

Supplemental information

Tetrathiafulvalene-based covalent organic frameworks for ultrahigh iodine capture

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Section 1: Materials and characterization

1.1 Materials

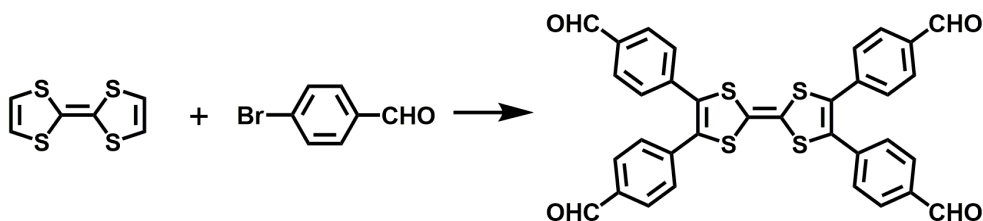
All starting materials and solvents, unless otherwise noted, were obtained from J&K scientific LTD. The reagents and purity of the solvents were of 95% and used without further purification. 2,3,6,7-tetra(4-formylphenyl)tetrathiafulvalene (TFP-TTF)¹, 2',5'-dimethyl-[1,1':4',1''-terphenyl]-4,4''-diamine (DTDA)², and 2,4,6-tris(4-aminophenyl)amine (TAPA)³ were synthesized using a modified literature method. All products were isolated and handled under nitrogen using either glovebox or Schlenk line techniques.

1.2 Instruments

A Bruker AV-400 NMR spectrometer was applied to record the liquid ¹H NMR spectra. Solid-state ¹³C 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 recorded on a SHIMADZU DTG-60 thermal analyzer under N₂. The operational range of the instrument was from 30 °C to 600 °C at a heating rate of 10 °C min⁻¹ with N₂ flow rate of 30 mL min⁻¹. PXRD data were collected on a PANalytical B.V. Empyrean powder diffractometer using a Cu K α source ($\lambda = 1.5418 \text{ \AA}$) over the range of $2\theta = 2.0\text{--}40.0^\circ$ with a step size of 0.02° and 2 s per step. The sorption isotherm for N₂ 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 DMF for 12 h (3 \times 5.0 ml) and then acetone for another 36 h (3 \times 5.0 ml). The acetone was then extracted under vacuum at 85 °C to afford the samples for sorption analysis. To estimate pore size distributions for TTF-COFs, nonlocal density functional theory (NLDFT) was applied to analyze the N₂ isotherm on the basis of the model of N₂@77K on carbon with slit pores and the method of non-negative regularization. For scanning electron microscopy (SEM) images, JEOL JSM-6700 scanning electron microscope was applied. The transmission electron microscopy (TEM) images were obtained on JEM-2100 transmission electron microscopy. The Electrochemistry experiments were conducted on a CHI660C Electrochemical Workstation (Shanghai Chenhua Electrochemical

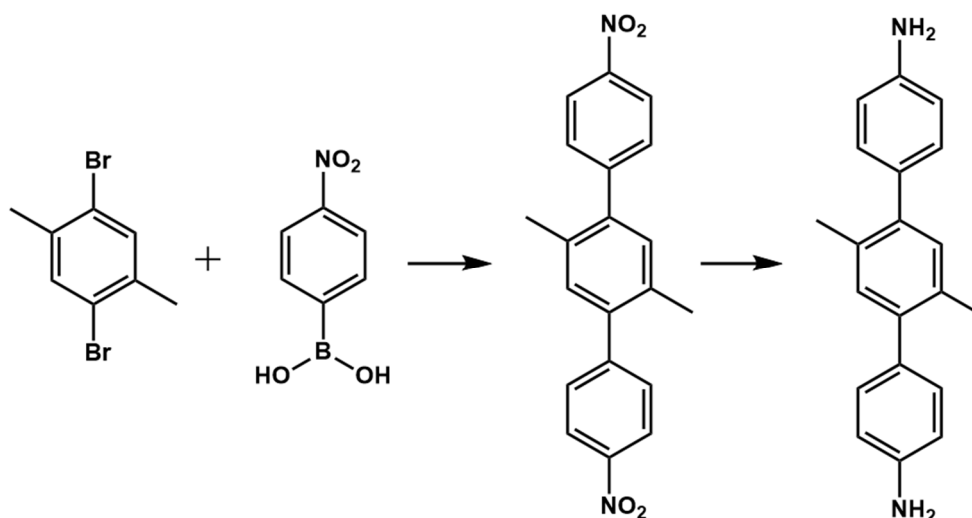
Instrument). Electron paramagnetic resonance (EPR) spectra were measured on JES-FA200. Raman scattering spectra were measured on INVIA, and the Raman band of the silicon wafer at 520.7 cm^{-1} was used to calibrate the spectrometer. X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALAB 250 XPS system.

1.3 Synthesis of 2,3,6,7-tetra(4-formylphenyl)tetrathiafulvalene (TFP-TTF)¹



A THF (80.0 ml) mixture of tetrathiafulvalene (8.0 mmol, 1.64 g), 4-bromobenzaldehyde (40.0 mmol, 7.4 g), $\text{Pd}(\text{OAc})_2$ (2.0 mmol, 0.45 g), $\text{PtBu}_3\text{HBF}_4$ (4.4 mmol, 1.74 g), and CsCO_3 (14.7 mmol, 9.6 g) was degassed by freeze-pump-thaw cycles, purged with argon, and refluxed 48 h. The mixture was extracted with chloroform and the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 , and concentrated under reduced pressure. The residue was purified by using silica gel chromatography with dichloromethane as eluent to afford the TFP-TTF (2.2 g, 40%) as red black solid. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ (ppm): 9.97 (s, 4 H), 7.78 (d, $J = 8.0$, 8 H), 7.36 (d, $J = 8.0$, 8 H).

1.4 Synthesis of 2',5'-dimethyl-[1,1':4',1''-terphenyl]-4,4''-diamine (DTDA)²

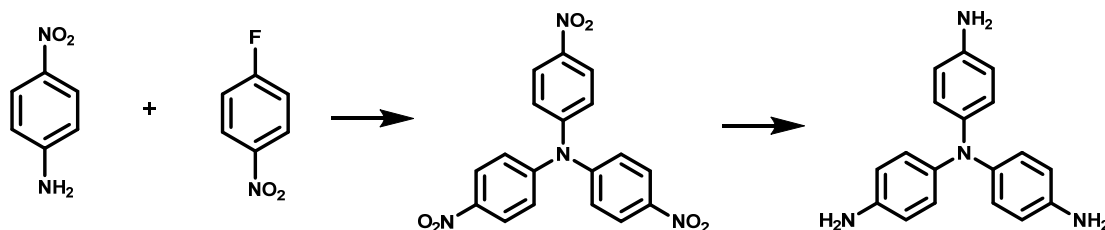


2',5'-dimethyl-4,4''-dinitro-1,1':4',1''-terphenyl. 1,4-Dibromo-2,5-dimethylbenzene (0.38 mmol, 0.10 g), 4-nitrophenyl boronic acid (0.95 mmol, 0.158 g), cesium carbonate (1.89 mmol, 0.617 g) and Pd(PPh₃)₄ (0.04 mmol, 0.044 g) were mixed in pre-degassed 1,4-dioxane (7.5 mL) and H₂O (1.5 mL) in a screw-capped Schlenk tube. The atmosphere was purified via 3 cycles of evacuation / N₂ fill before the tube was sealed. The mixture was heated at 100 °C for 12 h, and then partitioned between H₂O and EtOAc. The insoluble solid was filtered to afford the desired product 2',5'-dimethyl-4,4''-dinitro-1,1':4',1''-terphenyl as light brown solid (0.066 g, 50%). ¹H-NMR (DMSO, 400 MHz) δ (ppm): 8.31 (4 H, d, J = 6.76, Ph-H ortho to NO₂), 7.71 (4 H, d, J = 6.76, Ph-H meta to NO₂), 7.27 (2 H, s, Ph-H), 2.26 (6 H, s, CH₃).

DTDA. 2',5'-dimethyl-4,4''-dinitro-1,1':4',1''-terphenyl (0.15 mmol, 0.053 g) and 10% Pd/C (0.01 mmol, 0.016 g) and hydrazine monohydrate (1.5 mmol, 0.25 ml) was mixed in EtOH (30.0 mL). The resulting mixture was heated under reflux for 6 h under nitrogen and then filtered when it was still hot. The filtrate was evaporated to dryness to afford DTDA as white solid (0.022 g, 50%). ¹H-NMR (CDCl₃, 400 MHz) δ (ppm): 7.17 (4 H, d, J = 6.48, Ph-H meta to

NH₂), 7.11 (2 H, s, Ph-H), 6.74 (4 H, d, *J* = 6.52, Ph-H ortho to NH₂), 3.70 (4 H, br, NH₂), 2.27 (6 H, s, CH₃).

1.5 Synthesis of 2,4,6-tris(4-aminophenyl)amine (TAPA)³

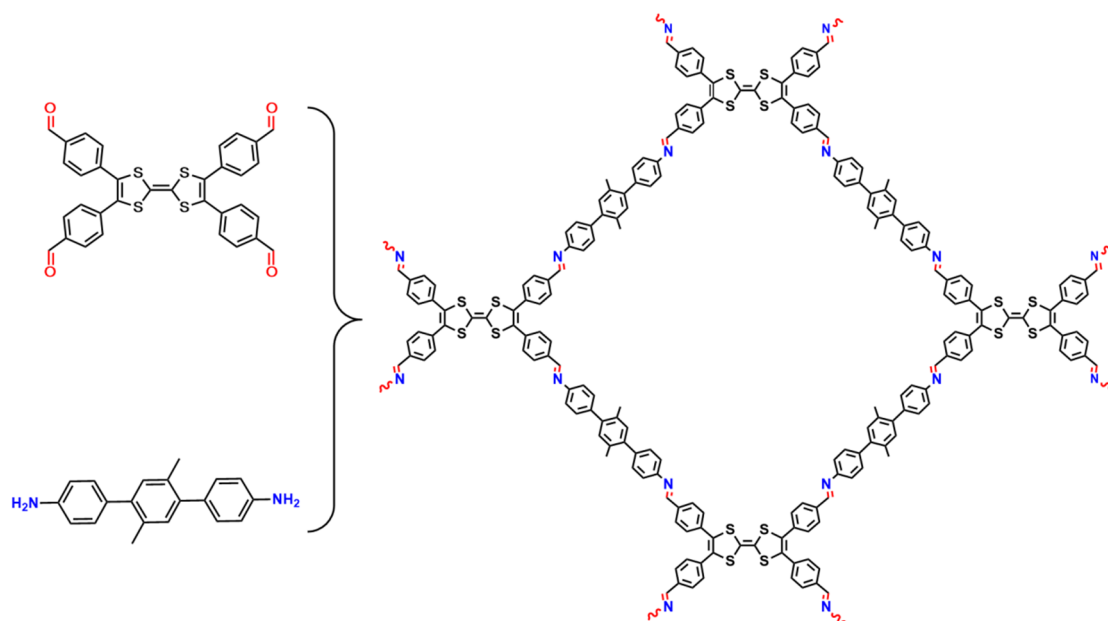


2,4,6-Tris(4-nitrophenyl)amine (TNPA). 1-Fluoro-4-nitrobenzene (8.0 mL, 0.08 mmol) was added to a suspension of 4-nitroaniline (5.0 g, 36.2 mmol) and K₂CO₃ (30.0 g) in dry DMSO (40.0 mL) in a 100-mL two-neck bottle under a flow of N₂. The mixture was heated at 120 °C for 48 h and then the solvent was removed under vacuum. The formed solid was suspended in methanol and collected via vacuum filtration. The compound was washed with H₂O and methanol. Afterwards, the product was dried under vacuum overnight to yield a yellow solid of TNPA. ¹H NMR (DMSO-*d*₆, 400 MHz) δ (ppm): 8.26 (d, *J* = 12 Hz, 6 H), 7.36 (d, *J* = 10.8 Hz, 6 H).

TAPA. A suspension of tris(4-nitrophenyl)amine (10.0 g, 26.3 mmol) and palladium on activated carbon (0.658 g, 0.006 mmol) in dry 1,4-dioxane (46.0 mL) and EtOH (23.0 mL) was heated at 80 °C for 1 h in a 250-mL two-neck bottle under a flow of N₂ and then hydrazine monohydrate (26.3 mL, 0.84 mmol) was added. The mixture was heated at 80 °C for 48 h. Palladium on activated carbon was removed via vacuum filtration. Afterwards, the product was crystallized at low temperature. The precipitate was collected via vacuum filtration and

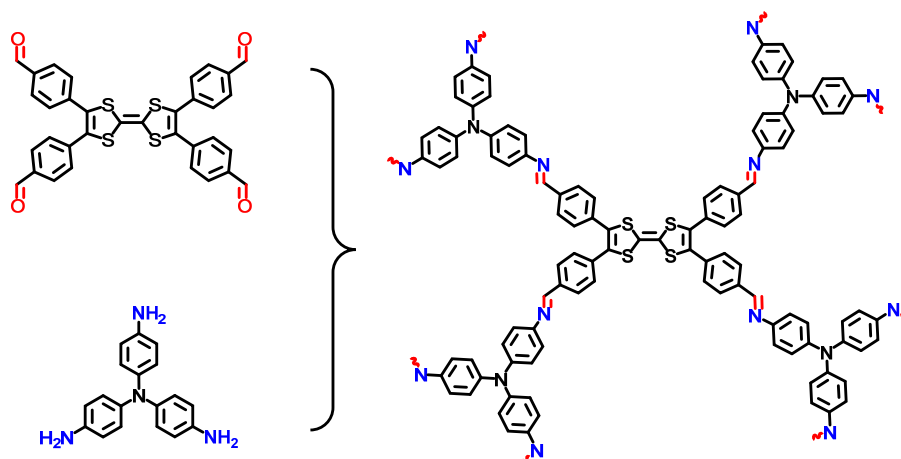
dried under vacuum overnight to yield a gray solid of TAPA. ^1H NMR (DMSO- d_6 , 400 MHz) δ (ppm): 6.58 (s, 6 H), 4.69 (s, 6 H), 6.44 (d, $J = 10.2$ Hz, 6 H).

1.6 Synthesis of JUC-560



DTDA (0.05 mmol, 0.017 g) and TFP-TTF (0.025 mmol, 0.019 g) were weighed into a Pyrex tube (volume: ca. 20.0 ml with a body length of 18.0 cm and neck length of 9.0 cm). Then, the mixture of mesitylene (0.7 mL), 1,4-dioxane (0.3 mL) and 0.1 ml of aqueous acetic acid (6.0 mol/L) was added. The Pyrex tube was flash frozen in a liquid nitrogen bath and 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%. Anal. Calcd for $\text{C}_{37}\text{H}_{26}\text{N}_2\text{S}_2$: C: 78.97; H: 4.66; N: 4.98; S: 11.39. Found: C: 79.12; H: 4.61; N: 5.06; S: 11.21. Solid-state ^{13}C NMR (500 MHz) δ (ppm): 159.4, 150.8, 141.1, 131.9, 121.2, 20.2. FT-IR: (KBr), ν/cm^{-1} : 3024.24, 2866.98, 2733.86, 2361.54, 1774.92, 1603.03, 1555.49, 1483.80, 1307.52, 1102.72, 1012.02, 840.13.

1.7 Synthesis of JUC-561



TAPA (0.04 mmol, 0.013 g) and TFP-TTF (0.03 mmol, 0.022 g) were weighed into a Pyrex tube (volume: ca. 20.0 ml with a body length of 18.0 cm and neck length of 9.0 cm). Then, the mixture of *o*-DCB (0.2 mL), *n*-BuOH (0.8 mL) and aqueous acetic acid (9.0 mol/L, 0.1 mL) was added. The Pyrex tube was flash frozen in a liquid nitrogen bath and 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 five 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 81%. Anal. Calcd for C₈₇H₅₄N₈S₆: C: 74.44; H: 3.88; N: 7.98; S: 13.70. Found: C: 74.46; H: 3.85; N: 7.99; S: 13.69. Solid-state ¹³C NMR (500 MHz) δ (ppm): 157.9, 155.4, 144.6, 135.9, 128.3. FT-IR: (KBr), ν /cm⁻¹: 3033.02, 2840.64, 2740.43, 1902.19, 1701.77, 1602.56, 1494.04, 1309.71, 1209.51, 1109.29, 832.81.

1.8 General procedure for iodine vapor sorption. An open small vial (2.0 mL) containing the COF sample (0.02 g) was placed in a large vial (10.0 mL) containing iodine (1.0 g). The large vial was sealed and kept in an oven at 60 °C. After a certain period, the large vial was cooled to room temperature. Then the sample was vacuumed at room temperature for 12 h

to remove the iodine on the surface. The small vial containing the COF sample was weighed and placed back into the iodine-containing large vial. The large vial was sealed and put back in the oven at 60 °C to continue the adsorption till the mass of the small vial containing the COF sample did not change.

1.9 General procedure for recycling the COF samples. The iodine-captured COF sample was added to ethanol (20.0 mL) in a vial at 25 °C, and ethanol was refreshed every 2 h until no color of the solution was observed. The COF sample was collected by filtration, washed with ethanol, dried under vacuum at 120 °C overnight and reused for the next cycle.

1.10 General procedure for iodine escape investigation. An open vial (2.0 mL) containing the iodine-loaded COF sample was placed in an empty large vial (10.0 mL). The large vial was sealed and kept in room temperature. Then the sample was vacuumed at room temperature for 12 h to remove the iodine on the surface. After a certain period, the small vial containing the COF sample was weighed and placed back into the empty large vial. The large vial was sealed to continue the desorption. The investigation was carried out for a period of 8 days.

1.11 Cyclic voltammetry (CV) measurements. After grinding each as-synthesized COF (6.0 mg) and carbon black (4.0 mg) in agate mortar and pestle for 10 mins, the ground powder was subjected to a mixture of water (0.25 mL), ethanol (0.25 mL) and Nafion solution (50.0 µL) and sonicated for 2 h. Then the electrode was prepared by drop-casting such mixture onto the surface of a fiber paper which was dried before use. The CV measurements were performed using an electrochemical analyzer CHI 760i E and a standard three-electrode setup with a carbon working electrode, platinum wire auxiliary electrode and Ag/AgCl as the reference

electrode. The scan rate was $20 \text{ mV}\cdot\text{s}^{-1}$ with potential range 0 V to 1.5 V in supporting electrolyte (0.1 M NBu_4PF_6 in CH_2Cl_2).

Section 2: Optimization of molecular structures

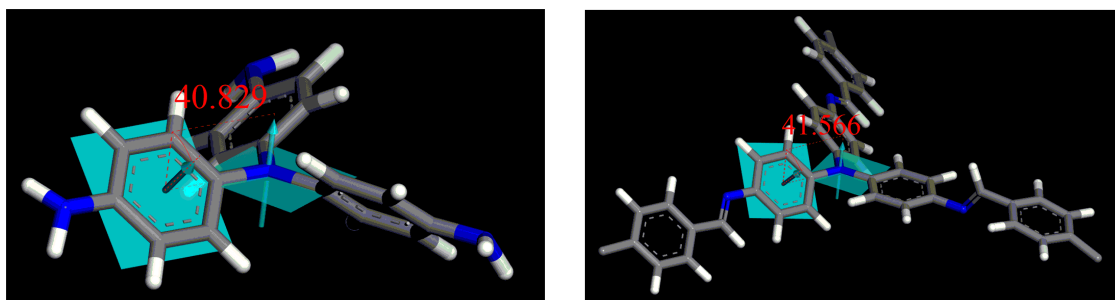


Figure S1. Twisted angles between benzene ring and central plane of TAPA (left) and JUC-561 (right) based on the optimization of molecular structures by Gaussian 09.

Section 3: SEM and TEM images

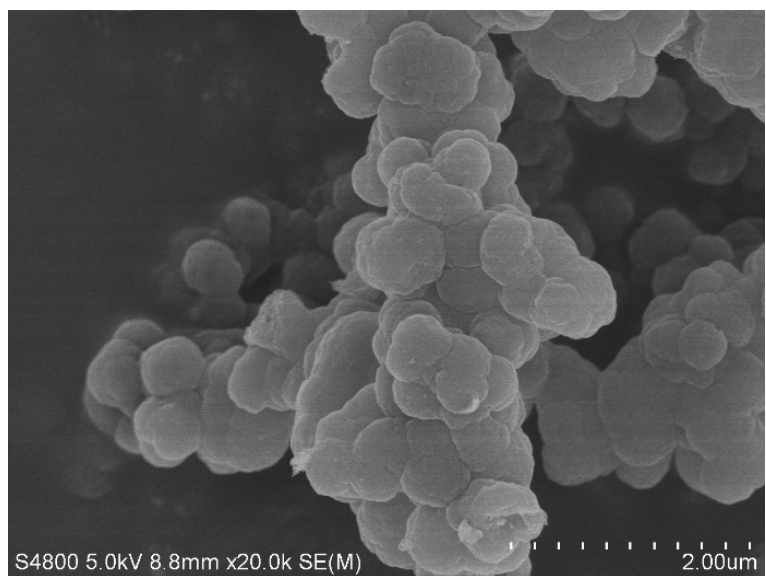


Figure S2. SEM image of as-synthesized JUC-560.

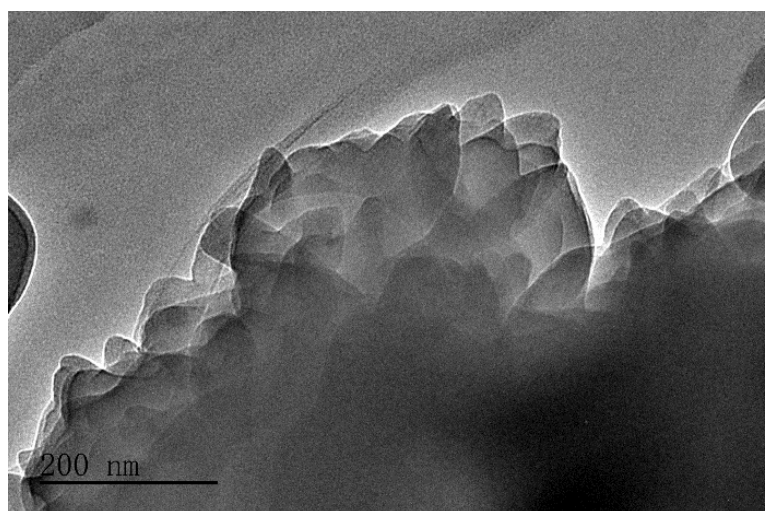


Figure S3. TEM image of as-synthesized JUC-560.

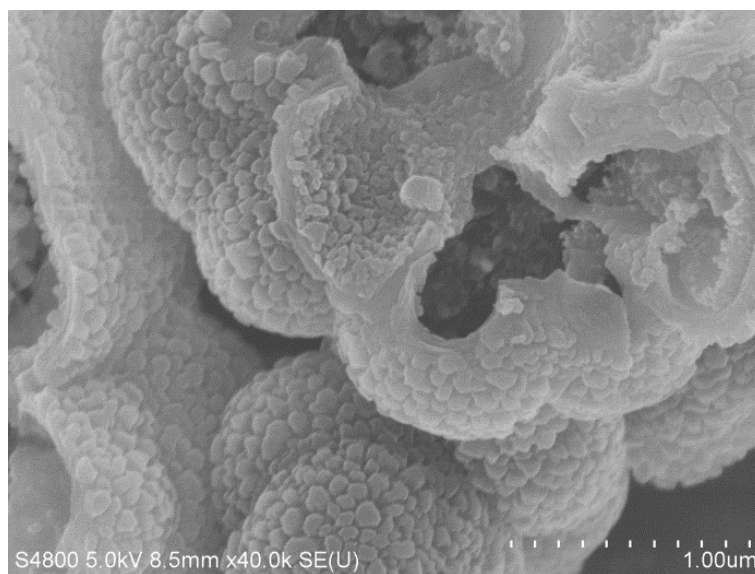


Figure S4. SEM image of as-synthesized JUC-561.

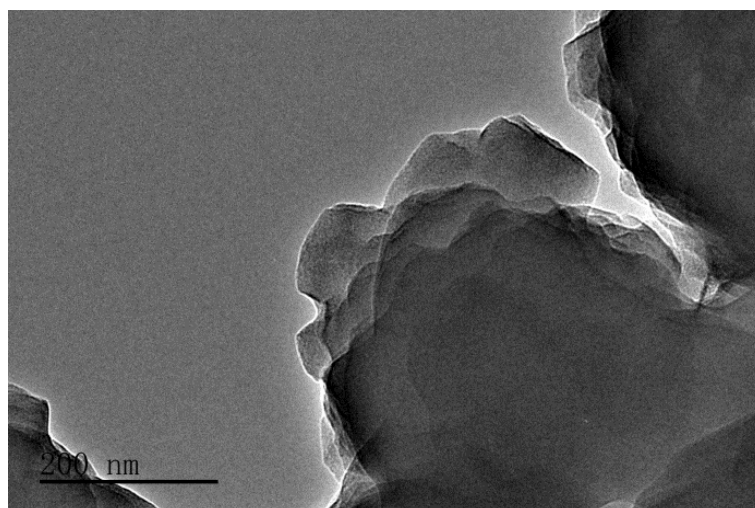


Figure S5. TEM image of as-synthesized JUC-561.

Section 4: FT-IR spectroscopy

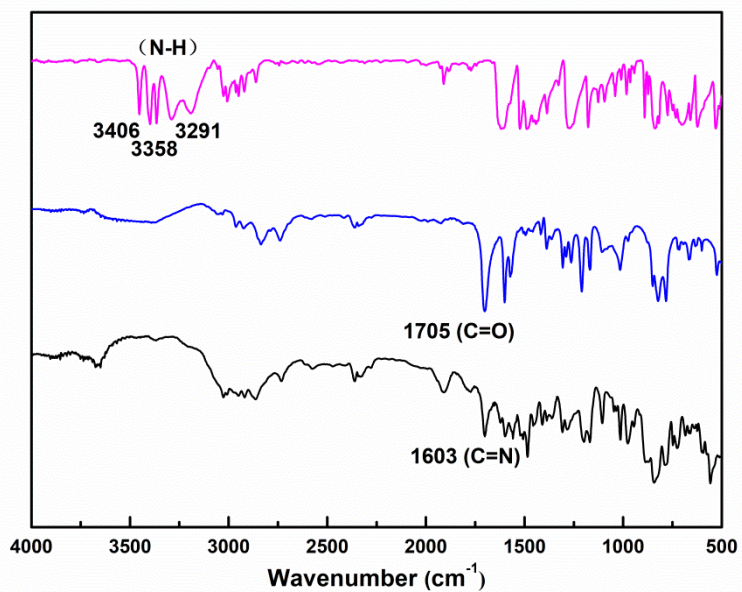


Figure S6. FT-IR spectra of JUC-560 (black), TFP-TTF (blue) and TAPT (pink).

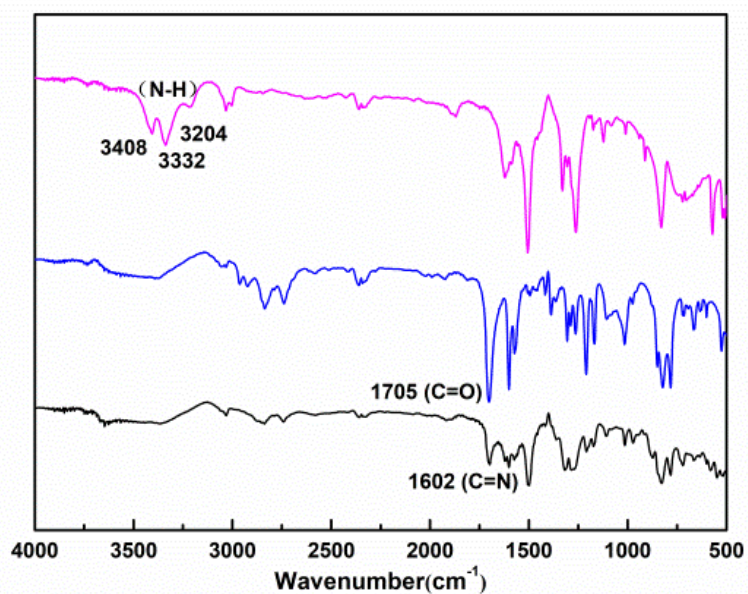


Figure S7. FT-IR spectra of JUC-561 (black), TFP-TTF (blue) and TAPA (pink).

Section 5: Solid-state ^{13}C NMR spectroscopy

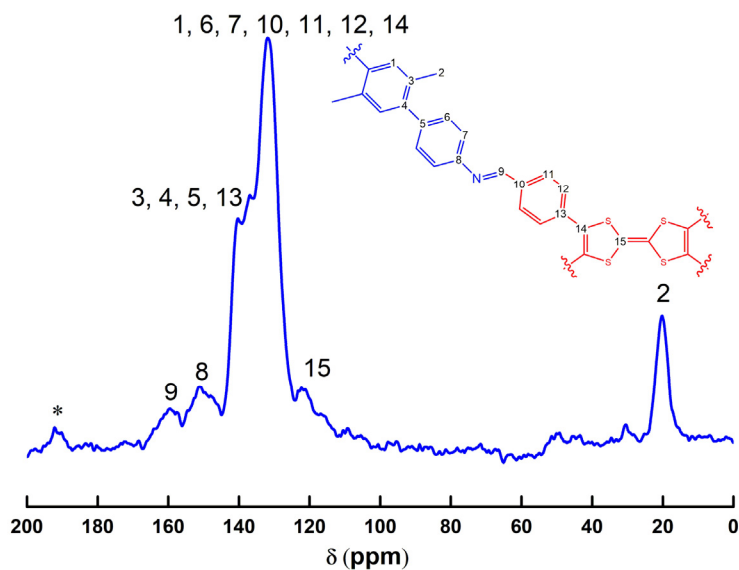


Figure S8. Solid state ^{13}C NMR of JUC-560. Asterisks (*) indicate peaks arising from spinning side bands.

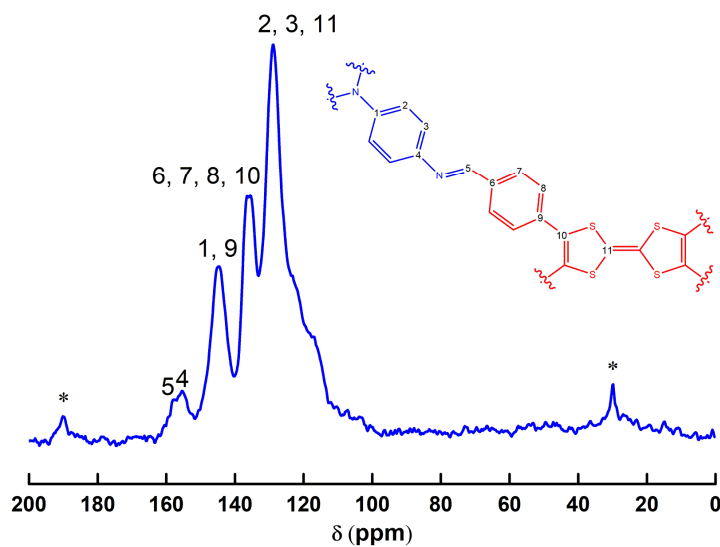


Figure S9. Solid state ^{13}C NMR of JUC-561. Asterisks (*) indicate peaks arising from spinning side bands.

Section 6: Structural analysis

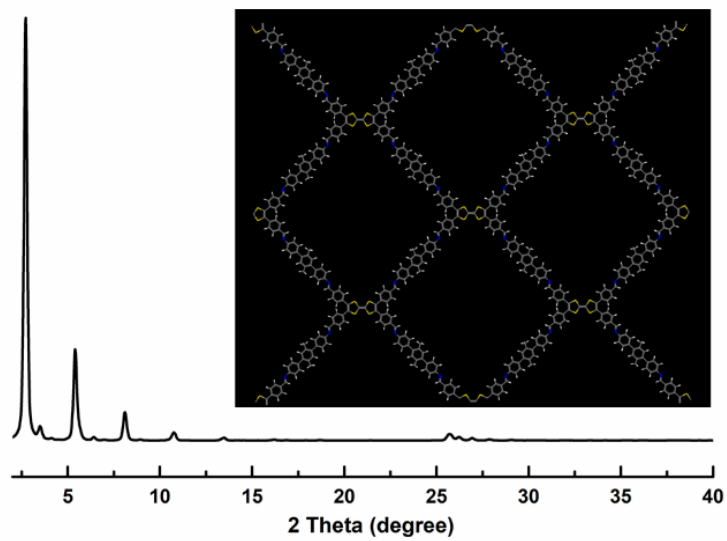


Figure S10. Calculated PXRD pattern of JUC-560 based on the AA-stacking **sql** net.

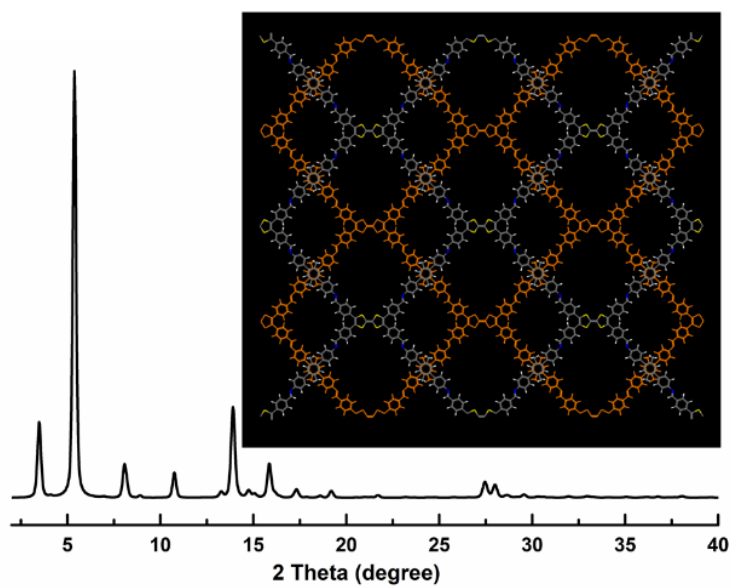


Figure S11. Calculated PXRD pattern of JUC-560 based on the AB-stacking **sql** net.

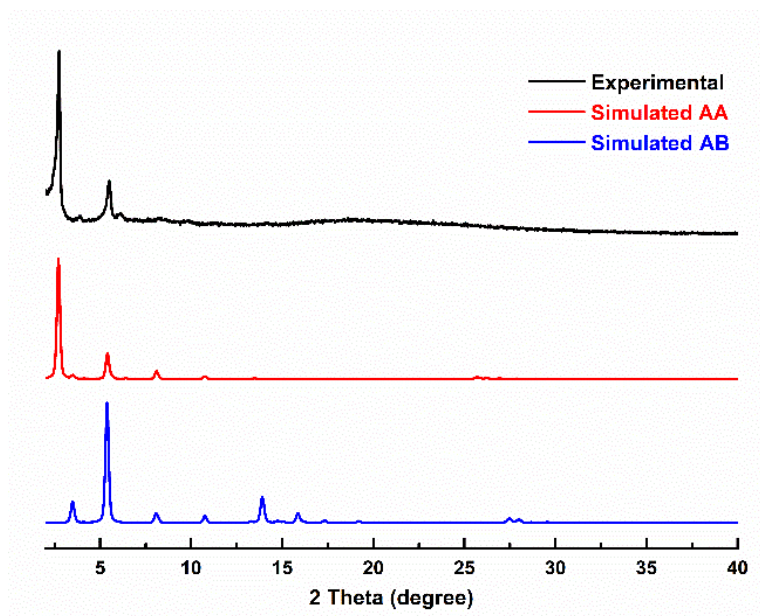


Figure S12. Comparison of PXRD patterns of JUC-560.

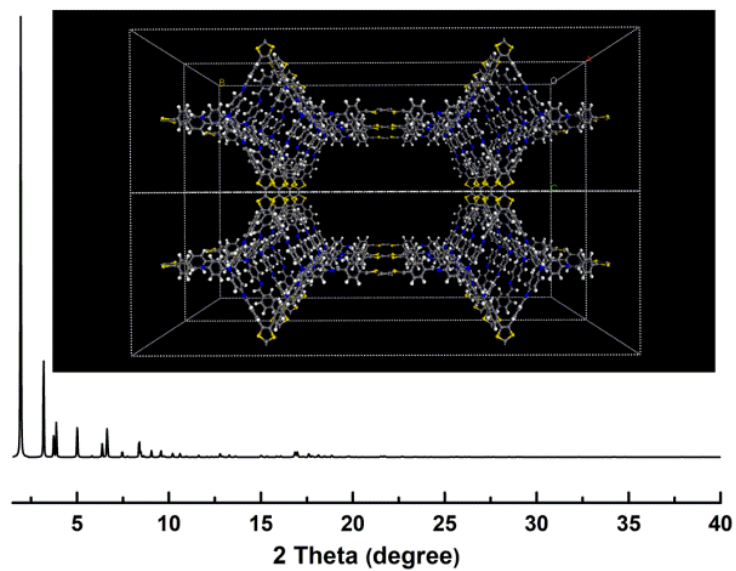


Figure S13. Calculated PXRD pattern of JUC-561 based on the **ffc** net.

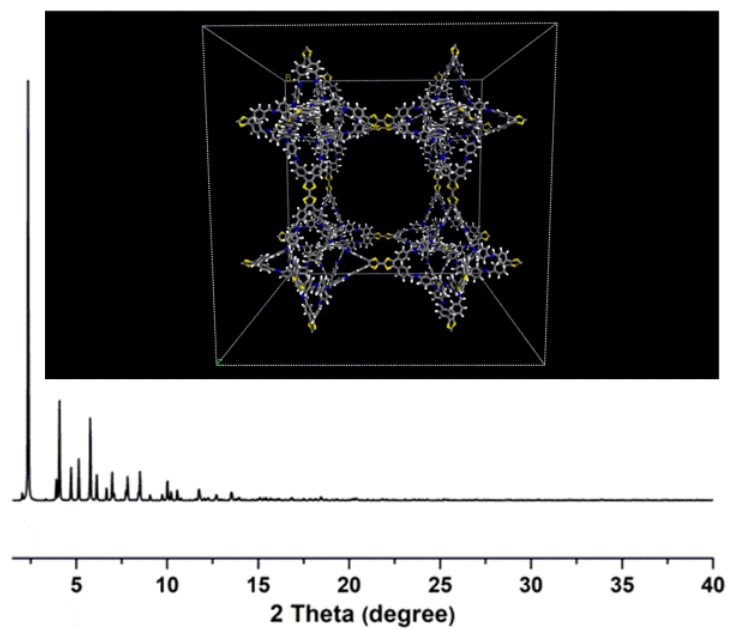


Figure S14. Calculated PXRD pattern of JUC-561 based on the **tbo** net.

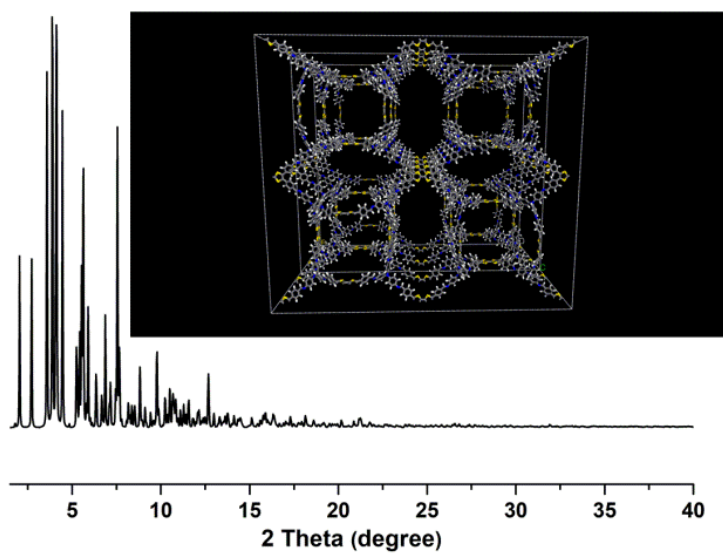


Figure S15. Calculated PXRD pattern of JUC-561 based on the **fjh** net.

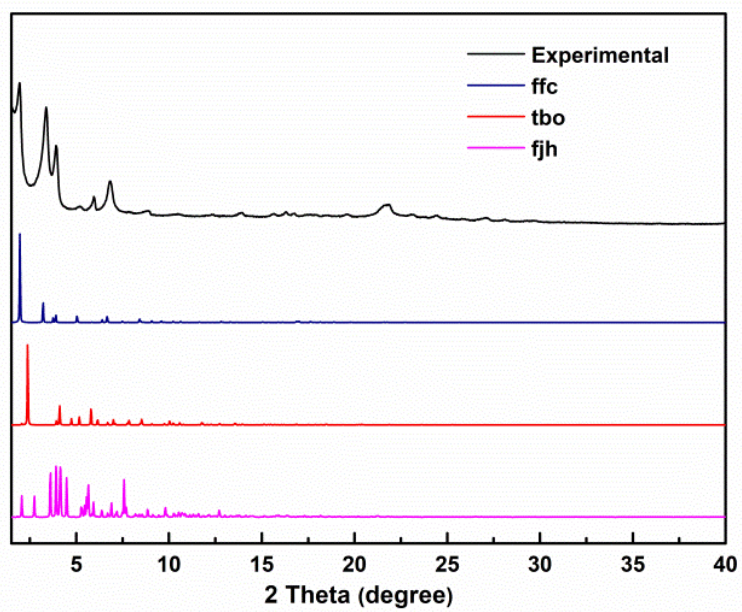


Figure S16. Comparison of PXRd patterns of JUC-561 based on different nets.

Section 7: Structural stability

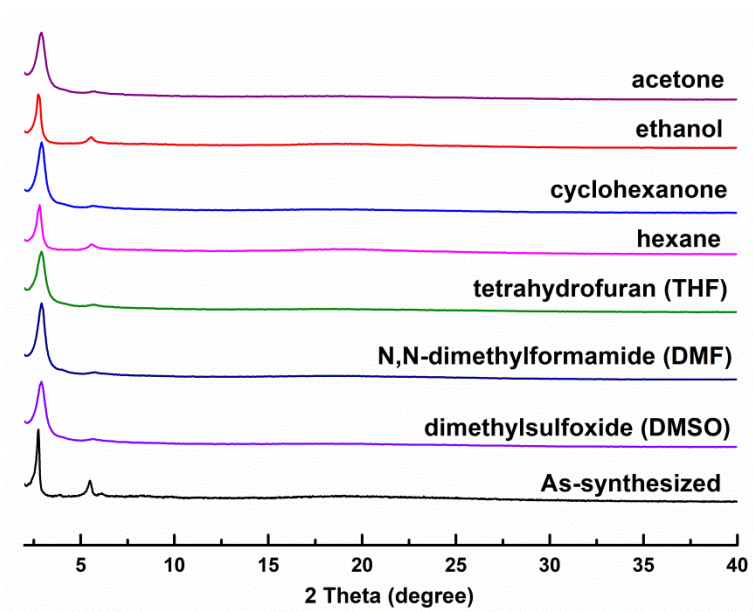


Figure S17. PXRD patterns of JUC-560 after the treatment in different organic solvents for 24 h.

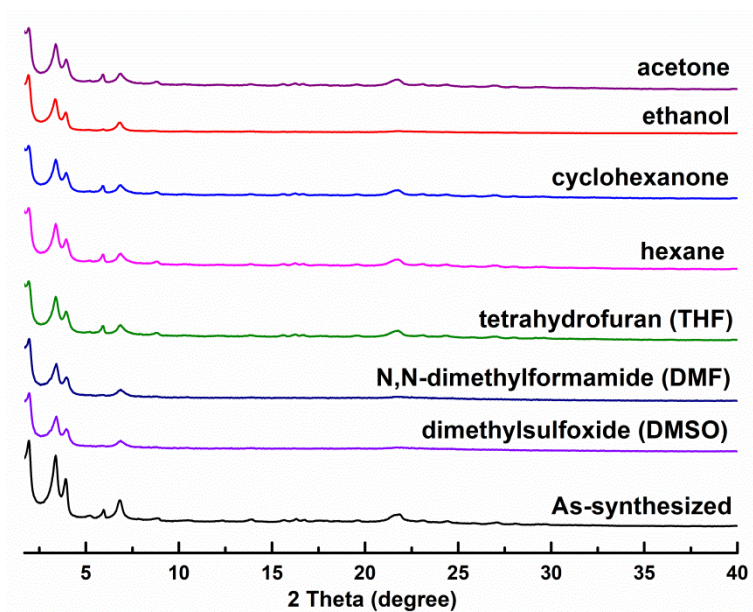


Figure S18. PXRD patterns of JUC-561 after the treatment in different organic solvents for 24 h.

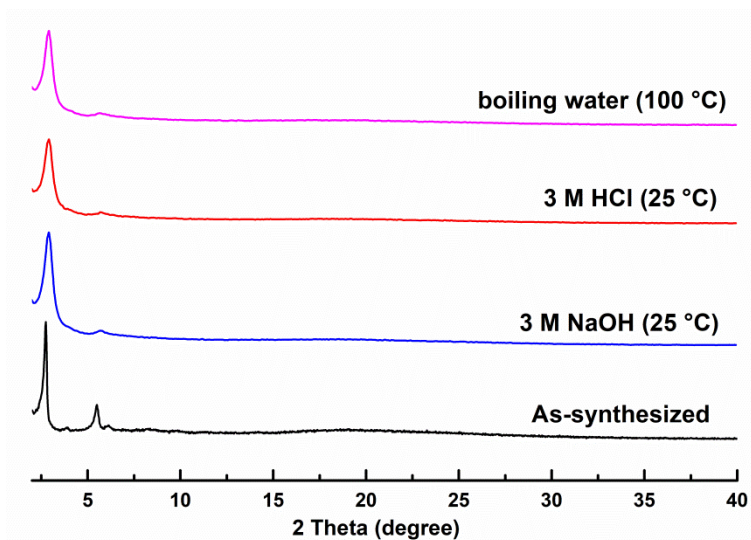


Figure S19. PXRD patterns of JUC-560 after the treatment in boiling water (100 °C), strong acid (3 M HCl, 25 °C) and strong base (3 M NaOH, 25 °C) for 24 h.

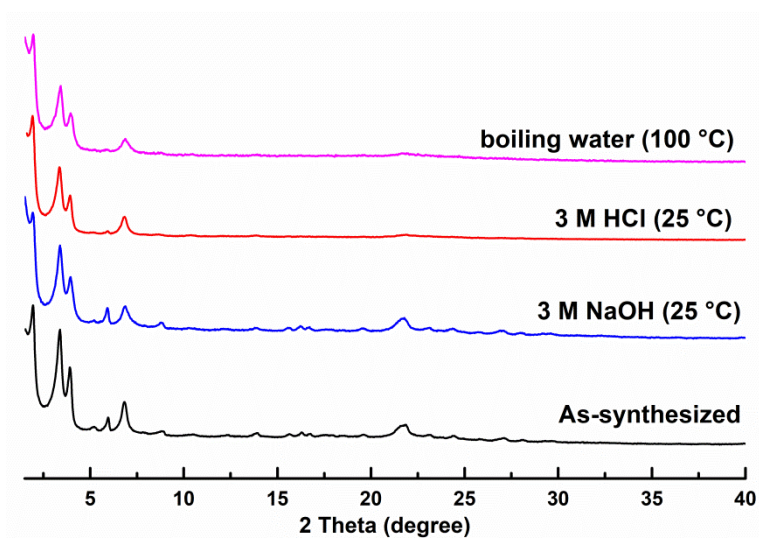


Figure S20. PXRD patterns of JUC-561 after the treatment in boiling water (100 °C), strong acid (3 M HCl, 25 °C) and strong base (3 M NaOH, 25 °C) for 24 h.

Section 8: Thermal gravity analysis

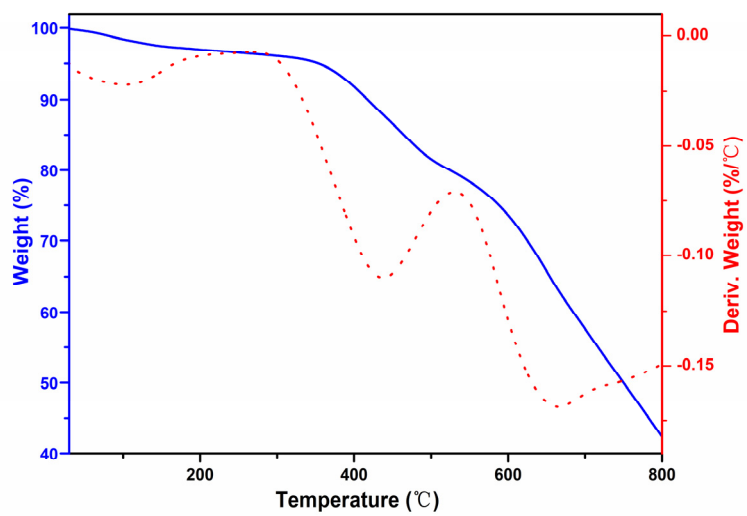


Figure S21. TGA curve of JUC-560.

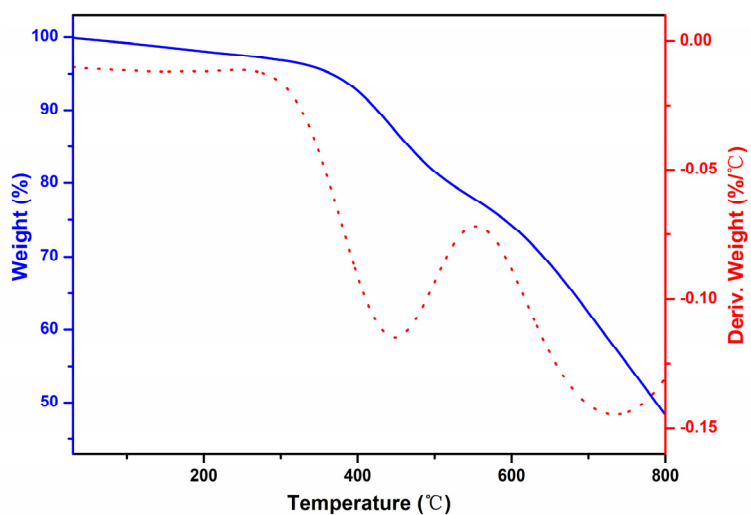


Figure S22. TGA curve of JUC-561.

Section 9. Nitrogen gas adsorption

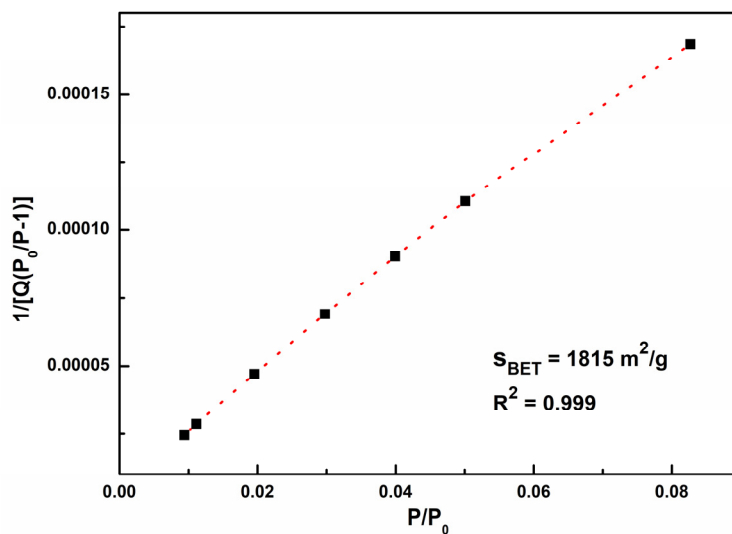


Figure S23. BET plot of JUC-560 calculated from N_2 adsorption isotherm at 77 K.

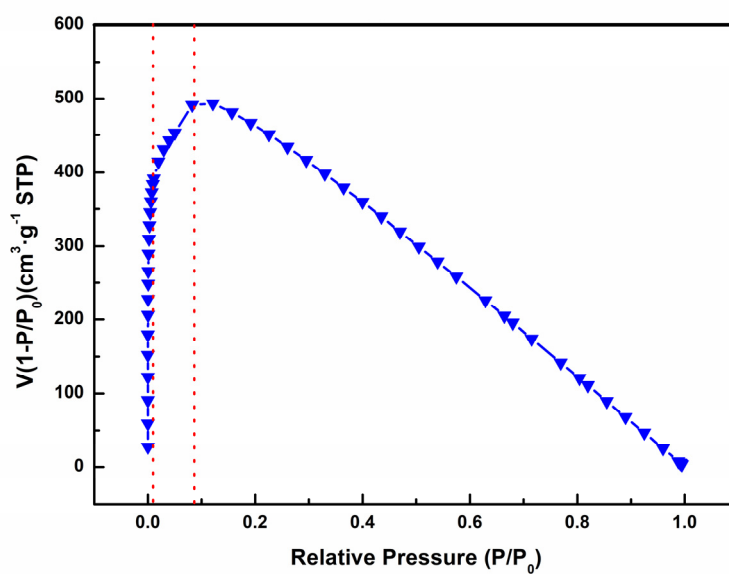


Figure S24. Rouquerol BET of JUC-560 calculated from N_2 adsorption isotherm at 77 K.

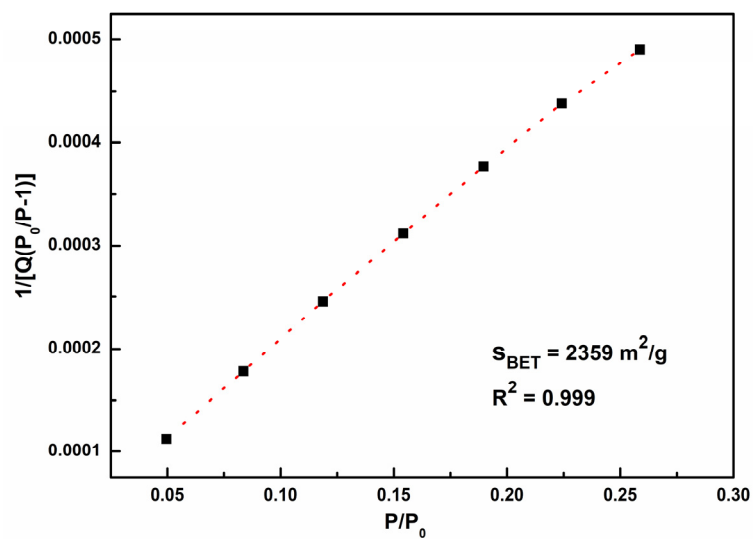


Figure S25. BET plot of JUC-561 calculated from N_2 adsorption isotherm at 77 K.

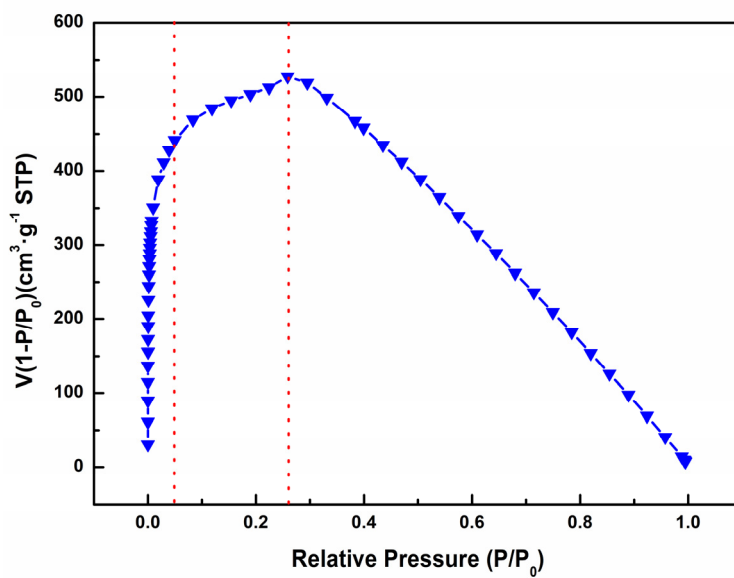


Figure S26. Rouquerol BET of JUC-560 calculated from N_2 adsorption isotherm at 77 K.

Section10. Adsorption of iodine

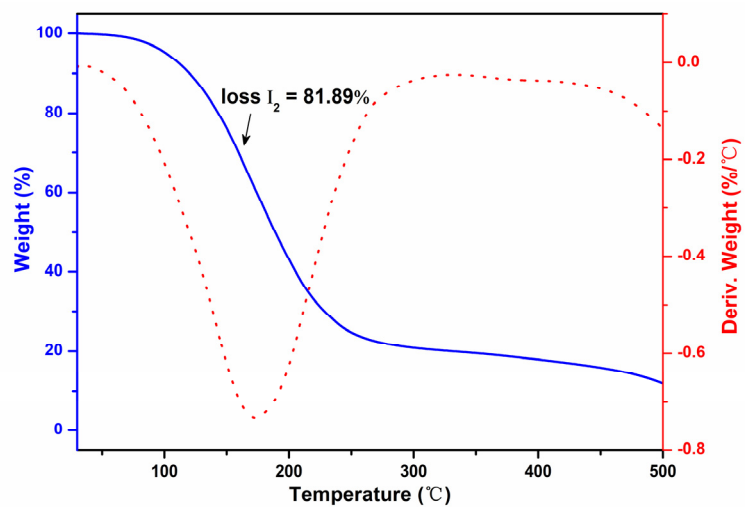


Figure S27. TGA curve of JUC-560 after iodine capture.

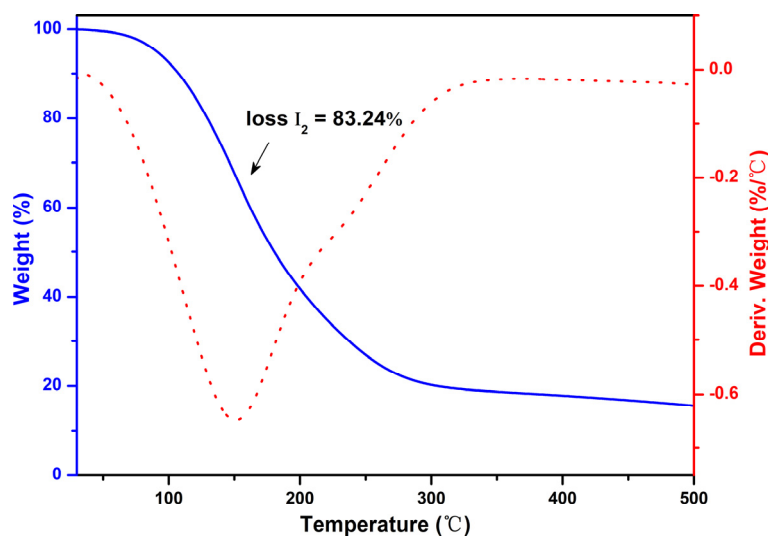


Figure S28. TGA curve of JUC-561 after iodine capture.

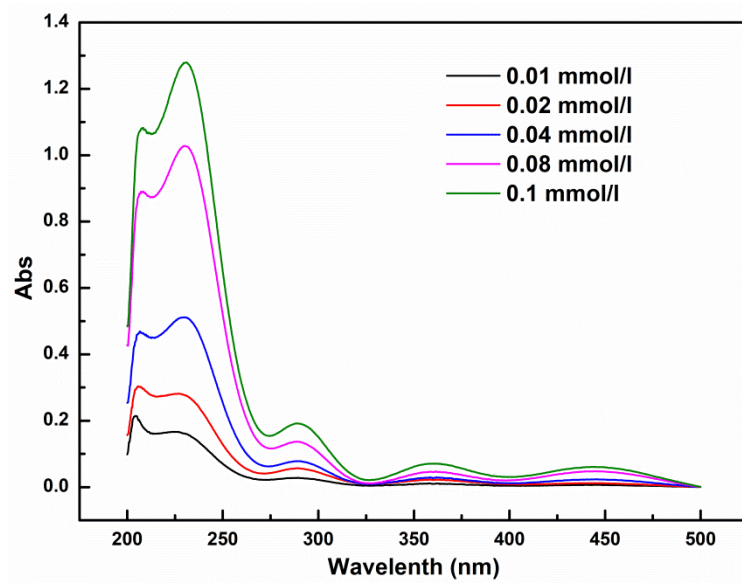


Figure S29. UV-Vis spectra of I₂ in ethanol at different concentrations recorded at room temperature, which are the data for a standard curve.

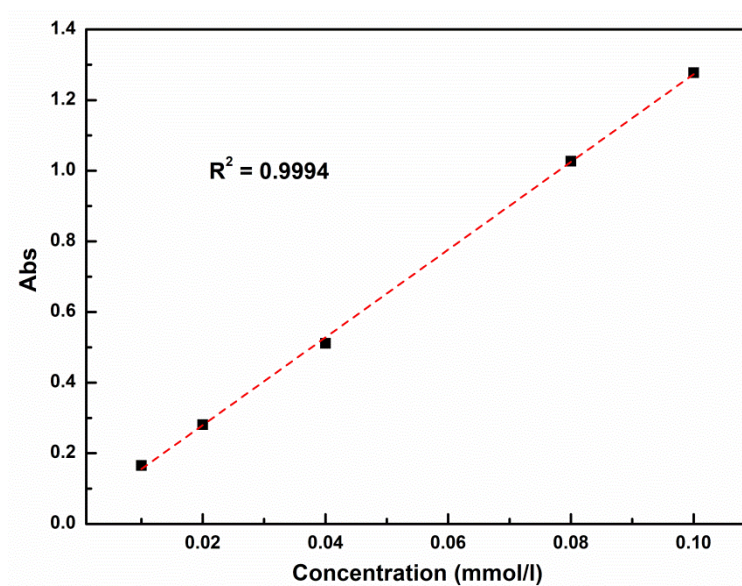


Figure S30. Calibration curve of iodine obtained from UV-Vis spectra.

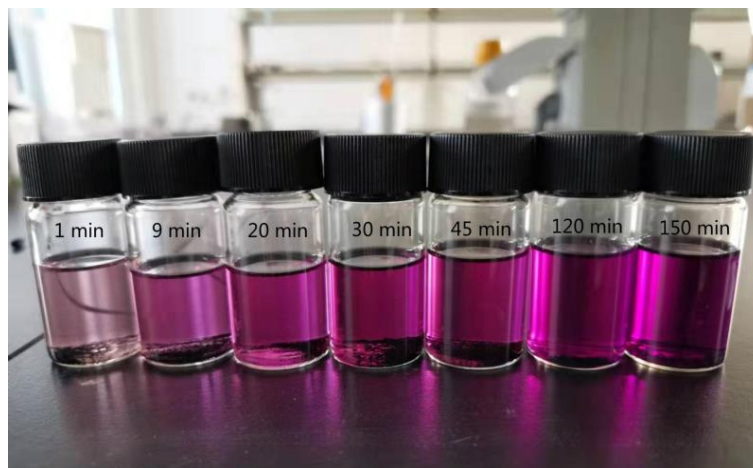


Figure S31. Visual detection of iodine release from JUC-560 in ethanol solution.

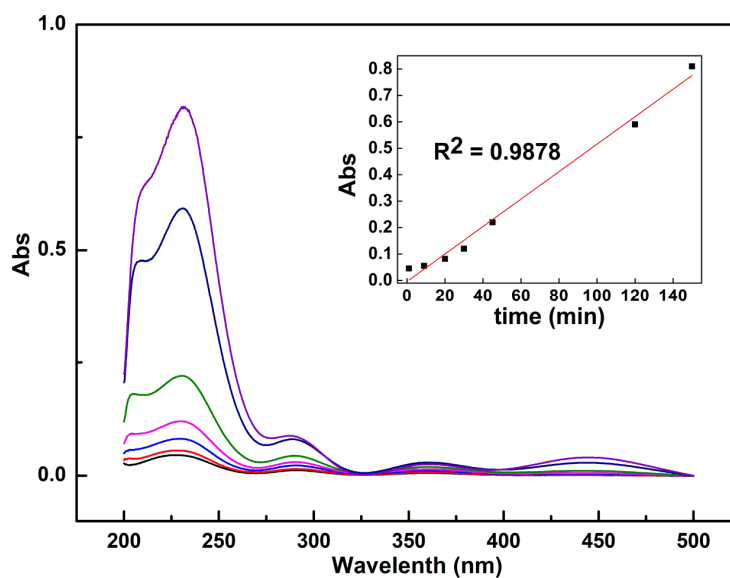


Figure S32. UV/Vis spectra of ethanol solutions containing iodine-loaded JUC-560.

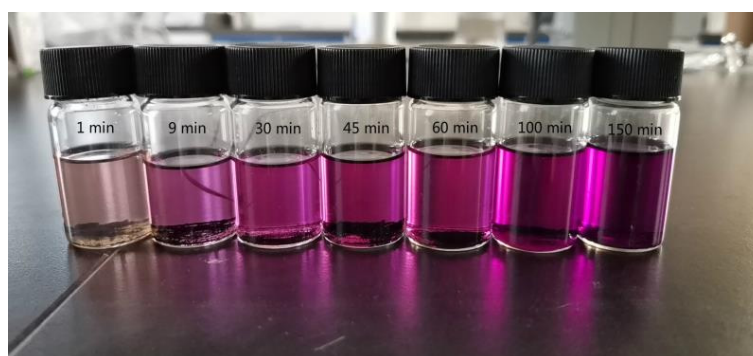


Figure S33. Visual detection of iodine release from JUC-561 in ethanol solution.

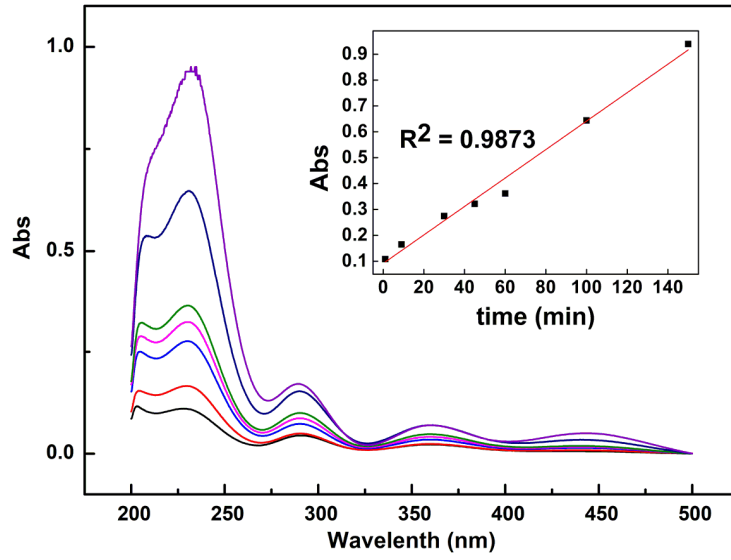


Figure S34. UV/Vis spectra of ethanol solutions containing iodine-loaded JUC-561.

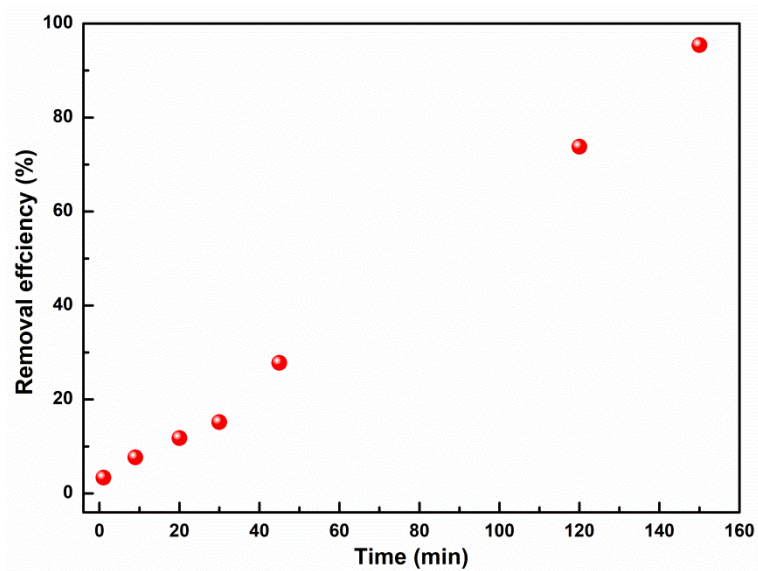


Figure S35. Removal efficiency of iodine by JUC-560.

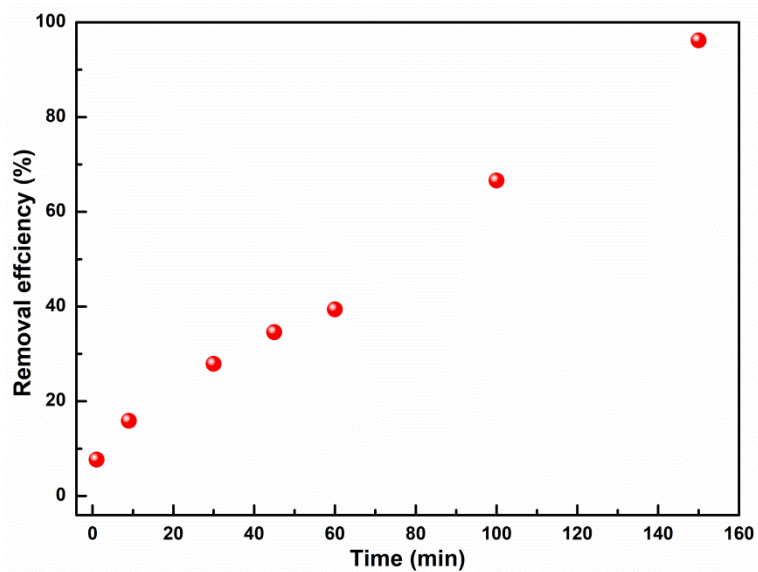


Figure S36. Removal efficiency of iodine by JUC-561.

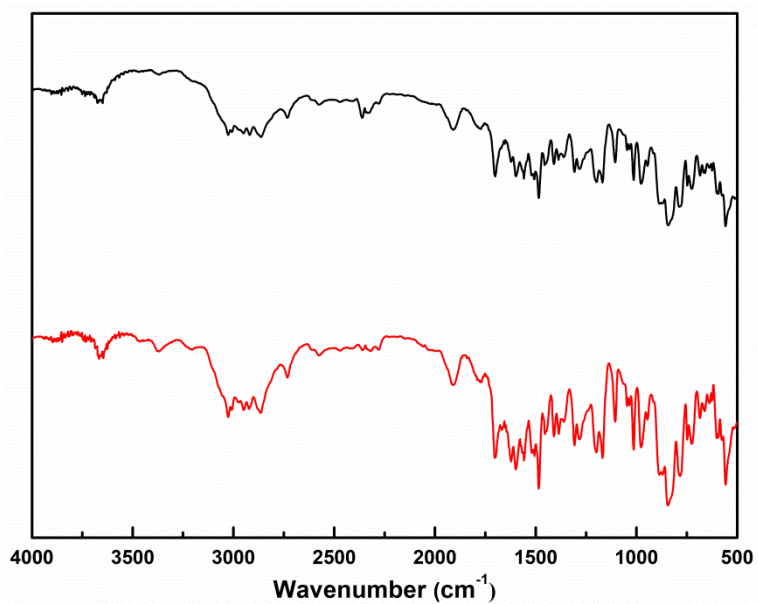


Figure S37. Comparison of IR spectroscopy of JUC-560 before (black) and after (red) cyclic application.

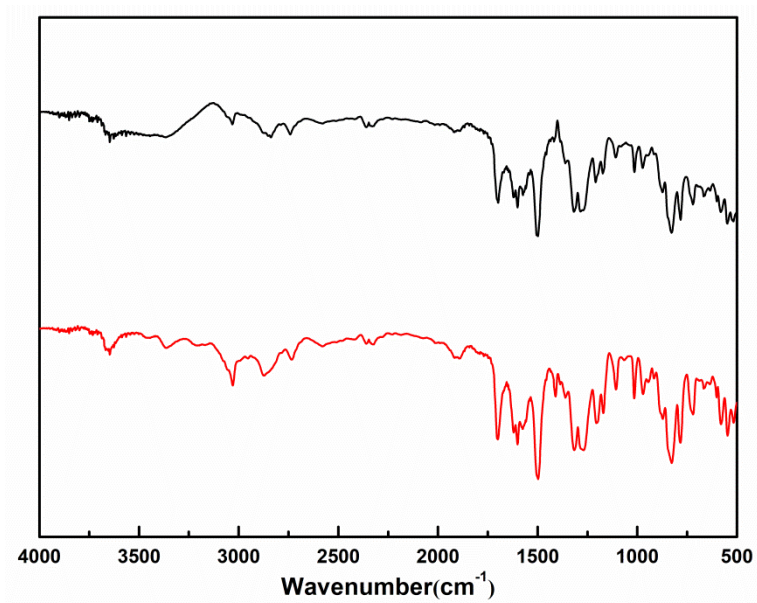


Figure S38. Comparison of IR spectroscopy of JUC-561 before (black) and after (red) cycled application.

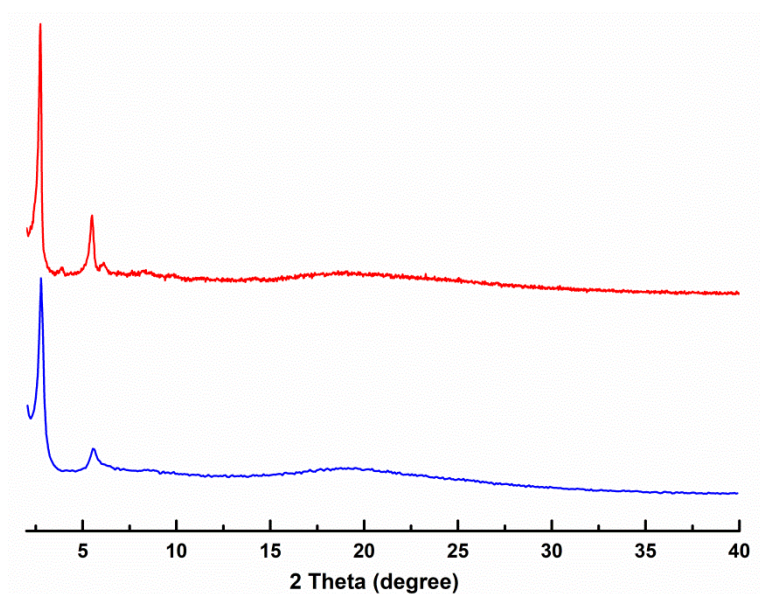


Figure S39. Comparison of PXRD patterns of JUC-560 before (red) and after (blue) cycled application.

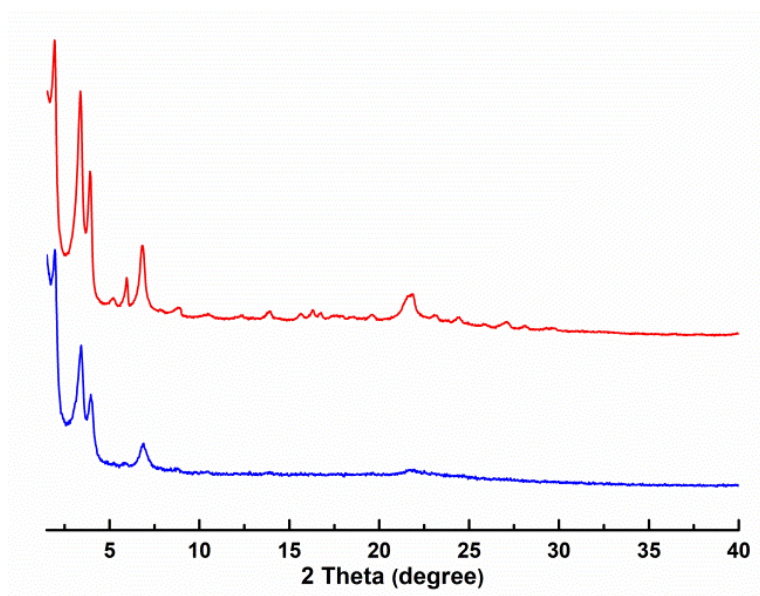


Figure S40. Comparison of PXRD patterns of JUC-561 before (red) and after (blue) cycled application.

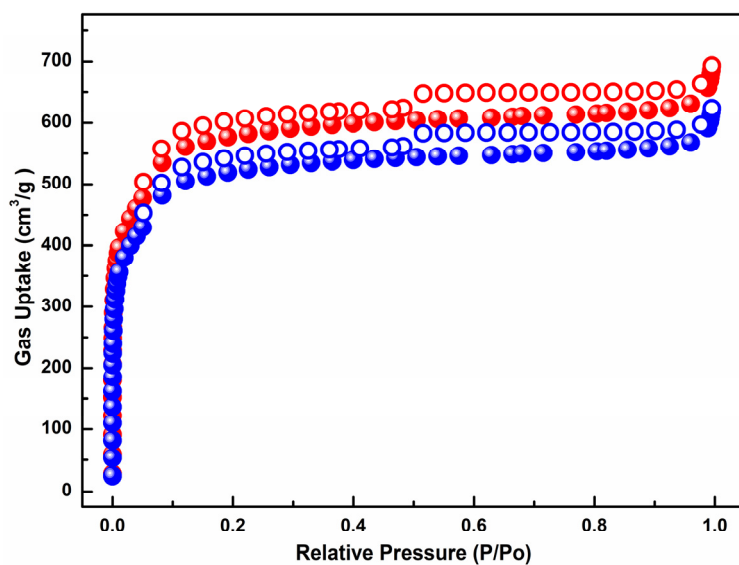


Figure S41. Comparison of nitrogen sorption isotherms of JUC-560 before (red) and after (blue) cycled application.

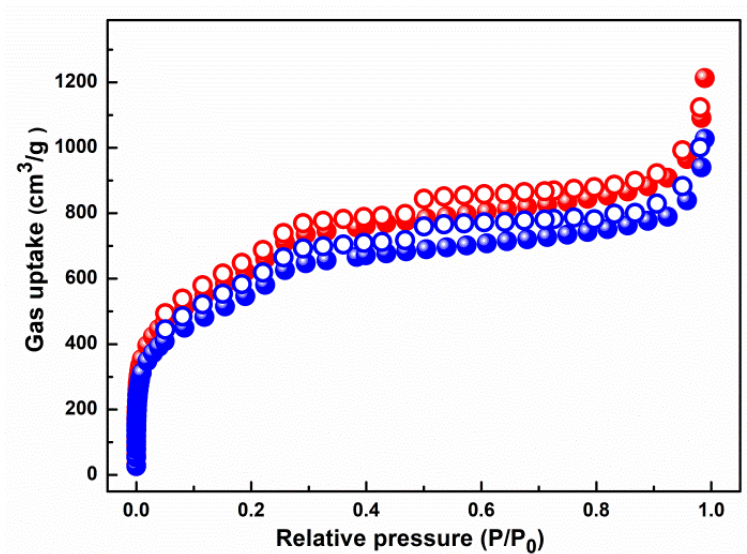


Figure S42. Comparison of nitrogen sorption isotherms of JUC-561 before (red) and after (blue) cycled application.

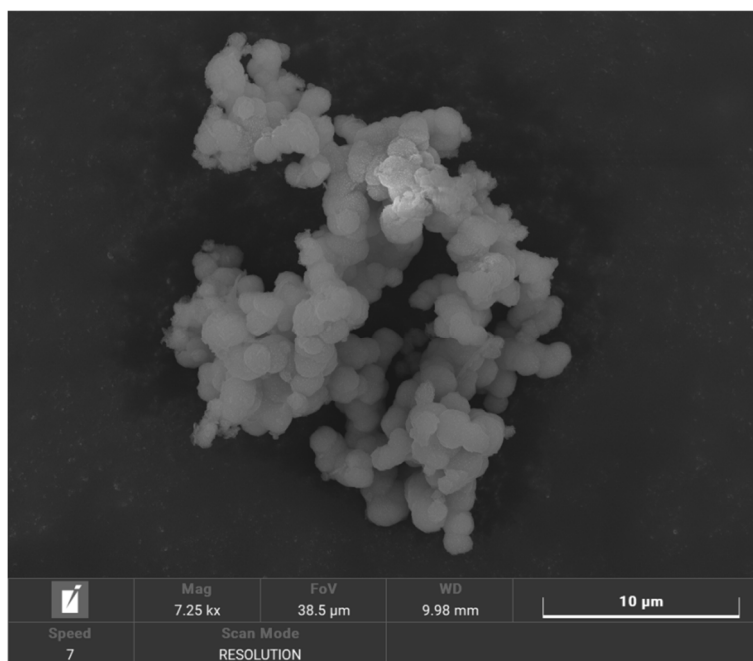


Figure S43. SEM image of I₂@JUC-560.

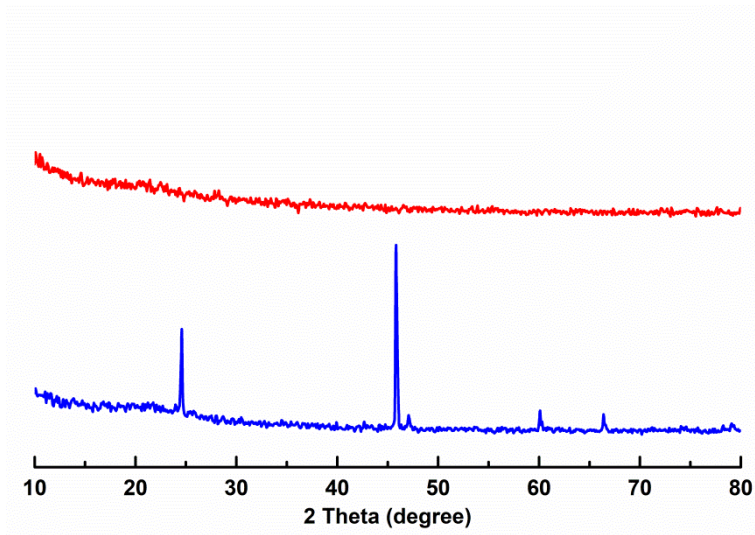


Figure S44. Comparison of PXRd patterns of I₂@JUC-560 (red) and I₂ (blue).

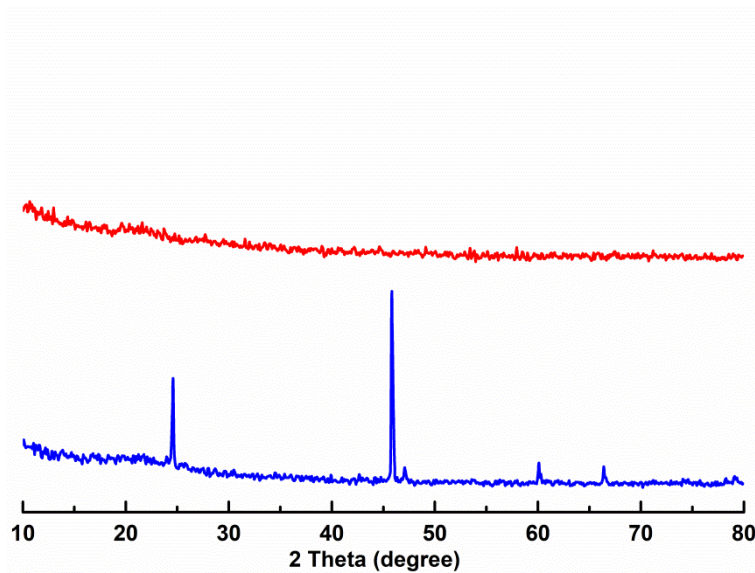


Figure S45. Comparison of PXRd patterns of I₂@JUC-561 (red) and I₂ (blue).

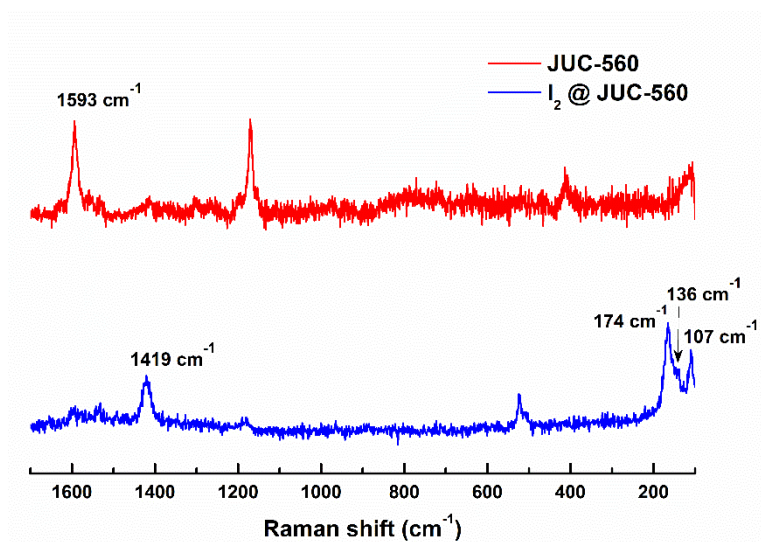


Figure S46. The full Raman spectra of the pristine (red) and iodine-loaded JUC-560 (blue). For the pristine COF-560, a symmetric vibration of TTF at 1593 cm⁻¹ could be observed. After loading I₂, the symmetric vibration of TTF almost disappeared, and a new peak for the oxidation state of TTF at 1419 cm⁻¹ appeared, which clearly indicates the complete charge-transfer from TTF to I₂.

Table S1. Comparison of experimental and simulated values of JUC-560 and JUC-561.

		Pore size (nm)	Pore volume (cm ³ g ⁻¹)	Iodine uptake (g g ⁻¹)
JUC-560	experimental	2.54	1.11	5.17
	theoretical	2.62	1.16	5.47
JUC-561	experimental	2.46	1.92	8.15
	theoretical	2.55	2.04	9.47

Table S2. Summary of iodine adsorption capacity for reported adsorbents.

Adsorbent	Temperature (°C)	I ₂ uptake (g g ⁻¹)	BET (m ² g ⁻¹)	Ref
JUC-561	75	8.19	2358	This work
TFB-DB COF	75	6.4	734	S4
QTD-COF-V	75	6.29	-	S5
TPB-DMTP	75	6.26	1927	S6
SCU-COF-2	75	6.0	413	S7
TJNU-201	77	5.625	2510	S8
COF-LZU1	77	5.30	858	S9
JUC-560	75	5.20	1815	This work
TAPA-PDA COF	77	5.09	685	S10
TTA-TTB	75	4.95	1733	S6
ETTA-TPA	75	4.79	1822	S6
PCMP-Y5	85	4.75	1212	S11
COF-DL229	75	4.7	1749	S12
H-C-CTPs	75	4.6	640	S13
CMP-LS5	70	4.4	1185	S14
COF-320	75	4.0	2400	S15
Meso-COF-3	75	4.0	982	S15
COP₁⁰	60	3.80	-	S16
KOH-AC	77	3.76	1973	S17
TFBCz-PDA	75	3.7	1441	S6
Meso-COF-2	75	3.5	1056	S15
COF-300	75	3.5	1360	S15
HCMP-3	85	3.36	50	S18
CMP-LS4	70	3.32	462	S14
Meso-COF-4	75	3.3	926	S15
Azo-PPN	77	2.90	400	S19
Meso-COF-1	75	2.90	816	S14
PAF-24	75	2.76	321	S20
PAF-23	75	2.71	273	S20
TTA-TFB	75	2.7	1163	S6
COF-TpgDB	75	2.6	210	S21
PAF-25	75	2.60	403	S20

TpPa-1	77	2.45	765	S9
CMP-LS6	70	2.44	679	S14
Cg-5C	25	2.39	360	S22
Azo-Trip	77	2.38	501	S23
Uassis-PC800	77	2.25	3053	S24
NiMoS chalcogels	60	2.25	490	S25
BN foam	77	2.12	561	S26
MALP-1	77	2.09	1179	S27
CMPN-3	70	2.08	1368	S28
MALP-4	77	2.04	1093	S27
NiP-CMP	77	2.02	2630	S29
MALP-3	77	1.87	1141	S27
NTP	75	1.80	1067	S30
ZIF-8	75	1.20	1875	S31
[Cd₂(COO)₄N₄]	50	0.66	1105	S32
HKUST-1	75	0.64	1798	S33
Ag⁺@Zeolite Mordenitres	95	0.28	-	S34

Table S3. Estimated iodine adsorption kinetics of reported adsorbents.

Porous adsorbent	Rate constant (g g⁻¹ h⁻¹)	Ref
QTD-COF-V	2.51	S5
JUC-561	0.70	This work
JUC-560	0.49	This work
SCU-COF-2	0.21	S7
Azo-PPN	0.18	S19
NiP-CMP	0.17	S29
TTA-TTB	0.15	S6
TFBCz-PDA	0.15	S6
TTA-TTB	0.14	S6
TPB-DMTP	0.13	S6
ETTA-TPA	0.12	S6
NTP	0.11	S30
Ag⁺-loaded-Zeolite	0.02	S34

Section S11: Electrochemical behavior

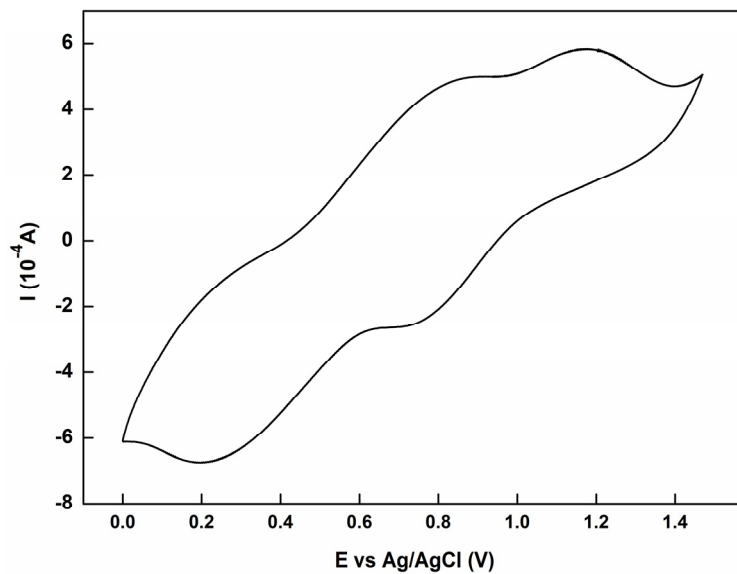


Figure S47. CV of JUC-560.

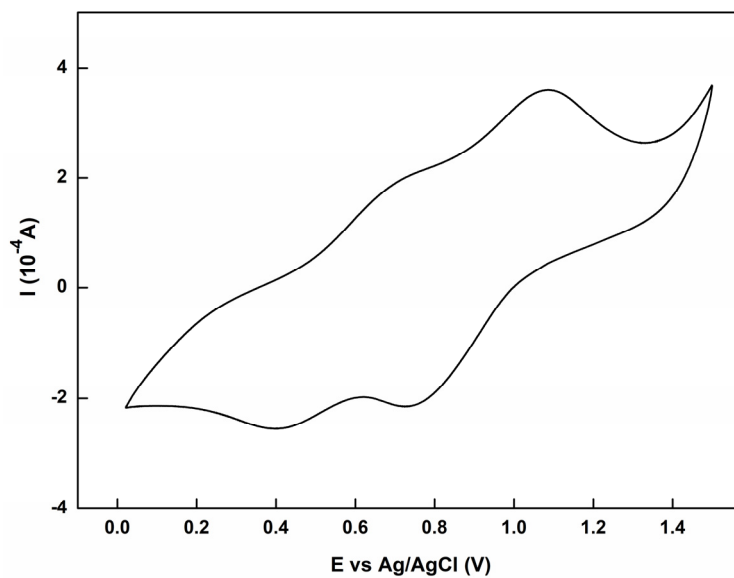


Figure S48. CV of JUC-561.

Section S12. Theoretical study

Table S4. Optimized geometries of TTF·I₂ (a), TTF^{•+}·I₂ (b), TTF^{•+}·I⁻ (c), TTF^{•+}·I₃⁻ (d), and TTF^{•+}·I₅⁻ (e).

	Interatomic forces	Distance (Å)
a	I1-C	3.758
	I1-S	3.914
	I2-C	3.769
	I2-S	3.924
b	I1-C	3.817
	I1-S	4.017
	I2-C	4.058
	I2-S	3.982
c	I-C	3.280
	I-S	3.897
d	I1-C	3.679
	I1-S	3.959
	I2-C	3.648
	I3-C	3.959
	I3-S	3.774
e	I1-C	3.950
	I2-C	3.853
	I3-C	3.689
	I3-S	3.823
	I4-C	3.835
	I5-C	3.718

Section S13: Unit cell parameters

Table S5. Unit cell parameters and fractional atomic coordinates for JUC-560 calculated based on the eclipsed **sql** net.

Space group		<i>Cmmm</i>	
Calculated unit cell		$a = 50.7796 \text{ \AA}, b = 43.0907 \text{ \AA}, c = 3.4757 \text{ \AA}, \alpha = \beta = \gamma = 90^\circ$	
Measured unit cell		$a = 50.9209 \text{ \AA}, b = 43.2634 \text{ \AA}, c = 3.4837 \text{ \AA}, \alpha = \beta = \gamma = 90^\circ$	
Pawley refinement		$R_p = 1.31\%, R_{wp} = 2.53\%$	
atoms	x	y	z
C1	0.48679	0	0.5
C2	0.08193	0.57157	0.5
H3	0.06243	0.58124	0.5
C4	0.10243	0.5931	0.5
H5	0.09775	0.61751	0.5
C6	0.12857	0.58316	0.5
C7	0.13376	0.55156	0.5
H8	0.15376	0.54308	0.5
C9	0.11309	0.53044	0.5
C10	0.08672	0.53915	0.5
N11	0.14698	0.63467	0.5
C12	0.15066	0.60503	0.5
C13	0.16156	0.68822	0.5
H14	0.14116	0.69531	0.5
C15	0.18125	0.71071	0.5
H16	0.17459	0.73429	0.5
C17	0.2082	0.70253	0.5
C18	0.21417	0.67054	0.5
H19	0.23396	0.66188	0.5
C20	0.19439	0.64817	0.5
H21	0.19991	0.62401	0.5
C22	0.16788	0.6569	0.5
C23	0.2565	0.71882	0.5
H24	0.2631	0.69521	0.5
C25	0.22376	0.75876	0.5
H26	0.20395	0.76737	0.5
C27	0.22964	0.72688	0.5
C28	0.43599	1.01604	0.5
S29	0.46825	1.0347	0.5
H30	0.1783	0.59182	0.5

H31	0.12058	0.50687	0.5
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Table S6. Unit cell parameters and fractional atomic coordinates for JUC-560 calculated based on the staggered **sql** net.

Space group		<i>Fmmm</i>	
Calculated unit cell		$a = 51.0253 \text{ \AA}, b = 43.2067 \text{ \AA}, c = 6.5014 \text{ \AA},$ $\alpha = \beta = \gamma = 90^\circ$	
atoms	x	y	z
C1	0.4868	0.5	0.5
C2	0.08187	0.07172	0.5
H3	0.0624	0.08139	0.5
C4	0.10235	0.09329	0.5
H5	0.09767	0.11774	0.5
C6	0.12844	0.08333	0.5
C7	0.13362	0.05168	0.5
H8	0.15358	0.04319	0.5
C9	0.11298	0.03052	0.5
C10	0.08665	0.03923	0.5
N11	0.1469	0.13493	0.5
C12	0.15051	0.10523	0.5
C13	0.1616	0.18854	0.5
H14	0.14126	0.19572	0.5
C15	0.18131	0.21098	0.5
H16	0.17473	0.23463	0.5
C17	0.20818	0.20268	0.5
C18	0.21407	0.17062	0.5
H19	0.2338	0.16188	0.5
C20	0.19426	0.1483	0.5
H21	0.19972	0.12409	0.5
C22	0.16782	0.15714	0.5
C23	0.25641	0.21875	0.5
C24	0.26296	0.19509	0.5
C25	0.22383	0.25889	0.5
H26	0.20409	0.26762	0.5
C27	0.22964	0.22696	0.5
C28	0.43604	0.51608	0.5
S29	0.46826	0.53476	0.5
H30	0.38222	0.50532	0.5

H31	0.71845	0.59852	0.5
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Table S7. Unit cell parameters and fractional atomic coordinates for JUC-561 calculated based on **ffc** net.

Space group		<i>Cmmm</i>	
Calculated unit cell		$a = 10.5167 \text{ \AA}, b = 89.0024 \text{ \AA}, c = 26.2881 \text{ \AA},$ $\alpha = \beta = \gamma = 90^\circ$	
Measured unit cell		$a = 10.5223 \text{ \AA}, b = 89.0138 \text{ \AA}, c = 26.2907 \text{ \AA},$ $\alpha = \beta = \gamma = 90^\circ$	
Pawley refinement		$R_p = 3.07\%, R_{wp} = 4.51\%$	
atoms	x	y	z
C1	0.7416	0.75768	0.11548
S2	0.77153	0.73253	0.05831
C3	0.66051	0.81505	0.43068
C4	0.66451	0.80694	0.38711
C5	0.75639	0.80215	0.36822
C6	0.84284	0.80523	0.39432
C7	0.83885	0.81346	0.43764
C8	0.74768	0.81849	0.45587
C9	0.7102	0.85183	0.45631
C10	0.68754	0.86761	0.45642
C11	0.70058	0.79429	0.2886
N12	0.76476	0.79388	0.32345
C13	0.64573	0.78642	0.79311
C14	0.65477	0.77749	0.8348
C15	0.73409	0.76717	0.84014
C16	0.80611	0.7663	0.8036
C17	0.79617	0.77509	0.76151
C18	0.71512	0.78514	0.75578
C19	0.66673	0.92618	0.45628
C20	0.62758	0.94115	0.45628
H21	0.58977	0.81875	0.44485
H22	0.59585	0.80429	0.36889
H23	0.91356	0.80143	0.38049
H24	0.90671	0.81606	0.45667
H25	0.71923	0.84616	0.42184
H26	0.67871	0.87369	0.42255
H27	0.6359	0.80165	0.29104
H28	0.58437	0.79437	0.78991

H29	0.59903	0.77852	0.86268
H30	0.86964	0.75876	0.80752
H31	0.85168	0.774	0.73355
H32	0.67992	0.92036	0.4223
H33	0.60998	0.94669	0.4223
C34	0.75	0.75	0.02429
S35	0.61445	1.01871	0.5
C36	0.54952	1.03686	0.5
C37	0.67626	0.87553	0.5
C38	0.72077	0.8436	0.5
C39	0.7166	0.90239	0.5
N40	0.65039	0.89154	0.5
C41	0.6063	0.94859	0.5
C42	0.68494	0.91857	0.5
N43	1.24323	1.32715	0.5
H44	1.2949	1.39964	0.5
C45	0.5	1.0078	0.5

Table S8. Unit cell parameters and fractional atomic coordinates for JUC-561 calculated based on **tbo** net.

Space group		<i>Fm-3m</i>	
Calculated unit cell		$a = b = c = 83.4586 \text{ \AA}$ $\alpha = \beta = \gamma = 90^\circ$	
N1	0.33195	0.33195	0.33195
C2	0.36298	0.32694	0.32694
H3	0.36577	0.33593	0.33593
C4	0.37644	0.31891	0.31891
H5	0.38851	0.32221	0.32221
C6	0.37431	0.30674	0.30674
C7	0.35773	0.30373	0.30373
H8	0.3549	0.29477	0.29477
C9	0.34445	0.31166	0.31166
H10	0.33243	0.3083	0.3083
C11	0.3463	0.32372	0.32372
C12	0.40358	0.29713	0.29713
N13	0.3873	0.29753	0.29753
C14	0.43291	0.28765	0.28765
H15	0.43774	0.29616	0.29616
C16	0.44439	0.27824	0.27824
H17	0.45688	0.28059	0.28059

C18	0.44032	0.26632	0.26632
C19	0.42303	0.26553	0.26553
H20	0.41729	0.2579	0.2579
C21	0.41149	0.27481	0.27481
H22	0.39887	0.27272	0.27272
C23	0.41578	0.28642	0.28642
S24	0.47629	0.26222	0.26222
C25	0.4544	0.25619	0.25619
C26	0.49094	0.25	0.75

Table S9. Unit cell parameters and fractional atomic coordinates for JUC-561 calculated based on **fjh** net.

Space group		<i>Fm</i> <i>m</i> <i>m</i>	
Calculated unit cell		$a = 86.5862 \text{ \AA}, b = 98.7415 \text{ \AA}, c = 33.7131 \text{ \AA},$ $\alpha = \beta = \gamma = 90^\circ$	
atoms	x	y	z
C1	0.27542	-0.14524	0.26433
C2	0.33063	-0.15788	0.26372
C3	0.29539	-0.19853	0.26701
C4	0.28398	-0.20844	0.26634
S5	0.26757	-0.23373	0.25037
C6	0.46311	-0.13099	0.4802
S7	0.48144	-0.12994	0.45454
C8	0.4491	-0.1427	0.42665
C9	0.43701	-0.14355	0.3992
C10	0.42485	-0.13419	0.40031
C11	0.42498	-0.12396	0.42911
C12	0.43718	-0.12307	0.45653
C13	0.44928	-0.13253	0.45536
N14	0.40074	-0.12717	0.37044
C15	0.41276	-0.13509	0.37012
C16	0.37517	-0.12068	0.34654
C17	0.36364	-0.12063	0.31716
C18	0.36604	-0.12745	0.28137
C19	0.38003	-0.13434	0.27488
C20	0.3915	-0.13451	0.30429
C21	0.38912	-0.12763	0.34031
C22	0.17271	-0.13168	0.26621
C23	0.18532	-0.14066	0.26704
C24	0.22298	-0.1822	0.25889
C25	0.23439	-0.19238	0.26004

C26	0.13075	-0.03231	0.48012
S27	0.13116	-0.01633	0.45446
C28	0.1177	-0.05247	0.45089
C29	0.11757	-0.06348	0.42486
C30	0.13085	-0.06675	0.40342
C31	0.14432	-0.05892	0.40878
C32	0.14445	-0.04792	0.43481
C33	0.13116	-0.04467	0.45625
N34	0.14202	-0.08096	0.3527
C35	0.13063	-0.07844	0.37665
C36	0.13084	-0.10243	0.32717
C37	0.13186	-0.11359	0.30164
C38	0.14444	-0.11499	0.27561
C39	0.15595	-0.10498	0.275
C40	0.15499	-0.0938	0.30025
C41	0.14247	-0.09238	0.32658
N42	0.35473	0.12644	-0.25047
C43	0.31625	-0.15382	0.24766
C44	0.34162	-0.13561	0.25013
C45	0.30483	-0.17564	0.25574
N46	0.30326	-0.16294	0.24584
C47	0.26886	-0.20569	0.25282
C48	0.29211	-0.18538	0.25455
C49	0.25787	-0.21739	0.25084
H50	0.35467	0.84778	-0.72202
H51	0.332	0.8314	-0.72424
H52	0.30751	0.79886	-0.72221
H53	0.28671	0.78086	-0.72309
H54	0.45893	0.84962	-0.57431
H55	0.43703	0.84813	-0.62422
H56	0.41515	0.8837	-0.56957
H57	0.43724	0.88533	-0.52028
H58	0.41369	0.85709	-0.65465
H59	0.37323	0.88494	-0.62435
H60	0.35232	0.88498	-0.67747
H61	0.3821	0.86017	-0.7544
H62	0.40275	0.85977	-0.701
H63	0.31681	0.82097	-0.73433
H64	1.17396	0.87896	-0.72113
H65	1.19687	0.86279	-0.72026
H66	1.22589	0.82854	-0.73125
H67	1.24646	0.81007	-0.72853
H68	1.10682	0.9503	-0.53188

H69	1.10664	0.93021	-0.57883
H70	1.15529	0.93846	-0.60826
H71	1.15538	0.95838	-0.56148
H72	1.12028	0.91442	-0.62348
H73	1.12064	0.89855	-0.65163
H74	1.12243	0.87835	-0.69814
H75	1.16615	0.89405	-0.74618
H76	1.16439	0.91428	-0.70034
C77	0.50774	-0.1297	-0.5
C78	0.13115	0.0068	-0.5
C79	0.25	-0.24318	0.25

Section S14: References

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