Supplemental information

Three-Dimensional Triptycene-Based Covalent Organic Frameworks with ceq or acs Topology

Hui Li,[1] Fengqian Chen,[1] Xinyu Guan,[1] Jiali Li,[1] Cuiyan Li,[1] Bin Tang,[2*] Valentin Valtchev,[3,4] Yushan Yan,[5] Shilun Qiu,[1] and Qianrong Fang[1*]

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

E-mail: qrfang@jlu.edu.cn

[2]*Deakin University, Institute for Frontier Materials, Geelong, Victoria 3216, Australia*

E-mail: bin.tang@deakin.edu.au

[3]*Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, 189 Songling Road, Laoshan District, Qingdao, Shandong 266101, P. R. China*

[4]*Normandie Université, ENSICAEN, UNICAEN, CNRS, Laboratoire Catalyse et Spectrochimie, 14000 Caen, France*

[5]*Department of Chemical and Biomolecular Engineering, Center for Catalytic Science and Technology, University of Delaware, Newark, DE 19716, USA*

Table of contents

Section S1. Materials and characterization

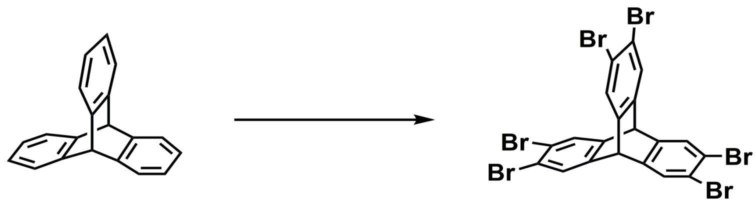
S1.1 Materials

All starting materials and solvents, unless otherwise noted, were purchased from J&K scientific LTD. The purity of the reagents and solvents were 95% and used without further purification. All products were isolated and handled under nitrogen using either glovebox or Schlenk line techniques.

S1.2 Instruments

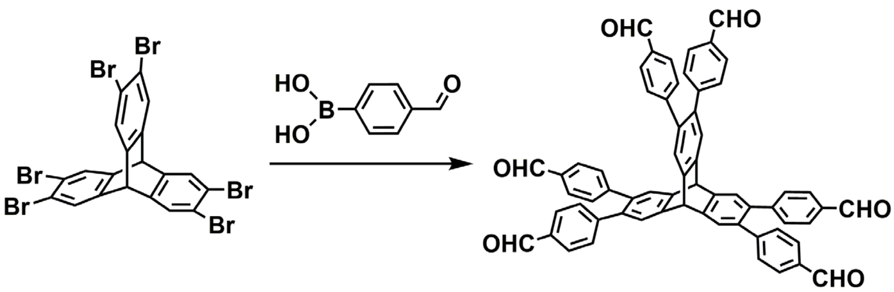
A Bruker AV-400 NMR spectrometer was used to collect the liquid ^{1}H NMR spectra. Solid-state ^{13}C NMR spectra were recorded on an AVIII 500 MHz solid-state NMR spectrometer. The FT-IR spectra (KBr) were obtained using a SHIMADZU IRAffinity-1 Fourier transform infrared spectrophotometer. Thermogravimetric analysis (TGA) was performed on a SHIMADZU DTG-60 thermal analyzer where the COFs were heated from 30 °C to 800 °C at a heating rate of 10 °C min^{-1} in nitrogen flow (30 mL min^{-1}). PXRD data were collected on a PANalytical B.V. Empyrean powder diffractometer using a Cu Kα source (λ = 1.5418 Å) over the range of 2θ = 2.0−40.0° with a step size of 0.02° and a counting time of 2 s per step. The sorption isotherm for N_2 was measured by using a Quantachrome Autosorb-IQ analyzer with ultra-high-purity gas (99.999% purity). Before gas adsorption measurements, the as-synthesized COFs (~50.0 mg) were immersed in acetone for 12 h (3 × 20.0 mL) and then acetone for another 12 h (3 × 5.0 mL). The acetone was then extracted under vacuum at 100 °C to afford the samples for sorption analysis. Other activation conditions have also been carried out, such as the use of THF or MeOH as exchange solvents and different degassing temperatures (80 or 120 °C); however, both COFs only obtain lower gas adsorption capacities under these conditions. To estimate pore size distributions for JUC-568 and JUC-569, nonlocal density functional theory (NLDFT) was employed to analyze the N_2 isotherm based on the model of N_2@77K on carbon with slit pores and the method of non-negative regularization. Scanning electron microscopy (SEM) images of the COFs were obtained using a JEOL JSM-6700 scanning electron microscope.

S1.3 Synthesis of 2,3,6,7,14,15-hexa(4′-formylphenyl)triptycene (HFPTP)[1]



(1) Synthesis of 2,3,6,7,14,15-hexabromotriptycene:

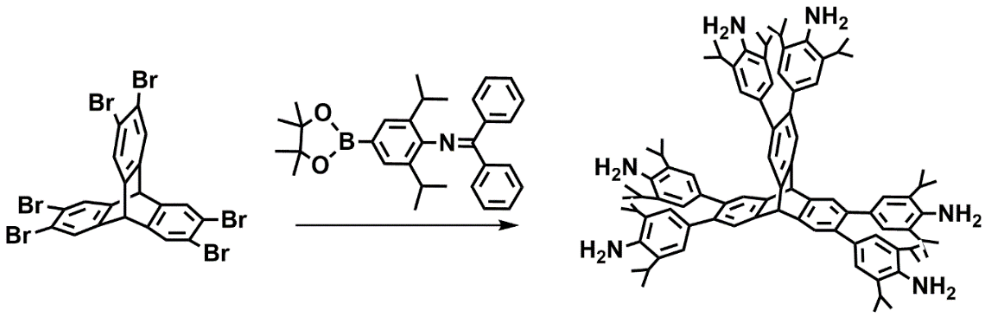
A mixture of triptycene (1.0 g, 3.9 mmol) and iron powder (80.0 mg, 1.45 mmol) was dissolved in 1,2-dichloroethane (60.0 mL). Bromine (1.32 mL, 25.7 mmol) was added slowly to the flask. Then the mixture was refluxed for 6 h. After the reaction was cooled to 25 °C, the solvent and excess bromine were removed under reduced pressure. The residue was loaded on a short column (silica, $CHCl_2$) to produce solid, which was recrystallized from $CHCl_3$ to give the pure product as colorless, needle-like crystals: (2.24 g, 3.1 mmol, 79%), m.p. > 350 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ (ppm) 7.62 (s, 6 H), 5.24 (s, 2 H).



(2) Synthesis of HFPTP:

A mixture of 2,3,6,7,14,15-hexabromotriptycene (500.0 mg, 0.69 mmol,), Cs_2CO_3 (2.9 g, 8.9 mmol), $Pd(PPh_3)_4$ (0.24 g, 0.2 mmol) and (4-formylphenyl) boronic acid (1.33 g, 8.9 mmol) was dissolved in anhydrous THF (50.0 mL) and the mixture was stirred and heated at 65 °C under an argon atmosphere for 17–18 h. Subsequently, the solvent was removed under reduced pressure and the residue was dissolved in CH_2Cl_2 (100.0 mL). The crude product was washed sequentially with saturated $NaHCO_3$ solution (100.0 mL), deionized H_2O (100.0 mL) and brine (100.0 mL). The organic phase was dried with $MgSO_4$ and filtered. The solvent was removed in a vacuum and the crude product was purified by column chromatography with silica gel (CH_2Cl_2/methanol, 25:1, v/v) and gave pure product as white crystals (426.0 mg, 0.48 mmol, 70 %), m.p. >300 °C. Rf = 0.55 (CH_2Cl_2/methanol, 20:1, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 9.94 (s, 6 H), 7.70 (d, J = 8.0

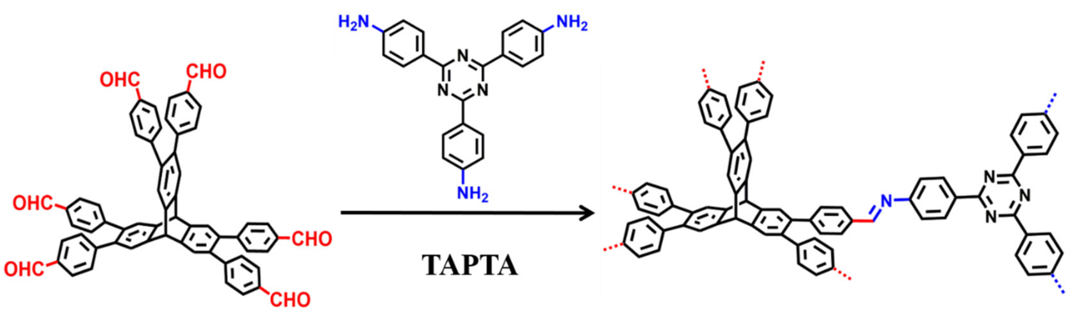
Hz, 12 H), 7.61 (s, 6 H), 7.22 (d, J = 8.0 Hz, 12 H), 5.75 (s, 2 H).



S1.4 Synthesis of 2,3,6,7,14,15-hexa (2′,6′-diisopropyl-4′-amino)triptycene (HDIATP)

A mixture of 2,3,6,7,14,15-hexabromotriptycene (500.0 mg, 0.69 mmol), Cs_2CO_3 (2.9 g, 8.9 mmol), $Pd(PPh_3)_4$ (0.16 g, 0.13 mmol) and *N*-(diphenylmethylene)-2,6-bis(1-methylethyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzenamine (3.5 g, 7.5 mmol) was dissolved in anhydrous THF (33.6 mL) and degassed H_2O (14.4 mL), the mixture was deoxygenated three times by a freeze-pump-thaw procedure, and then the mixture was stirred at 80 °C under an argon atmosphere for 72 h. After cooling to room temperature, the aqueous phase was removed by separation. Then ethyl acetate (25.0 mL) was added to precipitate the product. The organic phase was filtered and washed with ethyl acetate. The crude product was reserved for drying. Then crude product (900.0 mg, 0.4 mmol) was dissolved in 300.0 mL of THF and charged with 40.0 mL of 4 M aqueous HCl. The resulting solution was subjected to heating at 70 °C and kept at this temperature for 24 h. After cooling to room temperature, the resulting solution was neutralized with 1 M NaOH solution until pH = 7. Then white product was filtered off, washed with excess of ethanol and dried at 60 °C under vacuum (449.6 mg, 87%). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.54 (s, 6 H), 6.70 (s, 12 H), 5.63 (s, 2 H), 2.79 (s, 12 H), 1.04 (d, 72 H).

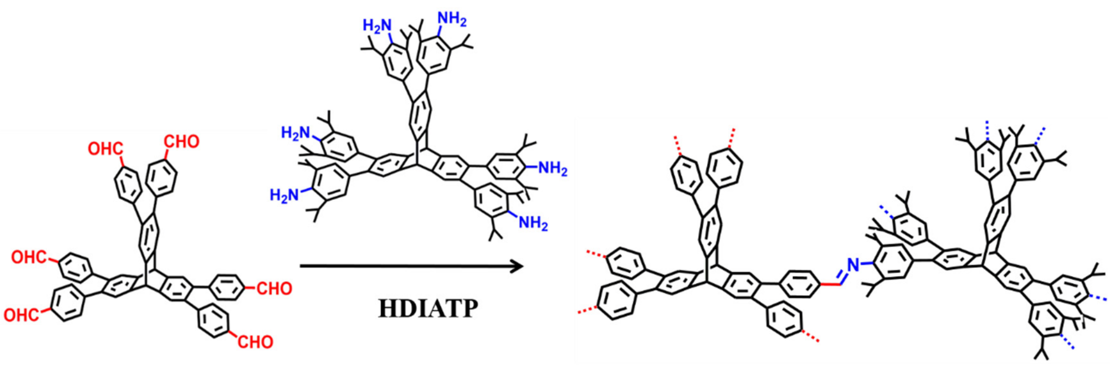
S1.5 Synthesis of JUC-568



HFPTP JUC-568

HFPTP (0.025 mmol, 22.0 mg) and TAPTA (0.05 mmol, 17.7 mg) were weighted into a Pyrex tube (volume: ca. 20.0 mL with a body length of 18.0 cm and neck length of 9.0 cm), and the mixture was added into 0.7 mL of mesitylene, 0.3 mL of dioxane and 0.1 mL of acetic acid (6 M). The Pyrex tube was flash frozen in a liquid nitrogen bath, evacuated to an internal pressure of ca. 19.0 mbar and flame-sealed, reducing the total length by ca. 10.0 cm. Upon warming to room temperature, the tube was placed in an oven at 120 °C for three days. As a result, a pale brown powder was isolated by centrifugation and washed with acetone (3 × 5.0 mL) and the yield is about 80%. The synthesis of JUC-568 is repeatable and scalable. When scaling up the amount of linkers while keeping solvent and catalyst in the same proportion, the high quality of JUC-568 can be obtained. Anal. Cald: C: 84.44; H: 4.19; N: 11.37. Found: C: 83.42; H: 4.16; N: 11.42.

S1.6 Synthesis of JUC-569



HFPTP JUC-569

HFPTP (0.025 mmol, 22.0 mg) and HDIATP (0.025 mmol, 32.3 mg) were weighted into a Pyrex tube (volume: ca. 20.0 mL with a body length of 18.0 cm and neck length of 9.0 cm), and the mixture was added into 0.2 mL of *o*-dichlorobenzene, 0.8 mL of *n*-butanol and 0.2 mL of acetic acid (9 M).

The Pyrex tube was flash frozen in a liquid nitrogen bath, evacuated to an internal pressure of ca. 19.0 mbar and flame-sealed, reducing the total length by ca. 10.0 cm. Upon warming to room temperature, the tube was placed in an oven at 120 °C for three days. As a result, a pale brown powder was isolated by centrifugation and washed with acetone (3 × 5.0 mL) and the yield is about 83%. Similar to JUC-568, the synthesis of JUC-569 is repeatable and scalable. When scaling up the amount of linkers while keeping solvent and catalyst in the same proportion, the high quality of JUC-569 can be also obtained. Anal. Cald: C: 90.97; H: 3.97; N: 5.06. Found: C: 90.86; H: 3.88; N: 5.26.

Section S2. SEM images

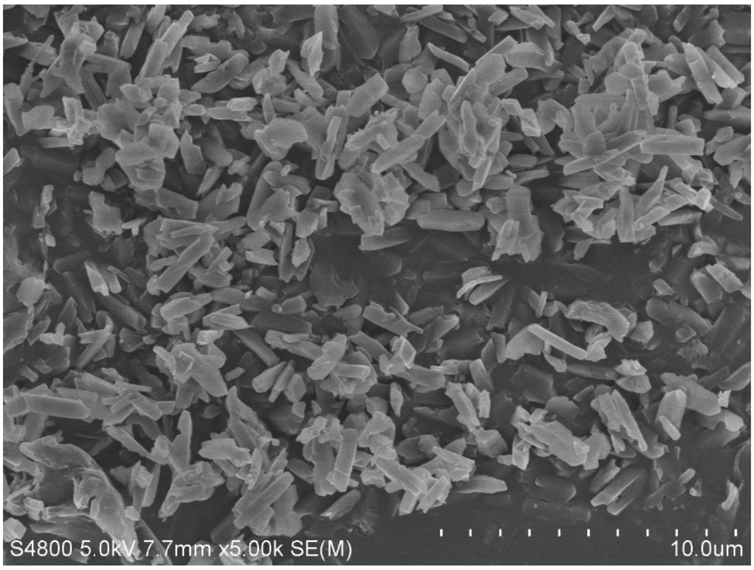


Figure S1. SEM image of JUC-568.

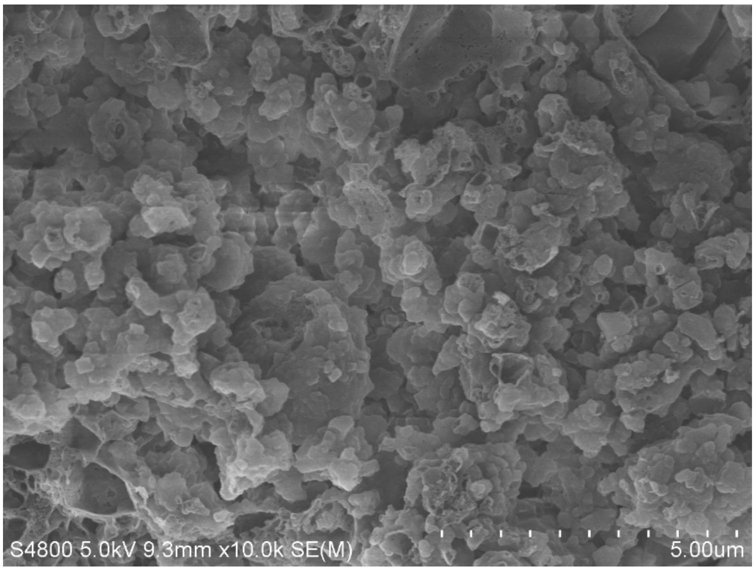


Figure S2. SEM image of JUC-569.

Section S3. FT-IR spectra

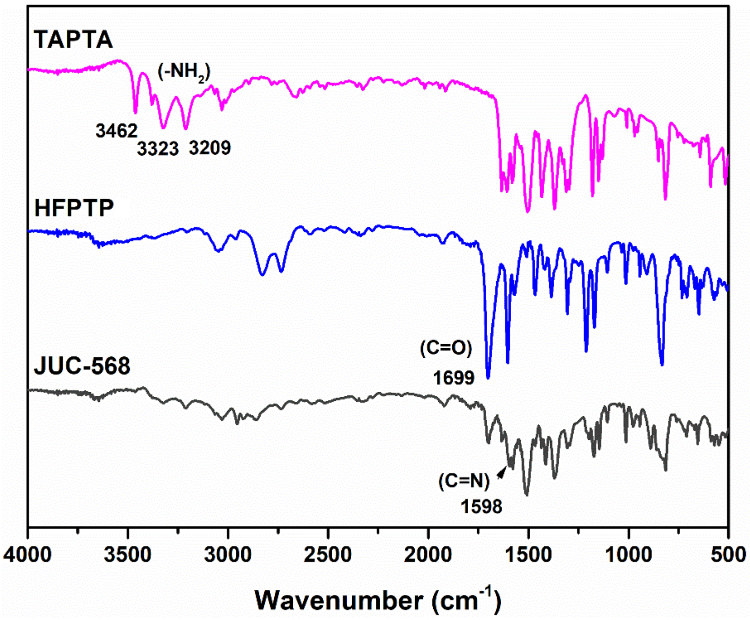


Figure S3. FT-IR spectra of JUC-568 (black), HFPTP (blue) and TAPTA (purple).

Section S4. Solid-state ^{13}C NMR spectra

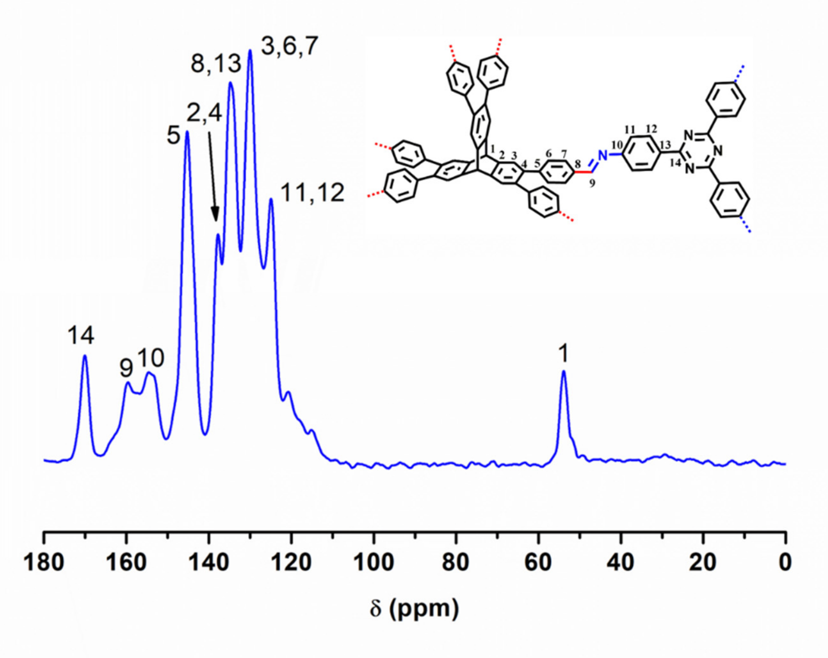


Figure S4. Solid state ^{13}C NMR of JUC-568.

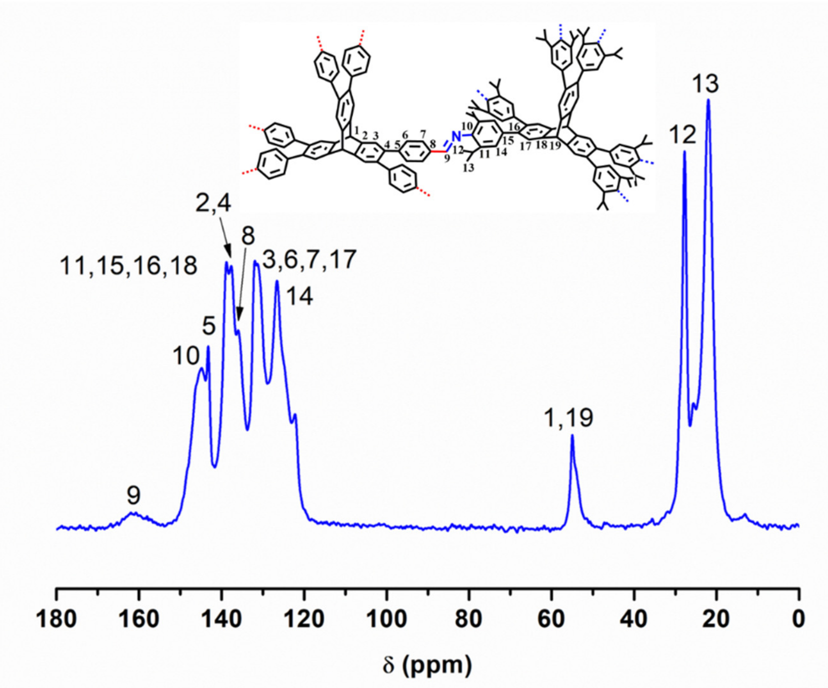


Figure S5. Solid state ^{13}C NMR of JUC-569.

Section S5. TGA curves

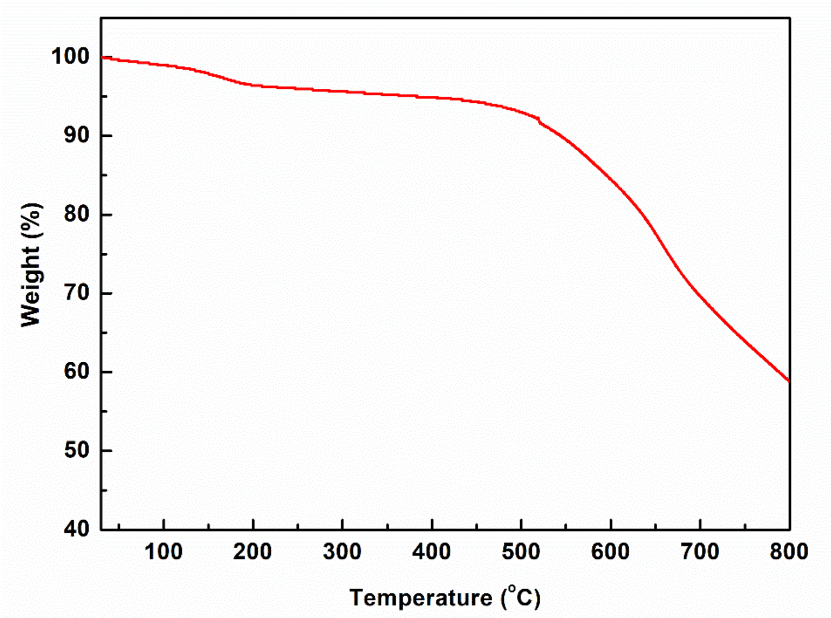


Figure S6. TGA curve of JUC-568.

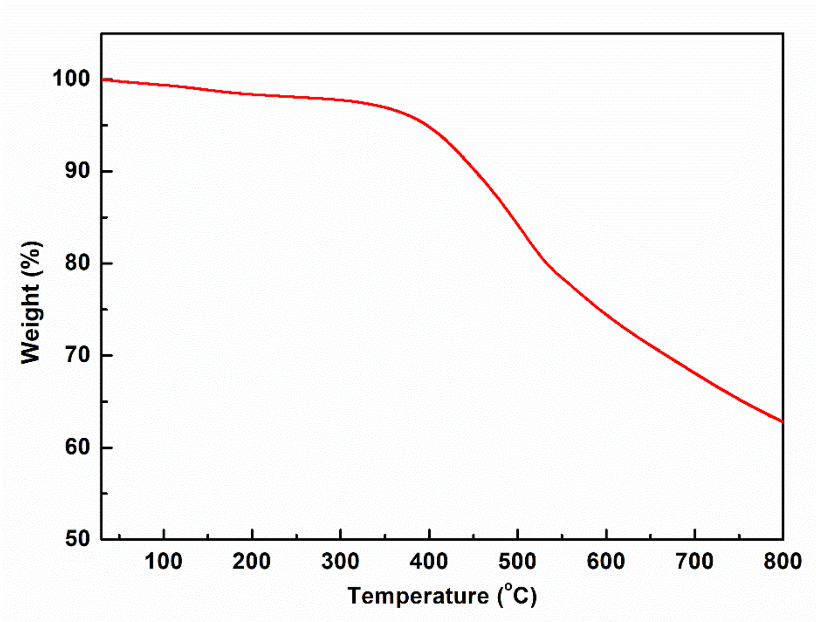


Figure S7. TGA curve of JUC-569.

Section S6: PXRD patterns and structures

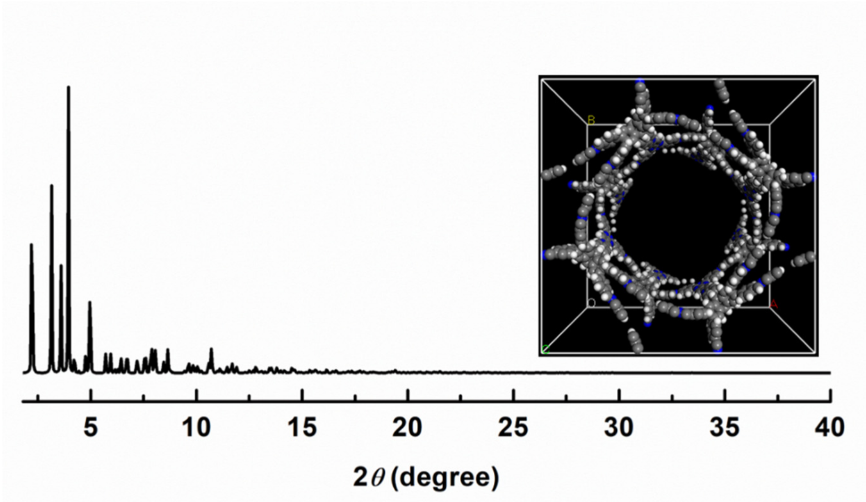


Figure S8. Calculated PXRD pattern of JUC-568 based on **sab** net.

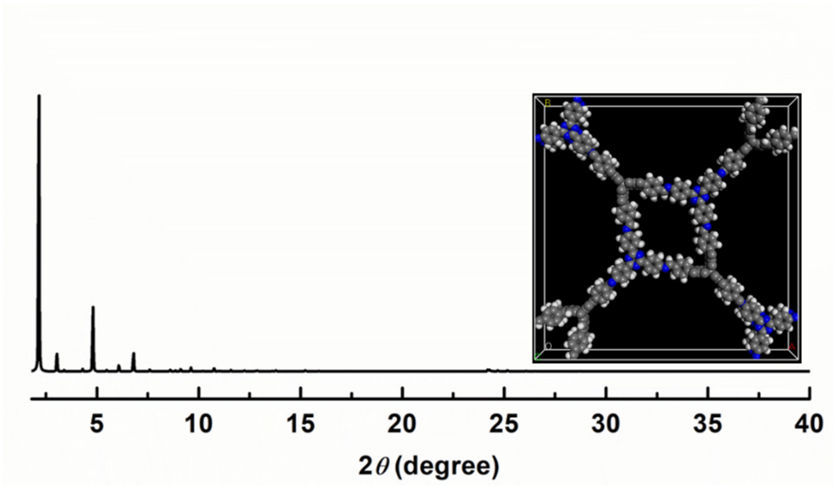


Figure S9. Calculated PXRD pattern of JUC-568 based on **dag** net.

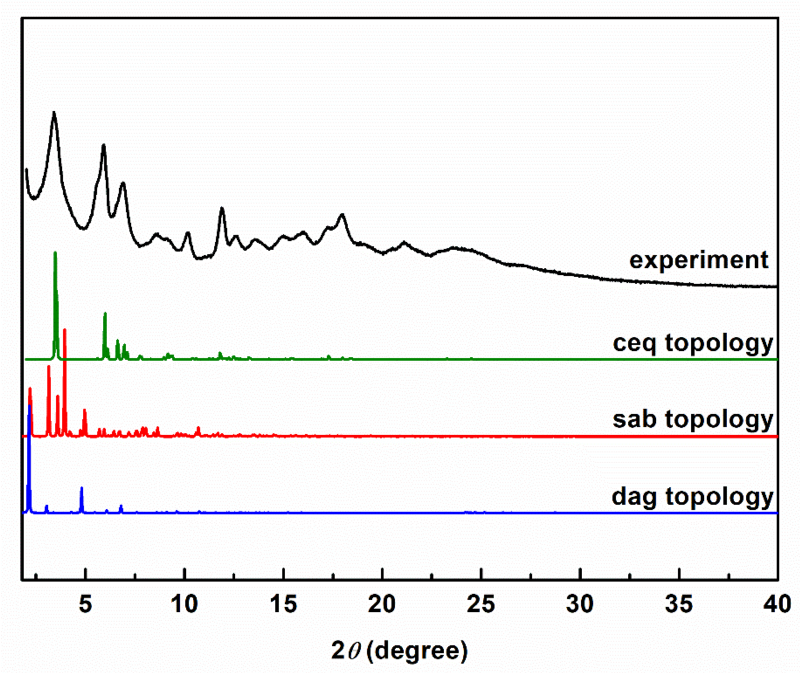


Figure S10. Comparison of PXRD patterns for JUC-568: experimental (black), **ceq** topology (green), **sab** topology (red), and **dag** topology (blue).

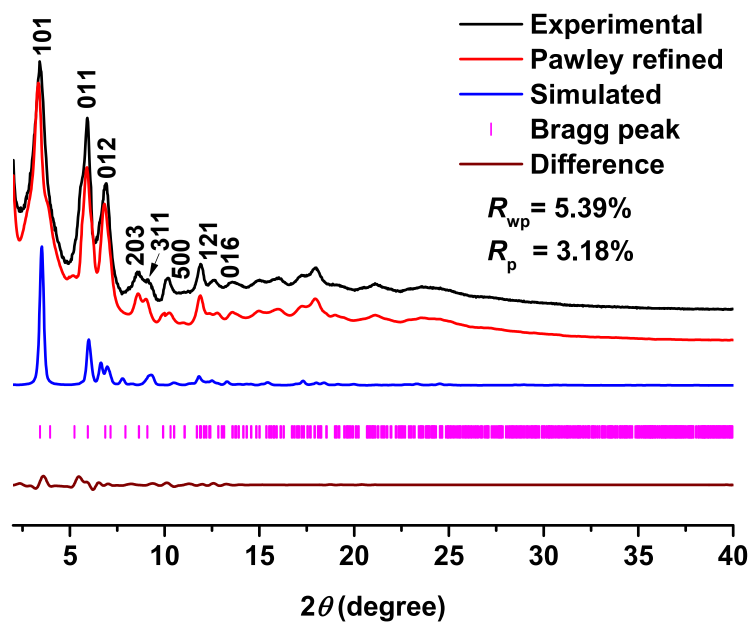


Figure S11. PXRD pattern of JUC-568.

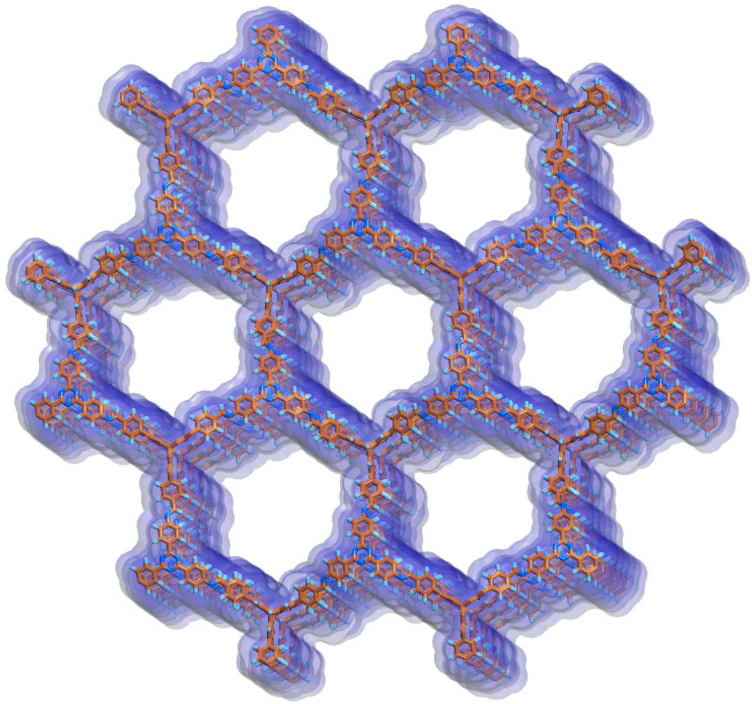


Figure S12. Extended structures of JUC-568 viewed along *c*-axis.

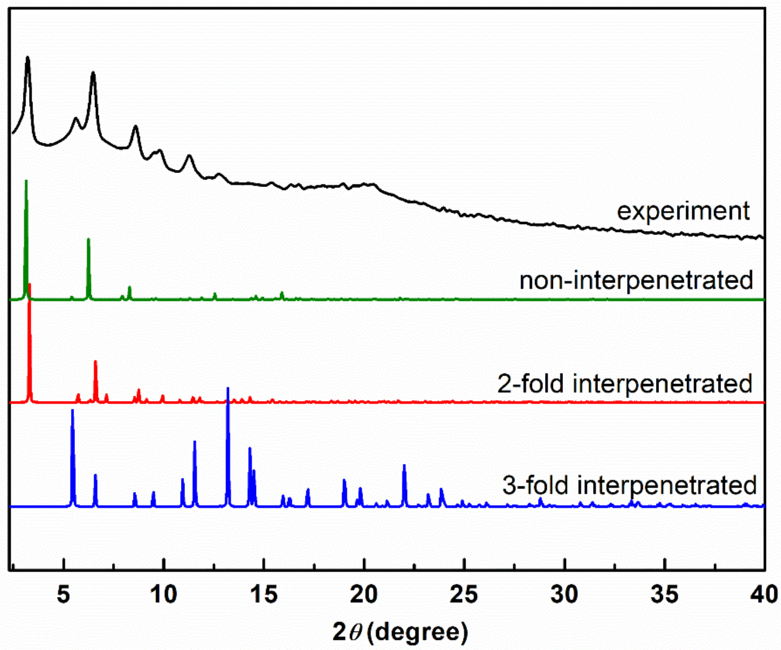


Figure S13. Comparison of PXRD patterns for JUC-569: experimental (black), non-interpenetrated (green), 2-fold interpenetrated (red) and 3-fold interpenetrated **acs** topology (blue).

Section S7. Nitrogen adsorption

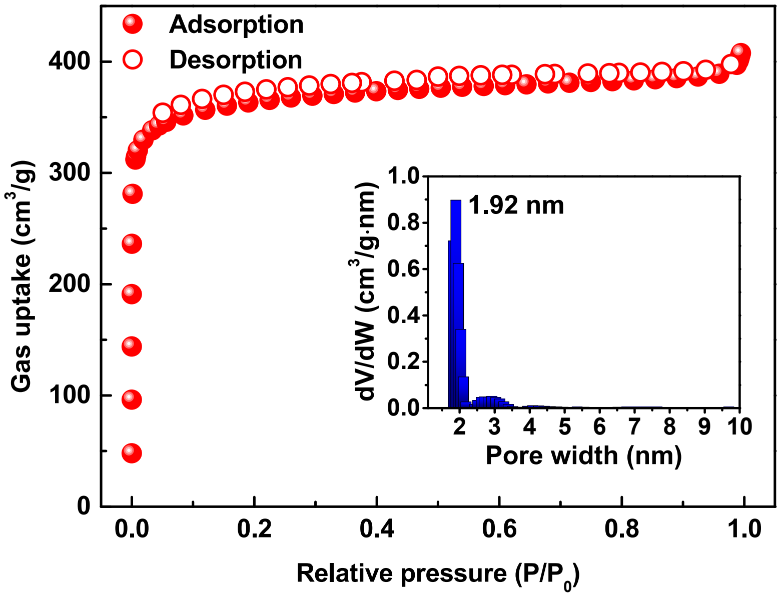


Figure S14. N_2 adsorption-desorption isotherm for JUC-568 at 77 K. Inserts: corresponding calculated pore-size distribution.

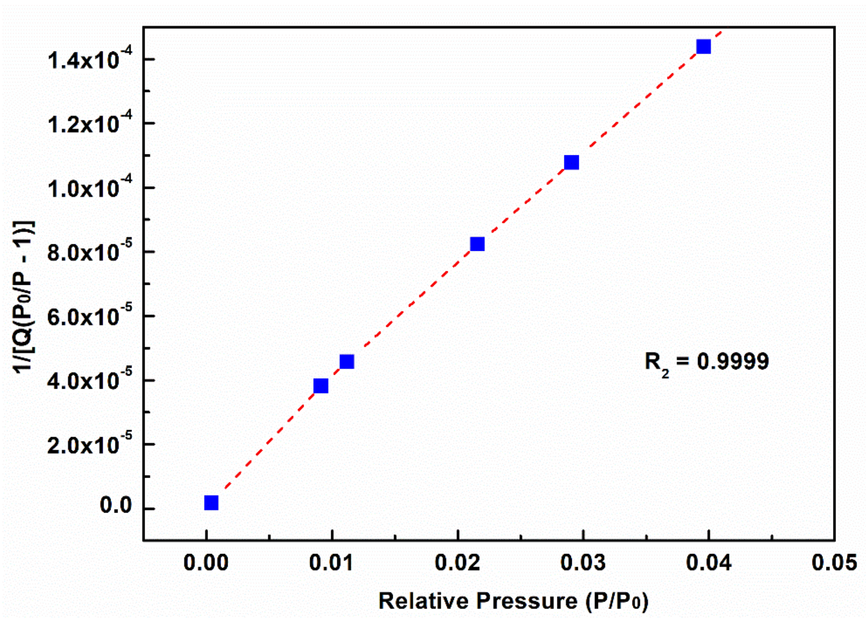


Figure S15. BET plot of JUC-568 calculated from N_2 adsorption isotherm at 77 K.

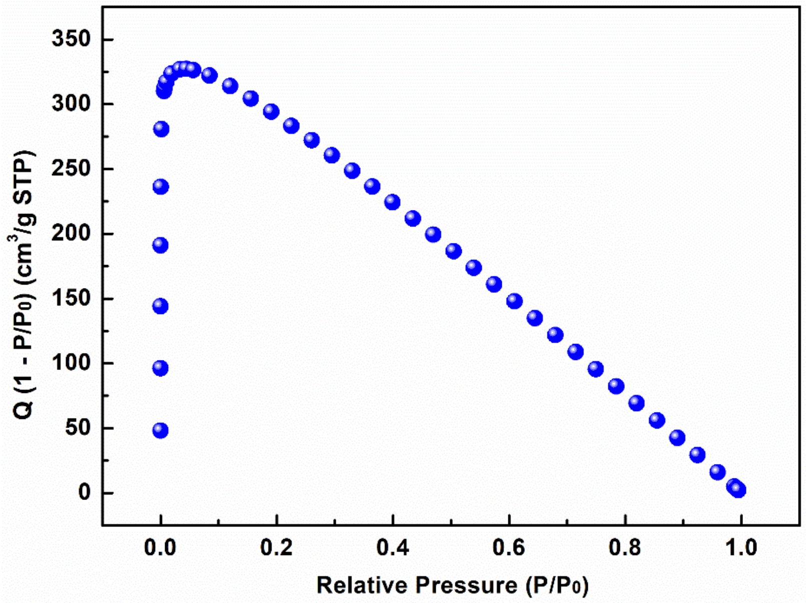


Figure S16. Rouquerol BET of JUC-568 calculated from N_2 adsorption isotherm at 77 K.

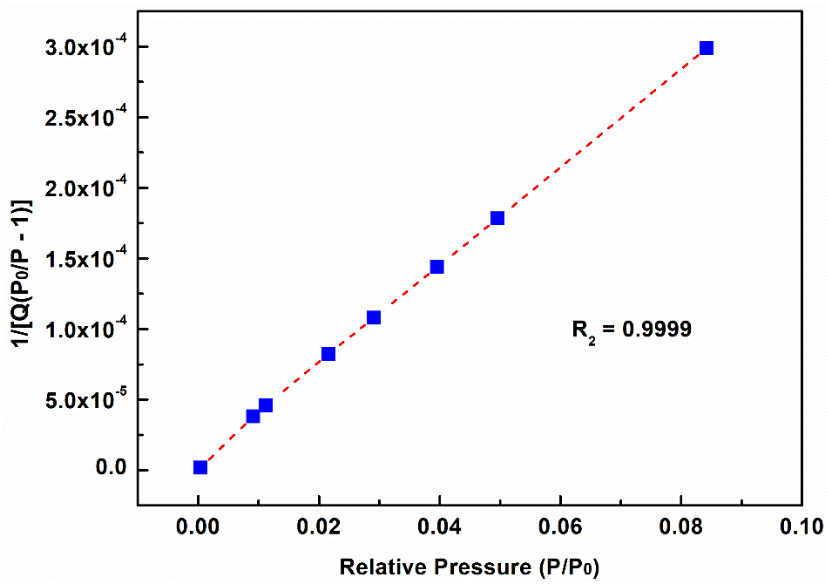


Figure S17. BET plot of JUC-569 calculated from N_2 adsorption isotherm at 77 K.

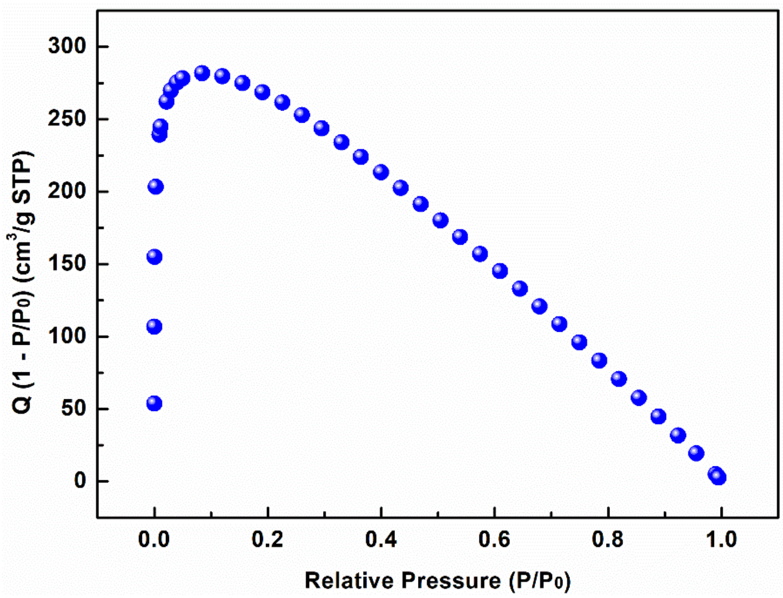


Figure S18. Rouquerol BET of JUC-569 calculated from N_2 adsorption isotherm at 77 K.

Section S8. A summary of H_2 storage capacity

Table S1. A summary of H_2 storage capacity at 77 K and 1 bar in current reported porous organic materials (POMs).

POMs	BET surface area	pore size	H_2 Uptake		Ref.
	(m^2/g)	(nm)	(wt %)	cm^3/g	
JUC-568	1433	1.92	2.45	274	This work
THPOP-1	1050	-	2.23	250	2
TTBI	2796	0.78	2.2	246	3
JUC-Z8	4743	3.01	2.14	240	4
DL-COF-1	2259	1.36	2.09	234	5
PAF-3	2932	1.27	2.07	232	6
NPAF	1790	0.6/1.0	1.87	209	7
SPT-CMP1	1631	1.1	1.72	193	8
PAF-1	5600	1.4	1.66	186	9
Trip-PIM	1065	0.7	1.65	185	10
TDCOF-5	2050	2.6	1.6	179	11
COF-JLU2	415	0.96	1.6	179	12
PPN-3	2840	1.25	1.58	177	13
JUC-569	1254	1.87	1.49	167	This work
BFCMP-2	1470	1.1/1.6	1.39	156	14
P2	834	-	1.36	152	15
PPN-12	1742	0.7	1.32	148	16
PSN-3	982	0.7	1.19	133	17
CPN-1	856	1.1	1.14	128	18
CTC-COF	1710	2.26	1.12	125	19
TPP2	468	-	1	112	20
PAF-19	250	1.33	0.55	62	21

Section S9: Unit cell parameters and fractional atomic coordinates

Table S2. Unit cell parameters and fractional atomic coordinates for JUC-568 calculated based on the **ceq** net.

Space group		*P*m	
Calulated unit cell		a = 49.5697 Å, b = 50.541 Å, c = 15.618 Å, $\alpha = \gamma$ = 90°, β = 120°	
Measured unit cell		a = 49.6389 Å, b = 50.656 Å, c = 15.702 Å, $\alpha = \gamma$ = 90°, β = 120°	
Pawley refinement		*R*p = *3.18*%, *wR*p = 5.39%	
atoms	x	y	z
C1	0.58833	0.45171	0.32605
N2	0.96767	0.14613	0.65393
C3	0.0228	0.16383	0.65521
C4	0.07962	0.18916	0.68385
C5	0.0523	0.18215	0.65588
C6	0.05302	0.19934	0.62868
C7	0.08051	0.2245	0.62941
C8	0.10763	0.23302	0.65733
C9	0.10711	0.21445	0.6846
C10	0.0202	0.1342	0.738
C11	0.96366	0.11086	0.73657
C12	0.9783	0.10385	0.87219
C13	0.98004	0.11993	0.84553
C14	0.69291	0.45174	0.36064
C15	0.71447	0.59637	0.38593
C16	0.23741	0.59982	0.67958
C17	0.2112	0.62408	0.65233
C18	0.18631	0.66555	0.6531
C19	0.18747	0.68324	0.68115
C20	0.21388	0.66031	0.70842
C21	0.23882	0.61849	0.70767
C22	0.16064	0.72019	0.68228
N23	0.13493	0.73501	0.65745
C24	0.73618	0.45171	0.41154
N25	0.68406	0.14989	0.0244
C26	0.63002	0.16358	0.97121
C27	0.60109	0.18888	0.91471
C28	0.6012	0.18198	0.94268
C29	0.57409	0.20091	0.94382
C30	0.54737	0.22755	0.91753
C31	0.54738	0.23605	0.88974

C32	0.57435	0.21577	0.88837
C33	0.71221	0.11417	0.96832
C34	0.76882	0.12959	0.02172
C35	0.90562	0.11355	0.0325
C36	0.87941	0.12999	0.03539
C37	0.67099	0.45172	0.30612
C38	0.67325	0.59634	0.28335
C39	0.43857	0.59919	0.76319
C40	0.43797	0.62383	0.78989
C41	0.46385	0.66372	0.81409
C42	0.49052	0.679	0.81175
C43	0.491	0.65477	0.78497
C44	0.46513	0.6147	0.76078
C45	0.51856	0.71586	0.83745
N46	0.52015	0.73115	0.86366
C47	0.67572	0.45169	0.26045
N48	0.34097	0.1455	0.31635
C49	0.34059	0.15761	0.37039
C50	0.31291	0.18411	0.40032
C51	0.34058	0.17433	0.39947
C52	0.36862	0.18872	0.42626
C53	0.36909	0.21384	0.45336
C54	0.34157	0.22536	0.45412
C55	0.31337	0.20952	0.42749
C56	0.25684	0.11395	0.28873
C57	0.25552	0.13354	0.23261
C58	0.13441	0.10933	0.09699
C59	0.16269	0.12738	0.12293
C60	0.6382	0.45173	0.32891
C61	0.61345	0.59638	0.32759
C62	0.32547	0.59951	0.56437
C63	0.35229	0.62775	0.56415
C64	0.3503	0.66903	0.53809
C65	0.32147	0.68208	0.51209
C66	0.29473	0.65461	0.51254
C67	0.2967	0.61334	0.53856
C68	0.31878	0.71988	0.48379
N69	0.34296	0.74143	0.48164
C70	0.32754	0.54828	0.59048
N71	0.65667	0.85294	0.97069
C72	0.65744	0.83408	0.0251
C73	0.68541	0.80891	0.08158
C74	0.6576	0.81542	0.05407

C75	0.6298	0.79755	0.05397
C76	0.62973	0.77257	0.08082
C77	0.65744	0.76492	0.10814
C78	0.68536	0.78375	0.10847
C79	0.74137	0.86622	0.02313
C80	0.73959	0.89016	0.96691
C81	0.87374	0.89684	0.97761
C82	0.84752	0.88095	0.98053
C83	0.36243	0.54825	0.69463
C84	0.3874	0.40362	0.71685
C85	0.67708	0.40032	0.23604
C86	0.64978	0.37617	0.2098
C87	0.65095	0.33454	0.18532
C88	0.67947	0.31678	0.18698
C89	0.70673	0.33964	0.21342
C90	0.70557	0.38148	0.2379
C91	0.68129	0.28021	0.16071
N92	0.65667	0.26643	0.13481
C93	0.41267	0.54828	0.73926
N94	0.02175	0.85186	0.68141
C95	0.96848	0.83776	0.62763
C96	0.91182	0.80949	0.59911
C97	0.93982	0.81931	0.59897
C98	0.94081	0.80356	0.57183
C99	0.91425	0.77738	0.54529
C100	0.88644	0.76611	0.54556
C101	0.88528	0.78302	0.5726
C102	0.96494	0.88529	0.70928
C103	0.01892	0.86944	0.76527
C104	0.03384	0.88703	0.90207
C105	0.03556	0.87031	0.87543
C106	0.30746	0.54829	0.67232
C107	0.28486	0.40372	0.67522
C108	0.75984	0.4007	0.43751
C109	0.7867	0.37412	0.43715
C110	0.8108	0.33434	0.463
C111	0.80822	0.32105	0.4894
C112	0.78122	0.34676	0.48964
C113	0.75708	0.38677	0.46376
C114	0.83403	0.28477	0.51731
N115	0.86014	0.26632	0.51855
C116	0.26213	0.54837	0.67835
N117	0.31386	0.85668	0.34403

C118	0.36783	0.84079	0.34268
C119	0.39753	0.81157	0.31488
C120	0.39702	0.82384	0.34241
C121	0.4244	0.81235	0.37014
C122	0.45171	0.78762	0.37046
C123	0.45213	0.77365	0.34307
C124	0.4249	0.78659	0.31519
C125	0.28363	0.86383	0.2598
C126	0.22873	0.88891	0.26156
C127	0.10947	0.89254	0.12821
C128	0.13776	0.87498	0.15415
C129	0.33094	0.54824	0.64017
C130	0.32933	0.40364	0.61549
C131	0.56228	0.40047	0.32463
C132	0.56311	0.36985	0.35152
C133	0.53707	0.32895	0.3503
C134	0.51007	0.31862	0.32216
C135	0.50949	0.34856	0.29537
C136	0.53545	0.38944	0.29657
C137	0.4817	0.2813	0.32013
N138	0.47993	0.25887	0.34427
C139	0.92786	0.04851	0.00195
C140	0.08133	0.04845	0.07522
C141	0.00433	0.04851	0.92576
C142	-0.0057	0.13827	0.68098
N143	-0.004	0.17096	0.62835
C144	-0.00682	0.12716	0.70974
C145	-0.00947	0.11988	0.76472
C146	0.00524	0.09795	0.90053
C147	0.0088	0.13004	0.84697
C148	0.01169	0.13368	0.81913
N149	-0.01165	0.11873	0.79228
C150	0.68379	0.13931	-0.00272
N151	0.63056	0.17274	-0.00163
C152	0.71283	0.12708	-0.00365
C153	0.76801	0.11872	-0.00656
C154	0.90288	0.09793	0.00367
C155	0.85019	0.12955	0.00956
C156	0.8228	0.13277	0.01356
N157	0.7955	0.11778	-0.00916
C158	0.31392	0.13659	0.31688
N159	0.36734	0.16545	0.36951
C160	0.28451	0.1271	0.28812

C161	0.22782	0.12185	0.23338
C162	0.10773	0.09773	0.09956
C163	0.16464	0.13255	0.15172
C164	0.19513	0.13678	0.17904
N165	0.19855	0.12108	0.20602
C166	0.66739	0.40823	0.33184
C167	0.33357	0.59175	0.669
C168	0.00443	0.90344	0.95003
C169	0.95239	0.90347	0.00215
C170	0.05668	0.90345	0.05196
C171	0.00439	0.90832	0.00178
C172	0.97663	0.95173	0.0022
C173	0.03217	0.95171	0.02895
C174	0.00437	0.95171	0.97402
H175	0.0794	0.1743	0.70586
H176	0.03114	0.19279	0.60589
H177	0.08082	0.238	0.60736
H178	0.12922	0.2202	0.70722
H179	0.04347	0.14297	0.73899
H180	0.94048	0.10029	0.73562
H181	0.95489	0.09547	0.87093
H182	0.95804	0.12474	0.82276
H183	0.71518	0.66894	0.38667
H184	0.21006	0.61024	0.62963
H185	0.16514	0.68497	0.63105
H186	0.21522	0.67539	0.73113
H187	0.26005	0.59988	0.72979
H188	0.16228	0.73609	0.70506
H189	0.62273	0.17268	0.91327
H190	0.57364	0.19475	0.96612
H191	0.52545	0.24247	0.9186
H192	0.57453	0.22113	0.86592
H193	0.68922	0.10719	0.94661
H194	0.79189	0.13495	0.04342
H195	0.92939	0.11268	0.05347
H196	0.88191	0.14365	0.05867
H197	0.67318	0.6689	0.28263
H198	0.41651	0.61165	0.79211
H199	0.46303	0.68339	0.83543
H200	0.51236	0.66738	0.78263
H201	0.4659	0.59512	0.7394
H202	0.53945	0.73162	0.83464
H203	0.28993	0.17161	0.3791

H204	0.39144	0.1801	0.42629
H205	0.39203	0.22484	0.47478
H206	0.29082	0.21741	0.42806
H207	0.25717	0.10558	0.31133
H208	0.25512	0.14086	0.20995
H209	0.13317	0.10413	0.07389
H210	0.18427	0.13797	0.12079
H211	0.61271	0.66894	0.3277
H212	0.37584	0.61768	0.58492
H213	0.37214	0.69179	0.53815
H214	0.27113	0.66529	0.49192
H215	0.27469	0.59146	0.53834
H216	0.29508	0.73056	0.4633
H217	0.70823	0.82396	0.08231
H218	0.60695	0.80315	0.03204
H219	0.607	0.75843	0.0804
H220	0.70801	0.77859	0.13063
H221	0.7421	0.85742	0.04589
H222	0.73885	0.90089	0.94422
H223	0.87144	0.90549	0.95417
H224	0.8239	0.87644	0.95945
H225	0.38815	0.33105	0.71758
H226	0.62641	0.38996	0.20803
H227	0.62869	0.31547	0.16426
H228	0.73012	0.32467	0.21543
H229	0.7279	0.39966	0.25905
H230	0.70465	0.26347	0.16294
H231	0.91052	0.82293	0.62067
H232	0.96332	0.81203	0.57124
H233	0.91545	0.76538	0.5236
H234	0.86251	0.77496	0.57271
H235	0.94282	0.89237	0.68673
H236	0.04107	0.86368	0.78787
H237	0.05575	0.88839	0.92499
H238	0.05882	0.85693	0.8769
H239	0.2841	0.33115	0.67517
H240	0.78911	0.38456	0.41604
H241	0.83254	0.31268	0.46266
H242	0.77868	0.3355	0.51064
H243	0.73535	0.40772	0.46427
H244	0.83113	0.2727	0.53807
H245	0.37569	0.82192	0.29231
H246	0.42444	0.82317	0.3925

H247	0.47375	0.77869	0.39297
H248	0.42516	0.77673	0.29293
H249	0.30593	0.85425	0.25887
H250	0.20648	0.90007	0.26243
H251	0.08761	0.89908	0.13013
H252	0.13881	0.8669	0.17709
H253	0.32941	0.33107	0.61484
H254	0.58484	0.37807	0.37433
H255	0.538	0.30455	0.372
H256	0.4879	0.33981	0.27247
H257	0.53466	0.41342	0.27488
H258	0.46049	0.27127	0.29703
H259	0.03481	0.14992	0.82072
H260	0.82532	0.14851	0.03671
H261	0.21634	0.154	0.17698
H262	0.66736	0.33563	0.33185
H263	0.33357	0.66436	0.66904
H264	0.00455	0.83087	0.94943
H265	0.9517	0.83091	0.00226
H266	0.05746	0.83088	0.05261
H267	0.00437	0.83572	0.0018

Table S3. Unit cell parameters and fractional atomic coordinates for JUC-569 calculated based on the **acs** net.

Space group		*P*-6	
Calulated unit cell		$a = b = 31.1095$ Å, $c = 18.4678$ Å, $\alpha = \beta = 90°$, $\gamma = 120°$	
Measured unit cell		$a = b = 31.1173$ Å, $c = 18.4733$ Å, $\alpha = \beta = 90°$, $\gamma = 120°$	
Pawley refinement		*R*p = 1.49%, *wR*p = 1.87%	
C1	0.13781	0.55855	-0.08563
C2	0.45054	0.50719	0.13145
C3	0.42558	0.52624	0.08539
C4	0.54732	0.44826	0.41489
C5	0.36247	0.64205	0.04005
C6	0.38805	0.6211	0.07984
C7	0.41358	0.59926	0.04035
C8	0.53311	0.47844	0.37144
C9	0.49121	0.54083	0.17887
N10	0.51531	0.52025	0.22679
C11	0.85984	0.40123	0.41472
C12	0.62138	0.52875	0.67477
C13	0.63561	0.49865	0.63102

C14	0.48189	0.61288	-0.13371
C15	0.64736	0.36719	0.54007
C16	0.63106	0.39684	0.5799
C17	0.61388	0.42649	0.54035
C18	0.50677	0.59384	-0.17993
C19	0.57014	0.51876	0.6735
C20	0.55551	0.55187	0.71857
H21	0.39211	0.49858	0.04735
H22	0.51698	0.41501	0.45073
H23	0.38829	0.62166	0.14434
H24	0.49132	0.47024	0.37256
H25	0.65156	0.56147	0.71152
H26	0.67732	0.50662	0.63245
H27	0.63166	0.39704	0.6444
H28	0.57539	0.59543	0.70731
H29	0.43775	0.46407	0.13044
H30	0.49447	0.65594	-0.135
H31	0.53982	0.62141	-0.21865
C32	0.66667	0.33333	0.42373
C33	0.33333	0.66667	-0.07627

Table S4. Unit cell parameters and fractional atomic coordinates for JUC-568 calculated based on the **sab** net.

Space group		*I*4cm	
Measured unit cell		$a = b = 54.6075$ Å, $c = 50.4626$ Å, $\alpha = \beta = \gamma = 90°$	
C1	0.88426	0.63416	0.92145
C2	0.83256	0.64903	0.79776
C3	0.21611	0.69769	0.40634
N4	-0.83019	0.41372	0.54948
C5	-0.82158	0.39312	0.56144
N6	-0.81029	0.37579	0.5465
C7	-0.8076	0.37874	0.51992
N8	-0.81634	0.39943	0.50826
C9	-0.8277	0.41698	0.52289
C10	-0.79074	0.36337	0.47666
C11	-0.79416	0.3602	0.50413
C12	-0.78402	0.33944	0.51653
C13	-0.77023	0.32263	0.50194
C14	-0.76618	0.3263	0.47461
C15	-0.77703	0.34643	0.46205
C16	-0.84627	0.45899	0.52558

C17	-0.83626	0.43996	0.51018
C18	-0.81383	0.36906	0.60301
C19	-0.82338	0.39011	0.59061
C20	-0.83409	0.40848	0.60645
C21	-0.8348	0.40603	0.63404
C22	-0.82453	0.3855	0.64638
C23	-0.81441	0.36674	0.6306
C24	-0.8339	0.44338	0.48256
C25	-0.84103	0.46545	0.47079
C26	-0.85046	0.4846	0.48625
C27	-0.85334	0.48109	0.51379
C28	0.13259	0.59372	0.43831
C29	0.13863	0.59511	0.46529
C30	0.14016	0.5738	0.48056
C31	0.13635	0.55076	0.46887
C32	0.12981	0.54944	0.44192
C33	0.12792	0.57081	0.42677
C34	0.14071	0.52845	0.48473
N35	0.14347	0.50725	0.47323
C36	0.17669	0.36065	1.77237
C37	0.19622	0.34874	1.75972
C38	0.2011	0.35325	1.73291
C39	0.18635	0.36951	1.71838
C40	0.16772	0.38252	1.73158
C41	0.163	0.37816	1.75844
C42	0.18977	0.37141	1.68936
N43	0.17465	0.38398	1.67485
C44	0.29787	0.23945	1.42026
C45	0.28365	0.25769	1.40821
C46	0.27372	0.27669	1.42345
C47	0.27814	0.27772	1.45095
C48	0.29378	0.26035	1.46256
C49	0.30349	0.24126	1.44734
C50	0.26553	0.29564	1.46817
N51	0.24823	0.30963	1.45894
C52	1.68006	0.14544	0.87292
C53	1.15754	0.63919	1.38955
C54	1.18847	0.67007	1.38401
C55	1.1699	0.65152	1.34549
C56	0.82534	0.71141	0.8951
C57	0.85889	0.67784	0.82173
C58	0.84505	0.61836	0.90521
H59	0.22401	0.7048	0.3869

H60	-0.79917	0.37983	0.46617
H61	-0.78704	0.33626	0.53862
H62	-0.76217	0.30582	0.51211
H63	-0.77464	0.34897	0.43978
H64	-0.84868	0.45647	0.54785
H65	-0.80555	0.35375	0.59054
H66	-0.84226	0.42549	0.5968
H67	-0.8438	0.42083	0.64666
H68	-0.80668	0.34962	0.64045
H69	-0.82613	0.42809	0.46968
H70	-0.8392	0.46799	0.44845
H71	-0.86147	0.49636	0.52644
H72	0.14231	0.61367	0.47484
H73	0.14452	0.57506	0.50261
H74	0.12603	0.53091	0.43236
H75	0.12256	0.56957	0.40498
H76	0.14169	0.52966	0.50726
H77	0.20817	0.33535	1.77126
H78	0.21712	0.34371	1.72275
H79	0.15639	0.39669	1.72039
H80	0.14798	0.38889	1.76899
H81	0.20585	0.36177	1.67942
H82	0.28014	0.25709	1.38595
H83	0.26201	0.2914	1.41362
H84	0.29862	0.26176	1.48448
H85	0.31601	0.22714	1.45701
H86	0.27092	0.29736	1.48991
H87	0.84002	0.72625	0.89511
H88	0.87366	0.69259	0.82164
H89	0.83043	0.60346	0.90492

Table S5. Unit cell parameters and fractional atomic coordinates for JUC-568 calculated based on the **dag** net.

Space group		$P4_2$/mnm	
Measured unit cell		$a = b = 58.1424$ Å, $c = 7.3498$ Å, $\alpha = \beta = \gamma = 90°$	
N1	-0.64648	0.38206	0.74305
C2	-0.60133	0.36994	0.74541
C3	-0.55965	0.3807	0.75278
C4	-0.57666	0.36355	0.74684
C5	-0.56979	0.34037	0.74264

C6	-0.54645	0.33456	0.74249
C7	-0.52952	0.35168	0.74543
C8	-0.53637	0.37489	0.75299
C9	-0.65254	0.31798	0.74911
C10	-0.69892	0.3305	0.76547
C11	0.25133	0.22187	0.71963
C12	0.26824	0.23879	0.73996
C13	0.58056	0.33456	-0.19556
C14	0.57618	0.35777	-0.23352
C15	0.55382	0.36512	-0.27037
C16	0.53555	0.34936	-0.26984
C17	0.54029	0.32581	-0.24778
C18	0.56274	0.31845	-0.21184
C19	0.5118	0.3581	-0.28321
C20	0.60188	0.3286	-0.0969
N21	0.49425	0.34476	-0.2539
C22	0.64341	0.32761	1.09673
C23	0.67222	0.37726	1.19264
H24	-0.56481	0.39961	0.7575
H25	-0.58329	0.32615	0.73932
H26	-0.54104	0.31572	0.73996
H27	-0.52275	0.38897	0.75931
H28	-0.6337	0.31268	0.73962
H29	-0.71783	0.33563	0.77029
H30	0.25632	0.20291	0.72143
H31	0.28704	0.23363	0.75615
H32	0.59091	0.37071	-0.23435
H33	0.55032	0.38402	-0.30112
H34	0.52582	0.31266	-0.25917
H35	0.56653	0.29932	-0.19579
H36	0.50857	0.37688	-0.31984
H37	0.67274	0.37731	1.34769
C38	0.22823	0.22823	0.69702
C39	0.26207	0.26207	0.74043
C40	0.27942	0.27942	0.69648
C41	0.21266	0.21266	0.59703
N42	0.29043	0.29043	0.82041
C43	-0.64056	0.35944	0.74169
N44	-0.60757	0.39243	0.7466
C45	-0.65858	0.34142	0.74431
C46	-0.6927	0.3073	0.77592
C47	0.66658	0.33342	1.18313
C48	0.68338	0.31662	0.9036

C49	0.69795	0.30205	1.19317

Table S6. Unit cell parameters and fractional atomic coordinates for JUC-569 with 2-fold interpenetrated **acs** net.

Space group		*P*3	
Measured unit cell		*a* = *b* = 30.8479 Å, *c* = 13.9668 Å, *α* = *β* = 90°, *γ* = 120°	
C1	0.09669	0.85557	0.23831
C2	0.07436	0.87846	0.1936
C3	0.20823	0.75292	0.40625
C4	0.02663	0.97599	0.07578
C5	0.04975	0.95521	0.12326
C6	0.07313	0.9341	0.07534
C7	0.1911	0.78077	0.36302
C8	0.14497	0.86806	0.2146
N9	0.16557	0.84166	0.25715
C10	0.51754	0.74287	0.43299
C11	0.25939	0.84645	0.67841
C12	0.27838	0.82147	0.63172
C13	0.31024	0.69388	0.57696
C14	0.29006	0.71697	0.6257
C15	0.27287	0.74403	0.57939
C16	0.21731	0.82107	0.73099
C17	0.19872	0.84861	0.78035
C18	0.6959	1.77786	1.11592
C19	0.74968	1.93116	1.31297
C20	0.75131	1.97728	1.27629
C21	0.78578	1.94332	1.39129
C22	0.71163	1.74101	1.14331
C23	0.68645	1.77531	1.01352
C24	-0.1845	0.90921	0.92563
C25	0.12428	0.93014	0.85609
C26	0.1441	0.90636	0.80598
C27	-0.18541	0.90093	0.12705
C28	0.14751	0.92751	0.10657
C29	0.17072	0.9042	0.14709
C30	0.09541	0.8327	0.89782
C31	0.07548	0.85744	0.94415
C32	0.21215	0.74473	0.6867
C33	0.02648	0.97597	0.9799
C34	0.04831	0.95425	0.93174
C35	0.07119	0.93246	0.97872

C36	0.19379	0.76993	0.73562
C37	0.13098	0.8576	0.82986
N38	0.15219	0.83216	0.78575
C39	0.51635	0.74594	0.63307
C40	0.2714	0.85251	0.37565
C41	0.28873	0.82432	0.41632
C42	0.31089	0.69476	0.48105
C43	0.29303	0.72073	0.43416
C44	0.2747	0.74625	0.48313
C45	0.22263	0.83096	0.34785
C46	0.2052	0.8615	0.30506
C47	-0.244	0.8226	0.72608
C48	-0.29892	0.92121	0.92297
C49	-0.31636	0.90753	1.02115
C50	-0.27666	0.97622	0.90758
C51	-0.20299	0.84876	0.65627
C52	-0.24669	0.77519	0.75843
C53	0.43089	0.49814	0.02403
C54	0.40891	0.52253	-0.01665
C55	0.54813	0.4144	0.25133
C56	0.35934	0.64194	-0.04234
C57	0.38033	0.61887	0.0046
C58	0.40348	0.59761	-0.04375
C59	0.52983	0.43847	0.1992
C60	0.46652	0.52224	0.09228
N61	0.48922	0.4972	0.13285
C62	0.8495	0.40836	0.30021
C63	0.5979	0.4902	0.64071
C64	0.61737	0.46882	0.58411
C65	0.64662	0.36352	0.45089
C66	0.62928	0.38958	0.49869
C67	0.61099	0.41598	0.45177
C68	0.55334	0.48705	0.6193
C69	0.53195	0.50762	0.68096
C70	1.08497	1.49082	1.20482
C71	1.03076	1.58458	0.99468
C72	1.02172	1.57928	0.89203
C73	1.04805	1.637	1.02496
C74	1.12321	1.51915	1.27798
C75	1.08532	1.44419	1.17723
C76	0.14892	0.56349	0.806
C77	0.48329	0.59661	0.83425
C78	0.51131	0.58121	0.78496

C79	0.14781	0.5774	0.00734
C80	0.45577	0.59309	0.07778
C81	0.47718	0.56929	0.12265
C82	0.44653	0.54786	0.66932
C83	0.41863	0.56106	0.72376
C84	0.54677	0.439	0.48627
C85	0.3598	0.64261	0.86197
C86	0.38367	0.62311	0.81354
C87	0.40715	0.6016	0.8598
C88	0.5282	0.46193	0.54111
C89	0.49183	0.5552	0.70224
N90	0.51632	0.53562	0.64966
C91	0.85064	0.40809	0.50643
C92	0.59998	0.51622	0.23979
C93	0.61761	0.49216	0.29401
C94	0.64642	0.36332	0.35516
C95	0.62836	0.38874	0.30754
C96	0.61047	0.41515	0.35489
C97	0.55566	0.48958	0.19312
C98	0.53604	0.51558	0.14111
C99	0.03276	0.43799	0.82092
C100	0.09838	0.57285	0.57608
C101	0.091	0.61701	0.58427
C102	0.14356	0.58529	0.51829
C103	0.05505	0.40499	0.83082
C104	0.01109	0.44134	0.91169
H105	0.03429	0.86776	0.21262
H106	0.18171	0.7114	0.42013
H107	0.05	0.95507	0.20488
H108	0.15037	0.76251	0.33912
H109	0.27886	0.88899	0.67349
H110	0.31507	0.84298	0.59062
H111	0.2872	0.71397	0.70707
H112	0.22584	0.88586	0.81548
H113	0.65926	1.76694	1.15444
H114	0.71063	1.90566	1.34312
H115	0.7696	1.98682	1.20255
H116	0.77399	2.00964	1.32753
H117	0.71159	1.97069	1.27071
H118	0.82407	1.97483	1.3678
H119	0.78852	1.9088	1.41005
H120	0.77275	1.95576	1.45677
H121	0.71326	1.72056	1.07663

H122	0.68346	1.71279	1.19608
H123	0.75019	1.76152	1.17815
H124	0.69701	1.74838	0.97896
H125	0.70987	1.81412	0.98076
H126	0.64506	1.76143	1.00054
H127	0.13617	0.97072	0.839
H128	0.1687	0.95957	0.05391
H129	0.04505	0.83722	1.0003
H130	0.19237	0.70215	0.69077
H131	0.04788	0.95385	0.85012
H132	0.15856	0.74836	0.78084
H133	0.29761	0.89435	0.36461
H134	0.32991	0.84208	0.43679
H135	0.29316	0.7215	0.35255
H136	0.22731	0.90387	0.31447
H137	-0.2807	0.81243	0.68855
H138	-0.33267	0.90106	0.87354
H139	-0.32634	0.86715	1.03484
H140	-0.35087	0.91136	1.03281
H141	-0.28552	0.93337	1.07266
H142	-0.27018	0.98485	0.82779
H143	-0.23945	0.99711	0.94721
H144	-0.30336	0.98867	0.93599
H145	-0.21871	0.85462	0.5867
H146	-0.18464	0.82524	0.64158
H147	-0.17397	0.88661	0.68665
H148	-0.22414	0.78243	0.82716
H149	-0.23059	0.76125	0.7005
H150	-0.28739	0.74568	0.77234
H151	0.37816	0.50277	-0.07241
H152	0.52705	0.37175	0.2542
H153	0.37895	0.61685	0.08613
H154	0.49266	0.41622	0.15993
H155	0.61879	0.51137	0.70782
H156	0.65533	0.47299	0.60202
H157	0.6296	0.39002	0.58031
H158	0.52856	0.49897	0.76086
H159	1.04679	1.47931	1.23719
H160	0.99379	1.55911	1.03243
H161	1.0335	1.55238	0.86186
H162	1.04439	1.61738	0.85614
H163	0.98019	1.56393	0.87762
H164	1.06603	1.66324	0.9615

H165	1.07665	1.64788	1.08507
H166	1.01471	1.64002	1.0515
H167	1.15572	1.55367	1.2438
H168	1.13741	1.49447	1.30955
H169	1.1061	1.53125	1.33723
H170	1.06542	1.43003	1.10563
H171	1.06517	1.41434	1.23441
H172	1.12564	1.45263	1.17061
H173	0.49879	0.61985	0.90216
H174	0.46608	0.63264	0.10018
H175	0.37953	0.55132	0.69929
H176	0.5248	0.41604	0.42149
H177	0.38463	0.6243	0.73195
H178	0.49144	0.46005	0.52138
H179	0.62227	0.55874	0.2333
H180	0.65429	0.51444	0.33481
H181	0.62781	0.38848	0.22592
H182	0.56276	0.55319	0.10675
H183	0.00117	0.42008	0.76624
H184	0.06455	0.542	0.53701
H185	0.06543	0.61151	0.6476
H186	0.07319	0.62091	0.51571
H187	0.12875	0.65231	0.59575
H188	0.13723	0.59272	0.44104
H189	0.15093	0.55259	0.52048
H190	0.17719	0.62011	0.549
H191	0.05819	0.39086	0.75717
H192	0.03012	0.37178	0.87866
H193	0.09387	0.42713	0.86419
H194	-0.00662	0.40358	0.94961
H195	-0.01874	0.45205	0.89745
H196	0.04172	0.47101	0.95885
C197	0.33333	0.66667	0.43753
C198	0.33333	0.66667	0.61957
C199	0.33333	0.66667	0.81931
C200	0.33333	0.66667	0.00107
C201	0	1	0.9368
C202	0	1	0.1191
C203	0.66667	0.33333	0.31187
C204	0.66667	0.33333	0.49411

Table S7. Unit cell parameters and fractional atomic coordinates for JUC-569 with 3-fold interpenetrated **acs** net.

Space group		*P*-6	
Measured unit cell		$a = b = 18.6536$ Å, $c = 13.4109$ Å, $\alpha = \beta = 90°$, $\gamma = 120°$	
C1	0.27066	-0.72164	0.89098
C2	-0.33595	-0.92686	0.18056
C3	-0.27147	-0.93134	0.13165
C4	-0.64369	-0.93303	0.38589
C5	-0.07751	-1.00518	0.05283
C6	-0.14389	-1.00805	0.10549
C7	-0.21082	-1.01039	0.05304
C8	-0.58548	-0.94306	0.33185
C9	-0.41089	-1.00061	0.20083
N10	-0.47633	-0.99391	0.24792
C11	-1.2664	-1.2726	0.38467
C12	-0.69587	-1.0658	0.74455
C13	-0.75356	-1.0585	0.68487
C14	-0.34997	-1.08078	0.86266
C15	-0.92171	-0.99096	0.55269
C16	-0.85584	-0.98707	0.60529
C17	-0.78942	-0.98592	0.55368
C18	-0.41732	-1.07872	0.81682
C19	-0.61116	-1.01034	0.733
C20	-0.5499	-1.02194	0.78889
C21	0.3322	-0.50934	0.2238
C22	0.4795	-0.67707	0.21649
C23	0.52478	-0.69049	0.1302
C24	0.4472	-0.74872	0.29016
C25	0.28173	-0.53344	0.32022
C26	0.29956	-0.47216	0.14639
H27	-0.21491	-0.87518	0.11227
H28	-0.62346	-0.87548	0.4238
H29	-0.14287	-1.00701	0.18626
H30	-0.52071	-0.89636	0.33765
H31	-0.71699	-1.11566	0.79791
H32	-0.81884	-1.10282	0.69335
H33	-0.35226	-1.13907	0.87585
H34	-0.85782	-0.98816	0.68609
H35	-0.56714	-1.05605	0.85856
H36	0.39338	-0.45755	0.24556
H37	0.52716	-0.62223	0.25756

H38	0.55309	-0.63442	0.08272
H39	0.48199	-0.74574	0.08596
H40	0.57539	-0.69977	0.15898
H41	0.40424	-0.80767	0.25215
H42	0.41404	-0.73823	0.35223
H43	0.4996	-0.75347	0.32219
H44	0.22198	-0.59039	0.30958
H45	0.27083	-0.48301	0.34576
H46	0.31584	-0.54534	0.37985
H47	0.29382	-0.421	0.18023
H48	0.23824	-0.51795	0.11631
H49	0.34445	-0.44596	0.0842
C50	-1	-1	0.39966
C51	0	-1	0.89977

Section S10. References

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