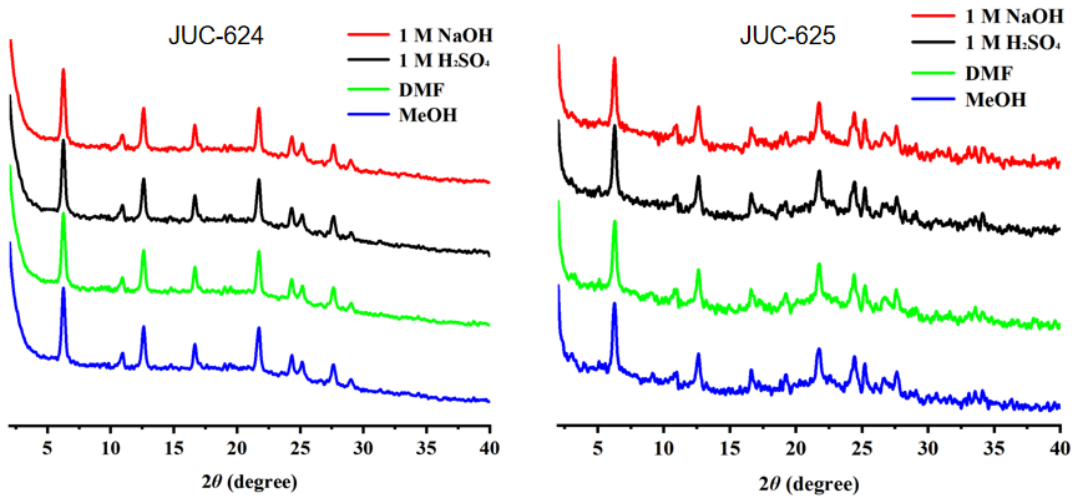


Figure S20. PXRD patterns of JUC-624 and JUC-625 after 24 hrs treatment in different solvents.

Section S8: Unit cell parameters and fractional atomic coordinates

Table S2. Unit cell parameters and fractional atomic coordinates for JUC-624 calculated based on the AA-stacked **kgd** net.

Space group		*P6*	
Calculated unit cell		$a = b = 16.2889$ Å, $c = 4.093$ Å, $\alpha = \beta = 90°$, $\gamma = 120°$	
Measured unit cell		$a = b = 16.2798$ Å, $c = 4.102$ Å, $\alpha = \beta = 90°$, $\gamma = 120°$	
Pawley refinement		Rp = 2.58%, Rwp = 3.53%	
atoms	x	y	z
C1	0.08945	0.09428	0.05663
N2	0.00424	0.83007	0.07566
C3	0.14863	0.84026	-0.17939
C4	0.21432	0.80911	-0.19362
C5	0.1987	0.72792	-0.01989
C6	0.11463	0.67864	0.16407
C7	0.05352	0.71504	0.19765
C8	0.0729	0.79944	0.04257
C9	0.23651	0.59993	-0.03113
C10	0.3029	0.5686	-0.03017
H11	0.15663	0.89517	-0.34629
H12	0.27388	0.84467	-0.35883
H13	0.09896	0.61567	0.30163
H14	0.99142	0.6781	0.3508
H15	0.16152	0.54823	-0.02967
C16	0.90572	0.99517	0.05663
N17	0.16993	0.17417	0.07566
C18	0.15974	0.30837	-0.17939
C19	0.19089	0.40521	-0.19362
C20	0.27208	0.47078	-0.01989
C21	0.32136	0.43599	0.16407
C22	0.28496	0.33848	0.19765
C23	0.20056	0.27346	0.04257
C24	0.40007	0.63658	-0.03113
C25	0.4314	0.7343	-0.03017
H26	0.10483	0.26146	-0.34629
H27	0.15533	0.42921	-0.35883
H28	0.38433	0.48329	0.30163
H29	0.3219	0.31332	0.3508

H30	0.45177	0.61329	-0.02967
C31	0.00483	0.91055	0.05663
N32	0.82583	0.99576	0.07566
C33	0.69163	0.85137	-0.17939
C34	0.59479	0.78568	-0.19362
C35	0.52922	0.8013	-0.01989
C36	0.56401	0.88537	0.16407
C37	0.66152	0.94648	0.19765
C38	0.72654	0.9271	0.04257
C39	0.36342	0.76349	-0.03113
C40	0.2657	0.6971	-0.03017
H41	0.73854	0.84337	-0.34629
H42	0.57079	0.72612	-0.35883
H43	0.51671	0.90104	0.30163
H44	0.68668	0.00858	0.3508
H45	0.38671	0.83848	-0.02967
C46	0.91055	0.90572	0.05663
N47	0.99576	0.16993	0.07566
C48	0.85137	0.15974	-0.17939
C49	0.78568	0.19089	-0.19362
C50	0.8013	0.27208	-0.01989
C51	0.88537	0.32136	0.16407
C52	0.94648	0.28496	0.19765
C53	0.9271	0.20056	0.04257
C54	0.76349	0.40007	-0.03113
C55	0.6971	0.4314	-0.03017
H56	0.84337	0.10483	-0.34629
H57	0.72612	0.15533	-0.35883
H58	0.90104	0.38433	0.30163
H59	0.00858	0.3219	0.3508
H60	0.83848	0.45177	-0.02967
C61	0.09428	0.00483	0.05663
N62	0.83007	0.82583	0.07566
C63	0.84026	0.69163	-0.17939
C64	0.80911	0.59479	-0.19362
C65	0.72792	0.52922	-0.01989
C66	0.67864	0.56401	0.16407
C67	0.71504	0.66152	0.19765
C68	0.79944	0.72654	0.04257
C69	0.59993	0.36342	-0.03113
C70	0.5686	0.2657	-0.03017

H71	0.89517	0.73854	-0.34629
H72	0.84467	0.57079	-0.35883
H73	0.61567	0.51671	0.30163
H74	0.6781	0.68668	0.3508
H75	0.54823	0.38671	-0.02967
C76	0.99517	0.08945	0.05663
N77	0.17417	0.00424	0.07566
C78	0.30837	0.14863	-0.17939
C79	0.40521	0.21432	-0.19362
C80	0.47078	0.1987	-0.01989
C81	0.43599	0.11463	0.16407
C82	0.33848	0.05352	0.19765
C83	0.27346	0.0729	0.04257
C84	0.63658	0.23651	-0.03113
C85	0.7343	0.3029	-0.03017
H86	0.26146	0.15663	-0.34629
H87	0.42921	0.27388	-0.35883
H88	0.48329	0.09896	0.30163
H89	0.31332	0.99142	0.3508
H90	0.61329	0.16152	-0.02967

Table S3. Unit cell parameters and fractional atomic coordinates for JUC-625 calculated based on the AA-stacked **kgd** net.

Space group		*P6*	
Calculated unit cell		$a = b = 16.3501$ Å, $c = 3.915$ Å, $\alpha = \beta = 90°$, $\gamma = 120°$	
Measured unit cell		$a = b = 16.3492$ Å, $c = 3.921$ Å, $\alpha = \beta = 90°$, $\gamma = 120°$	
Pawley refinement		Rp = 3.68%, Rwp = 4.68%	
atoms	x	y	z
C1	0.08945	0.09428	0.05663
N2	0.00424	0.83007	0.07566
C3	0.14863	0.84026	-0.17939
C4	0.21432	0.80911	-0.19362
C5	0.1987	0.72792	-0.01989
C6	0.11463	0.67864	0.16407
C7	0.05352	0.71504	0.19765
C8	0.0729	0.79944	0.04257
N9	0.23651	0.59993	-0.03113
C10	0.3029	0.5686	-0.03017
H11	0.15663	0.89517	-0.34629

H12	0.27388	0.84467	-0.35883
H13	0.09896	0.61567	0.30163
H14	0.99142	0.6781	0.3508
C15	0.90572	0.99517	0.05663
N16	0.16993	0.17417	0.07566
C17	0.15974	0.30837	-0.17939
C18	0.19089	0.40521	-0.19362
C19	0.27208	0.47078	-0.01989
C20	0.32136	0.43599	0.16407
C21	0.28496	0.33848	0.19765
C22	0.20056	0.27346	0.04257
N23	0.40007	0.63658	-0.03113
C24	0.4314	0.7343	-0.03017
H25	0.10483	0.26146	-0.34629
H26	0.15533	0.42921	-0.35883
H27	0.38433	0.48329	0.30163
H28	0.3219	0.31332	0.3508
C29	0.00483	0.91055	0.05663
N30	0.82583	0.99576	0.07566
C31	0.69163	0.85137	-0.17939
C32	0.59479	0.78568	-0.19362
C33	0.52922	0.8013	-0.01989
C34	0.56401	0.88537	0.16407
C35	0.66152	0.94648	0.19765
C36	0.72654	0.9271	0.04257
N37	0.36342	0.76349	-0.03113
C38	0.2657	0.6971	-0.03017
H39	0.73854	0.84337	-0.34629
H40	0.57079	0.72612	-0.35883
H41	0.51671	0.90104	0.30163
H42	0.68668	0.00858	0.3508
C43	0.91055	0.90572	0.05663
N44	0.99576	0.16993	0.07566
C45	0.85137	0.15974	-0.17939
C46	0.78568	0.19089	-0.19362
C47	0.8013	0.27208	-0.01989
C48	0.88537	0.32136	0.16407
C49	0.94648	0.28496	0.19765
C50	0.9271	0.20056	0.04257
N51	0.76349	0.40007	-0.03113
C52	0.6971	0.4314	-0.03017

H53	0.84337	0.10483	-0.34629
H54	0.72612	0.15533	-0.35883
H55	0.90104	0.38433	0.30163
H56	0.00858	0.3219	0.3508
C57	0.09428	0.00483	0.05663
N58	0.83007	0.82583	0.07566
C59	0.84026	0.69163	-0.17939
C60	0.80911	0.59479	-0.19362
C61	0.72792	0.52922	-0.01989
C62	0.67864	0.56401	0.16407
C63	0.71504	0.66152	0.19765
C64	0.79944	0.72654	0.04257
N65	0.59993	0.36342	-0.03113
C66	0.5686	0.2657	-0.03017
H67	0.89517	0.73854	-0.34629
H68	0.84467	0.57079	-0.35883
H69	0.61567	0.51671	0.30163
H70	0.6781	0.68668	0.3508
C71	0.99517	0.08945	0.05663
N72	0.17417	0.00424	0.07566
C73	0.30837	0.14863	-0.17939
C74	0.40521	0.21432	-0.19362
C75	0.47078	0.1987	-0.01989
C76	0.43599	0.11463	0.16407
C77	0.33848	0.05352	0.19765
C78	0.27346	0.0729	0.04257
N79	0.63658	0.23651	-0.03113
C80	0.7343	0.3029	-0.03017
H81	0.26146	0.15663	-0.34629
H82	0.42921	0.27388	-0.35883
H83	0.48329	0.09896	0.30163
H84	0.31332	0.99142	0.3508

Section S9. References

[1] B. C. Patra, S. Khilari, R. N. Manna, S. Mondal, D. Pradhan, A. Pradhan, A. Bhaumik, ACS Catalysis 2017, 7, 6120-6127.

[2] Q. Zhao, S. Chen, H. Ren, C. Chen, W. Yang, Industrial & Engineering Chemistry Research 2021, 60, 11070-11078.

[3] D. Zhou, X. Tan, H. Wu, L. Tian, M. Li, Angew Chem Int Ed Engl 2019, 58, 1376-1381.

[4] S. Maiti, A. R. Chowdhury, A. K. Das, ChemNanoMat 2019, 6, 99-106.

[5] S. Ruidas, B. Mohanty, P. Bhanja, E. S. Erakulan, R. Thapa, P. Das, A. Chowdhury, S. K. Mandal, B. K. Jena, A. Bhaumik, ChemSusChem 2021, 14, 5057-5064.