

Supporting Information

Thiophene-based Mesoporous Covalent Organic Framework for Efficient Iodine Vapor Capture

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Section S1. Experimental

S1.1 Measurements

PXRD patterns were collected on a Empyrean DY01610 Advance diffractometer operated at 40 kV and 35 mA using Cu K α radiation and in the range of 2-40°, the structure of COFs was simulated by Material Studio Software. **Fourier transform infrared (FT-IR)** spectra in the range of 4000 to 500 cm⁻¹ were collected by Universal ATR accessory. **N₂ adsorption and desorption** of COFs were performed at 77 K using ASAP 2460, Micromeritics Instrument Corp, USA. Pore size distributions and pore volumes were derived from the adsorption isotherms. **X-ray photoelectron spectroscopy (XPS)** spectra were obtained by the Kratos axis supra™ of Shimadzu. **Solid state ¹³C NMR (NMR)** spectra of all the samples were collected on a Bruker Avance III instrument with AS500 magnet equipped with a cryoprobe (300 MHz). **Scanning electron microscopy (SEM)** measurements was performed on a JEOL 8100 scanning electron microscope at an acceleration voltage of 10 kV. **Thermogravimetric analysis (TGA)** was carried out on the DTG-60AH from 30 to 800 °C under N₂ with a heating rate of 10 °C min⁻¹. **The ultraviolet–visible diffuse reflectance spectroscopy (UV–vis DRS)** was conducted on Shimadzu UV-2600 tested from 220 to 800 nm.

S1.2 Materials

All starting materials and solvents were obtained from commercial sources and used without further purification.

4',4''',4''''-(1,3,5-Triazine-2,4,6-triyl)tris((1,1'-biphenyl)-4-amine) (TTPB,97%), Thieno [3,2-b]thiophene-2,5-dicarboxaldehyde (TTDC, 97%), and [1,1':4',1'':3'',1''':4''',1''''-Quinquephenyl]-4,4''''-diamine, 5''-(4'-amino[1,1'-biphenyl]-4-yl)-(QDAB, 95%) were purchased from Shanghai Haohong Scientific Co., Ltd. N, N–dimethylformamide (DMF, 99.99%), tetrahydrofuran (THF, 99.99%), acetic acid (99%), 1,4-dioxane (99.8%), dichloromethane (98%), n-butanol(99%), methanol, acetone, iodine, bromatum kalium (KBr, 99%) were purchased from J&K Scientific or Sinopharm. The solvents mentioned above are anhydrous solvents.

S1.3 The adsorption experimental of I₂ vapor

The JLNU-COFs were activated with anhydrous methanol and acetone exchange solvents for 3 times and calcined at 80 °C for 4 h under nitrogen atmosphere to ensure the removal of water molecules from them. Then, an open vial (2 mL) containing the COF sample (20.0 mg) was placed in a large vial (10 mL) containing iodine (1 g), and the large vial was sealed and stored in a constant temperature oven at 75 °C. After a period of time, the vial containing the COF sample was weighed and placed back into the vial containing iodine. The vial was sealed and placed back into the oven at 75°C to continue adsorption until the mass of the vial containing the adsorbent remained constant. The iodine uptake capacity of JLNU-COFs was calculated according to equation (1).

$$a=(m_2-m_1)/m_1 \quad (1)$$

a (g g⁻¹) is the iodine adsorption capacity, m_1 (g) and m_2 (g) are the mass of the sample before and after iodine capture.

S1.4 Iodine release and recycling

JLNU-COFs absorbing iodine (4 mg) were immersed in ethanol (40 mL) and kept for a certain time. Then the absorbance of the supernatant at different time intervals was determined by UV-Vis spectrophotometer.

The I₂@JLNU-COFs were added to 50 mL of ethanol in a vial under a constant temperature water bath at 25°C, and the ethanol was changed every 2 h until the solution was colourless. The COFs samples were filtered, ethanol washed, and dried under vacuum at 100°C for 6 h, and then repeated in the next cycle.

Section S2. Supplemental figures and tables

S2.1 PXRD patterns

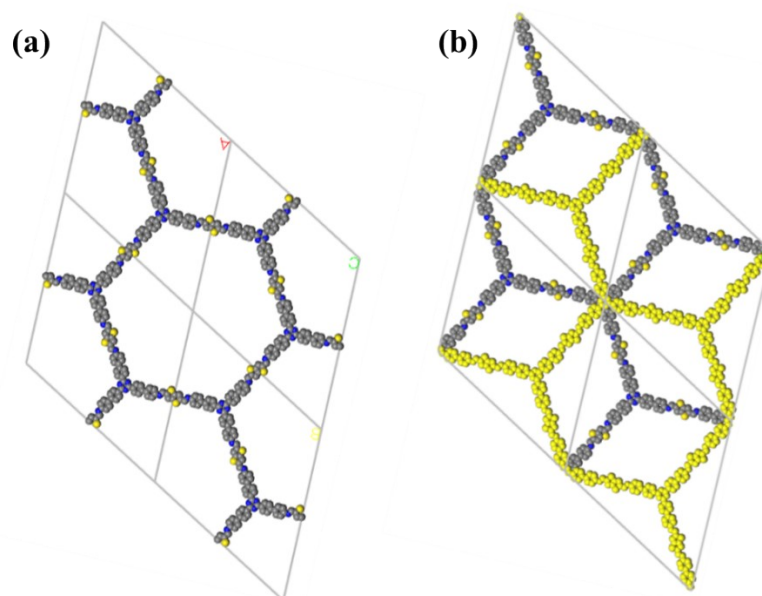


Fig. S1. Vertical projection view (up) of the structure for (a) AA stacking and (b) AB stacking of JLNU-312.

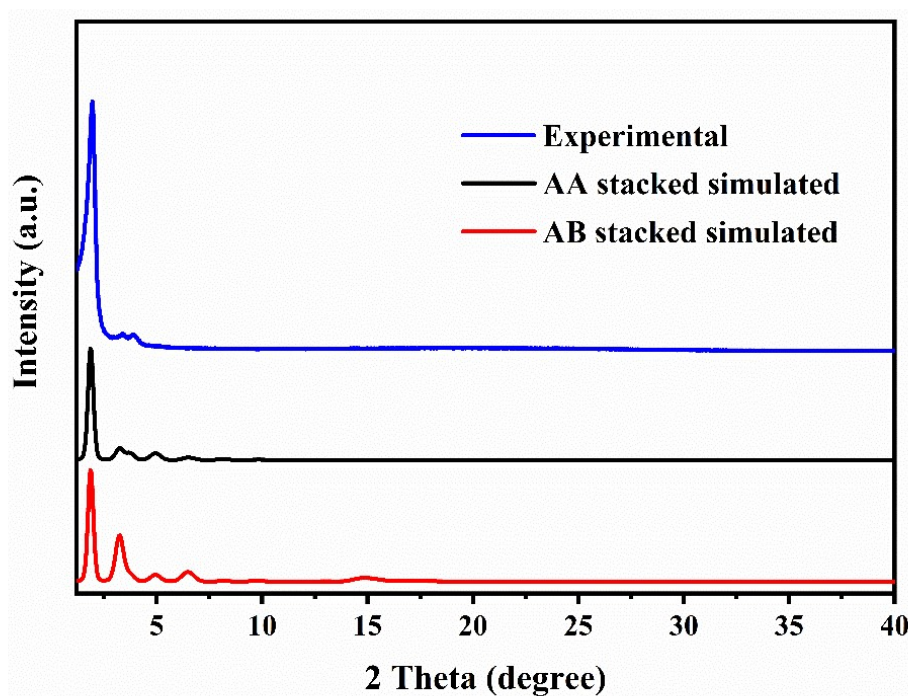


Fig. S2. Comparison of PXRD patterns for JLNU-312: calculated based on the AA stacked (black), AB stacked (red), and experiment (blue).

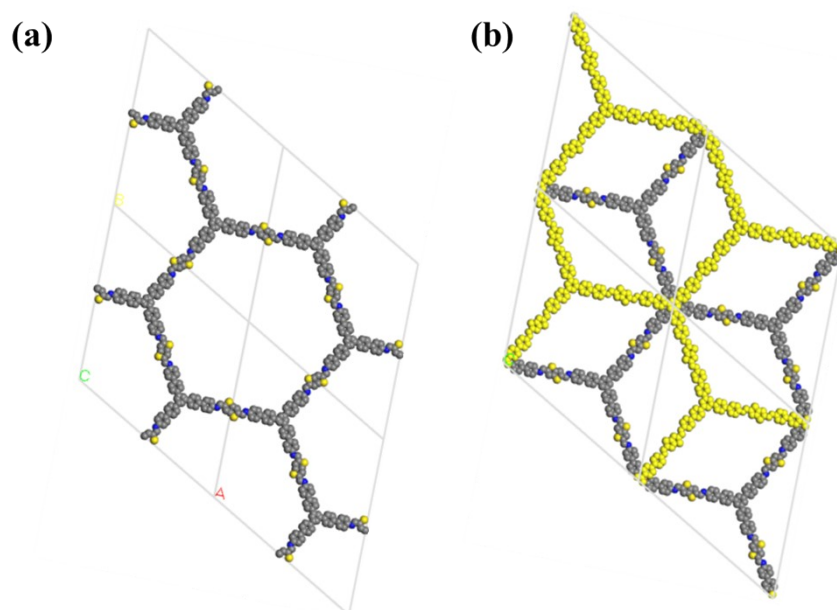


Fig. S3. Vertical projection view (up) of the structure for (a) AA stacking and (b) AB stacking of JLNU-313.

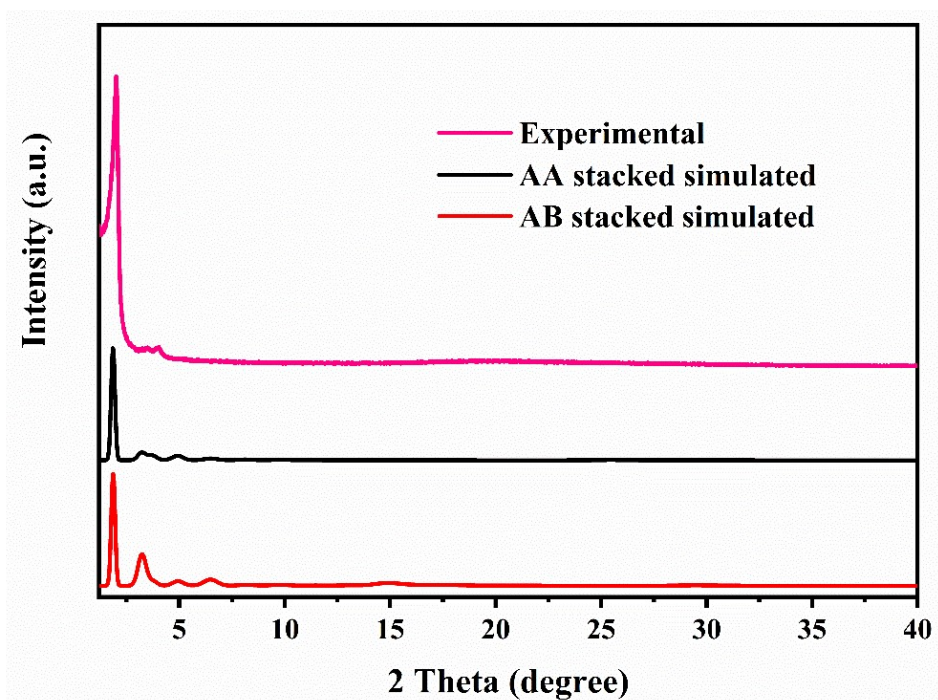


Fig. S4. Comparison of PXRD patterns for JLNU-313: calculated based on the AA stacked (black), AB stacked (red), and experiment (pink).

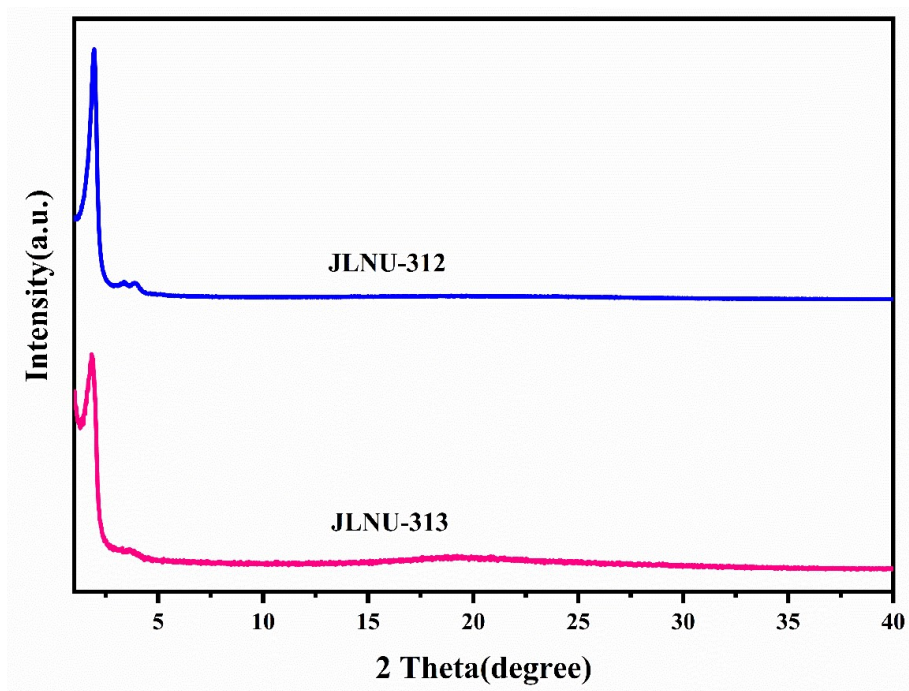


Fig. S5. Comparison of PXRD patterns for JLNU-312 (blue) and JLNU-313 (pink).

S2.2 ^{13}C NMR

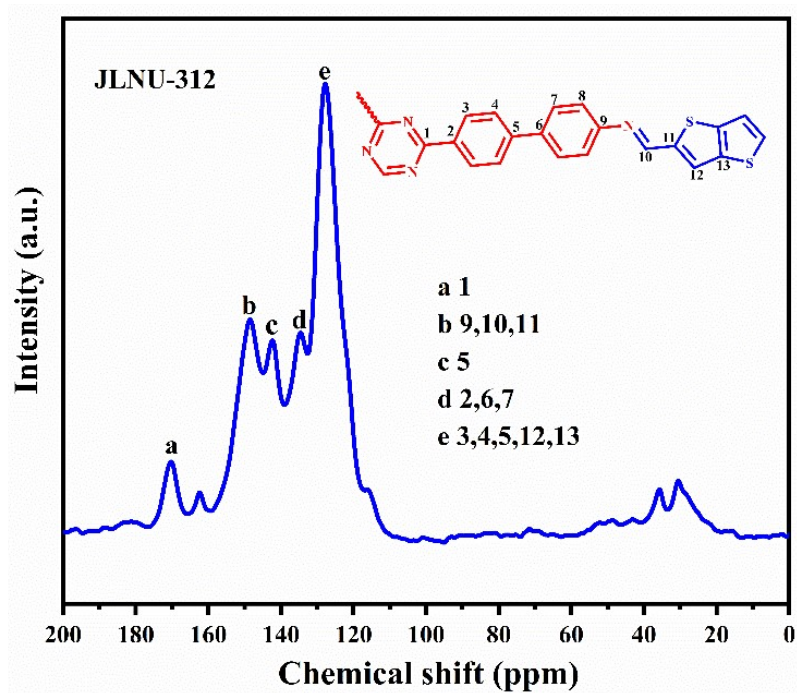


Fig. S6. Solid-state ^{13}C NMR spectrum of JLNU-312.

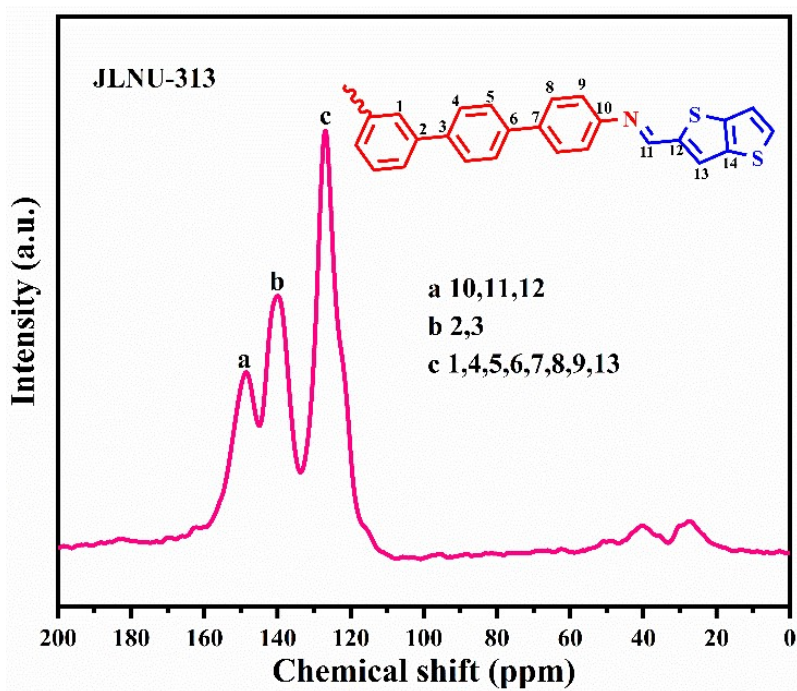


Fig. S7. Solid-state ^{13}C NMR spectrum of JLNU-313.

S2.3 Gas adsorption isotherms

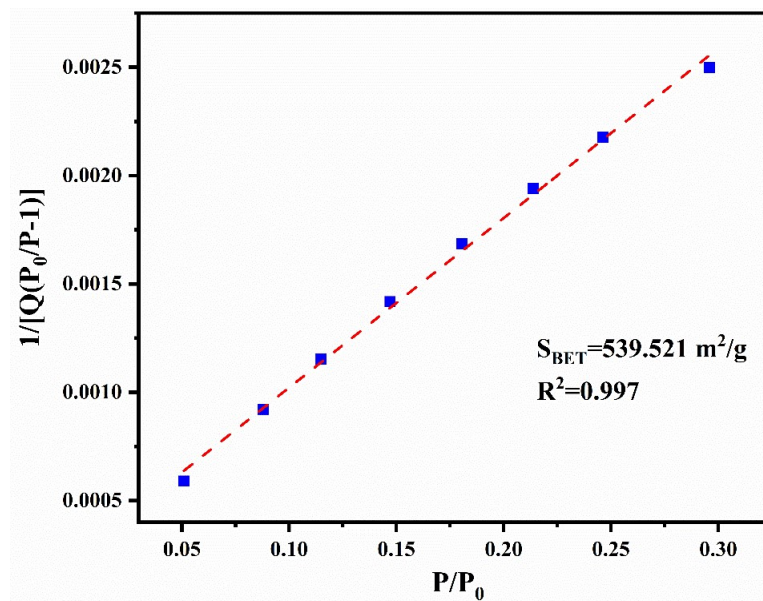


Fig. S8. BET plot of JLNU-312 calculated from N_2 adsorption isotherm at 77 K. (Before the test, the material was soaked in acetone for 8 h and then activated by vacuum heating (100 °C) for 8 h.)

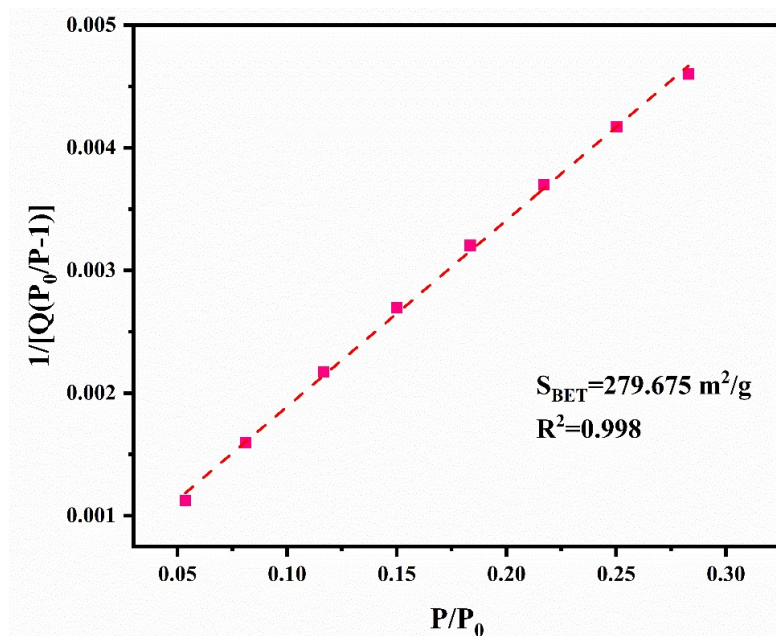


Fig. S9. BET plot of JLNU-313 calculated from N_2 adsorption isotherm at 77 K. (Before the test, the material was soaked in acetone for 8 h and then activated by vacuum heating (100 °C) for 8 h.)

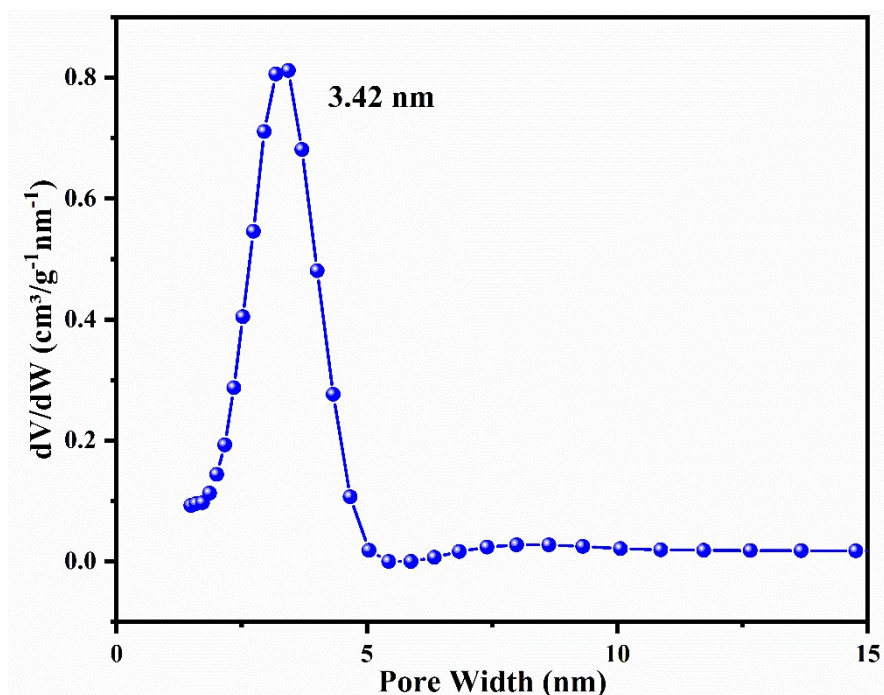


Fig. S10. The pore size distribution of JLNU-312. (Before the test, the material was soaked in acetone for 8 h and then activated by vacuum heating (100 °C) for 8 h.)

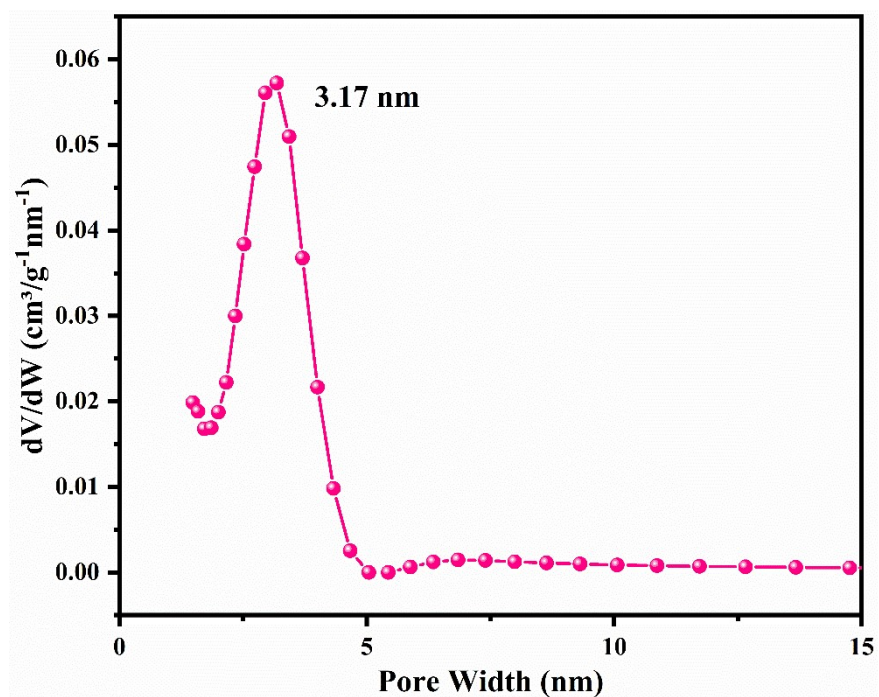


Fig. S11. The pore size distribution of JLNU-313. (Before the test, the material was soaked in acetone for 8 h, and then activated by vacuum heating (100 °C) for 8 h.)

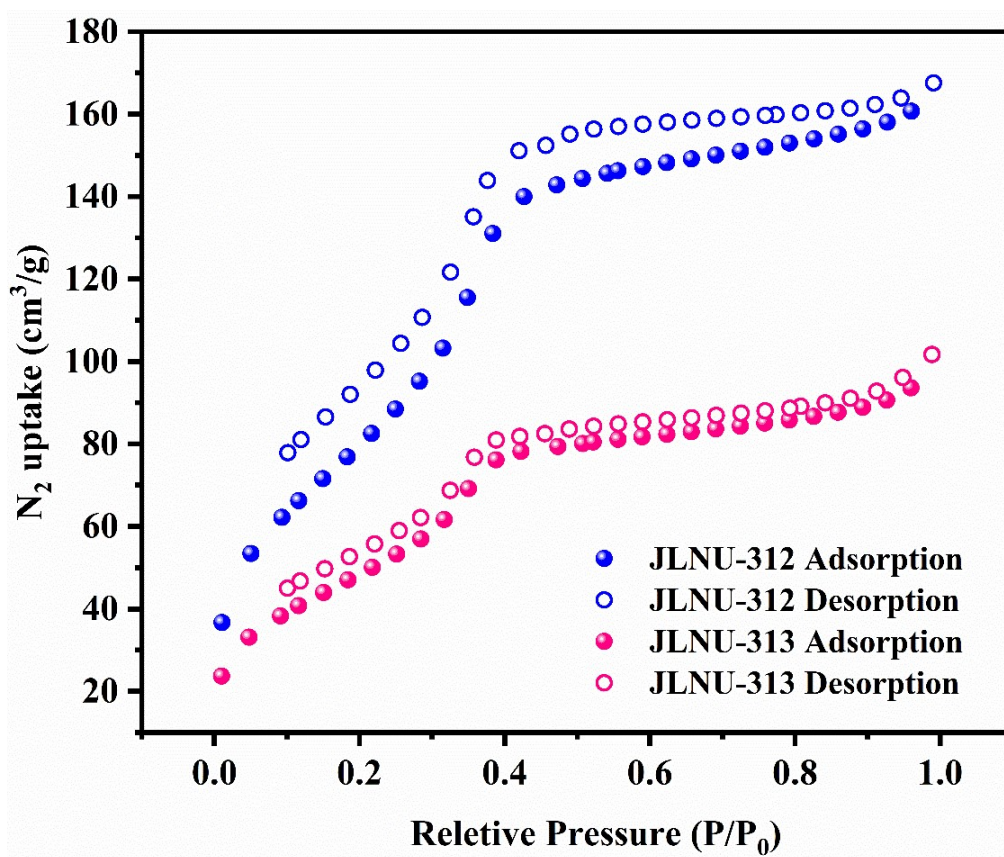


Fig. S12. N₂ adsorption-desorption isotherm of JLNU-312 (blue) and JLNU-313 (pink). (Before the test, the material was soaked in acetone for 8 h and then activated by heating (100 °C) under N₂ flow for 8 h.)

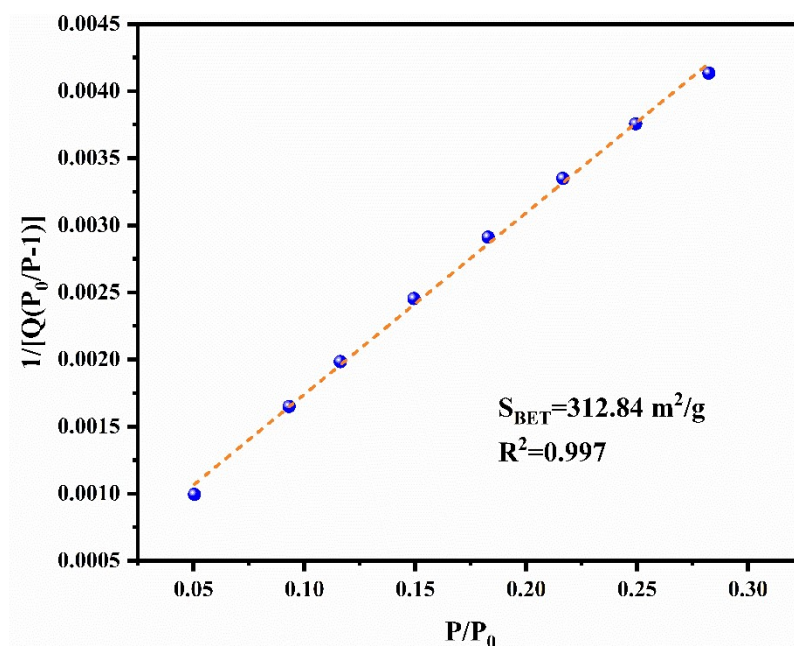


Fig. S13. BET plot of JLNU-312 calculated from N₂ adsorption isotherm at 77 K. (Before the test, the material was soaked in acetone for 8 h and then activated by heating (100 °C) under N₂ flow for 8 h.)

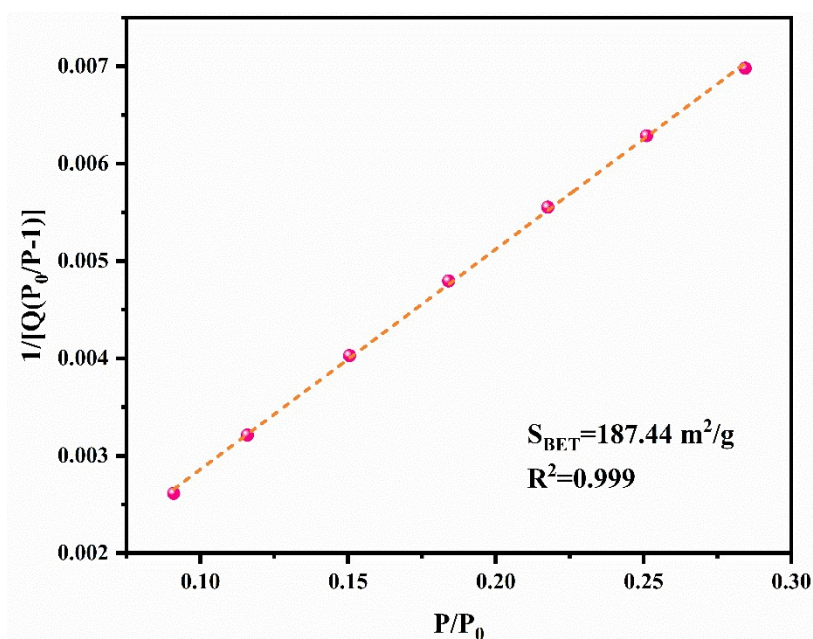


Fig. S14. BET plot of JLNU-313 calculated from N₂ adsorption isotherm at 77 K. (Before the test, the material was soaked in acetone for 8 h and then activated by heating (100 °C) under N₂ flow for 8 h.)

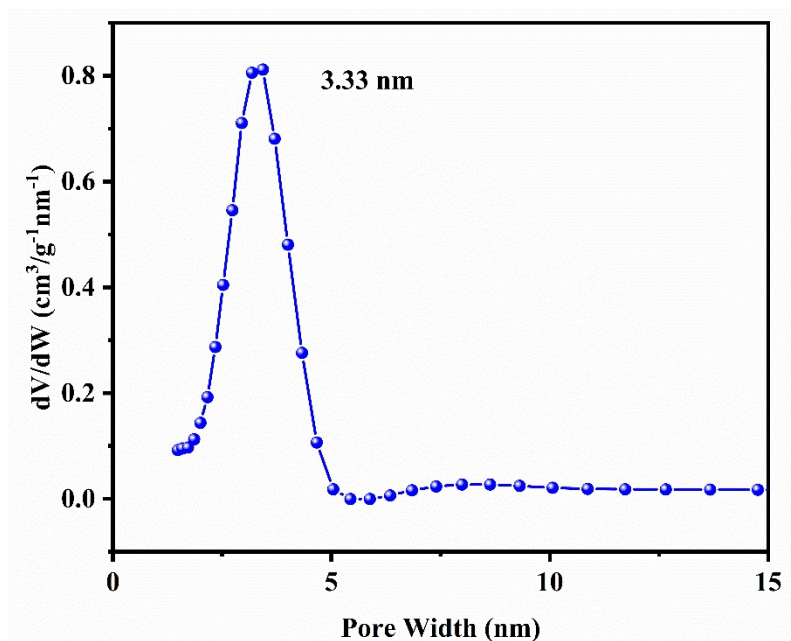


Fig. S15. The pore size distribution of JLNU-312. (Before the test, the material was soaked in acetone for 8 h and then activated by heating (100 °C) under N₂ flow for 8 h.)

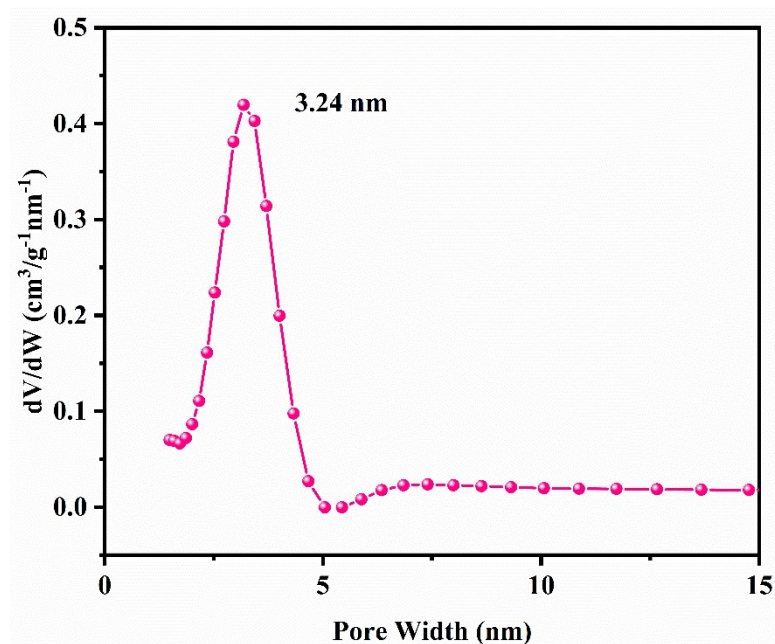


Fig. S16. The pore size distribution of JLNU-313. (Before the test, the material was soaked in acetone solvent for 8 h and then activated by heating (100 °C) under N₂ flow for 8 h.)

S2.4 TGA

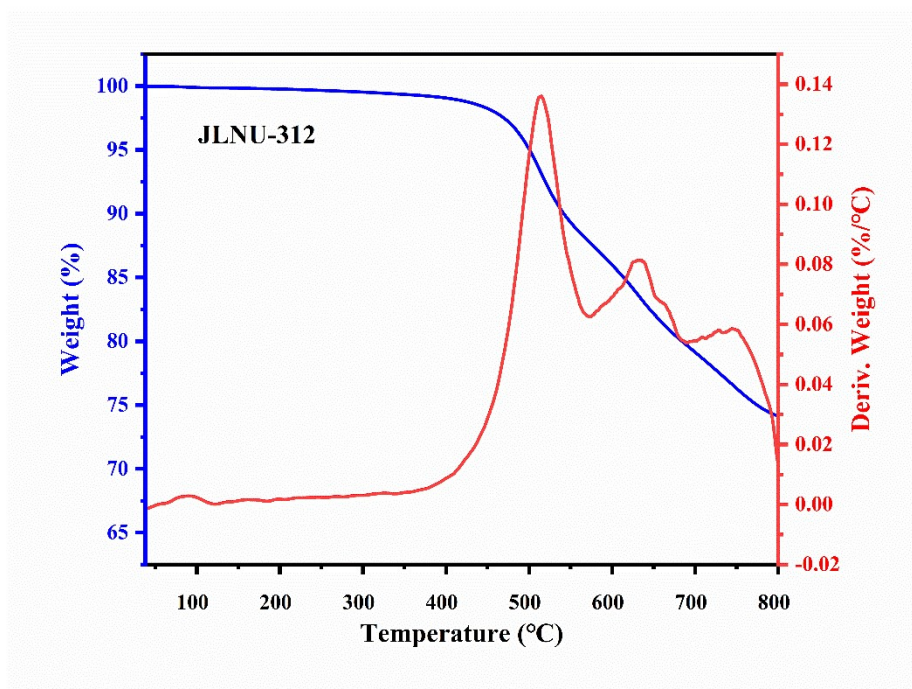


Fig. S17. TGA (blue) and DTG (red) curves of JLNU-312 under N₂.

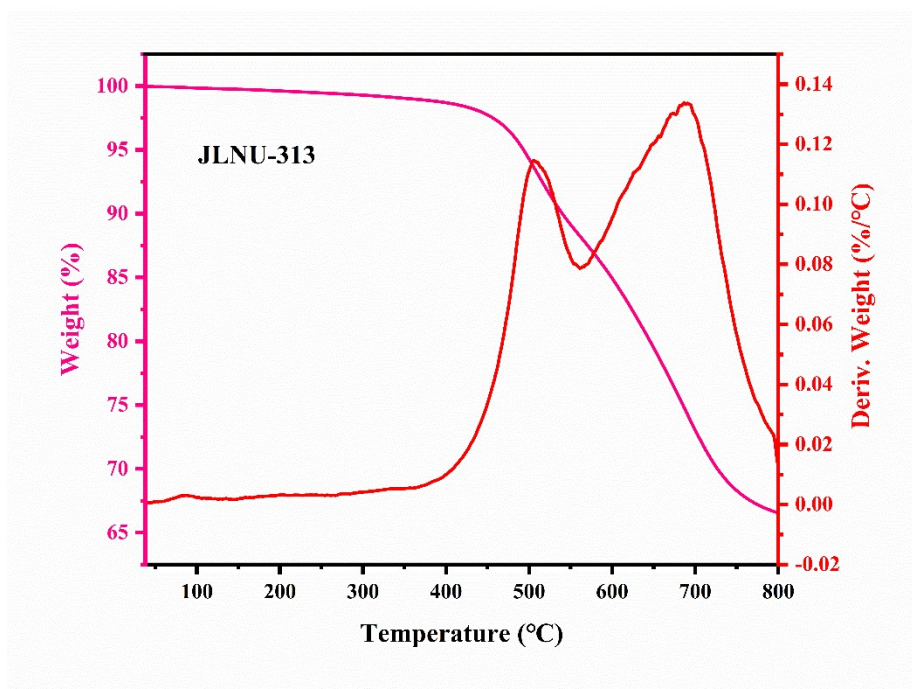


Fig. S18. TGA (pink) and DTG (red) curves of JLNU-313 under N₂.

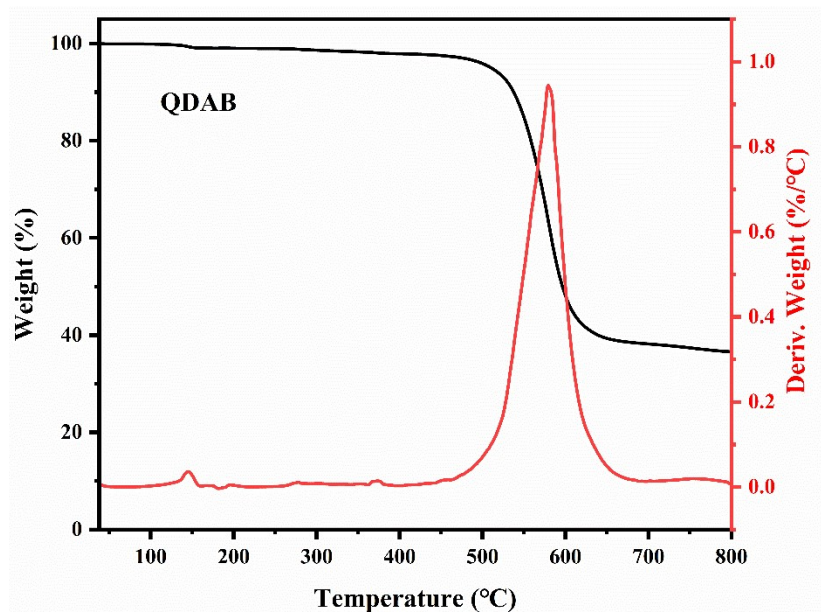


Fig. S19. TGA (black) and DTG (red) curves of QDAB under N₂.

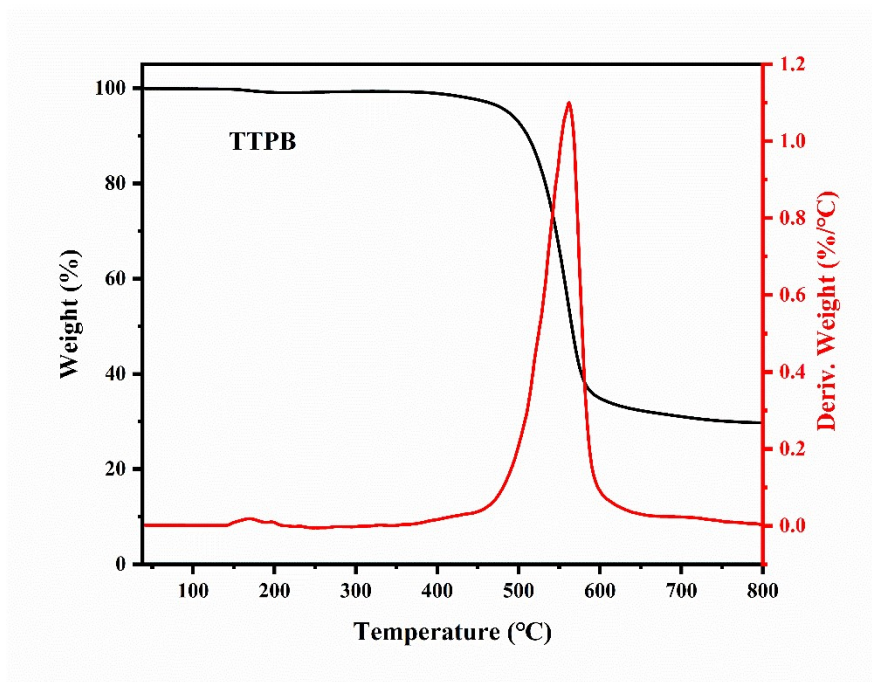


Fig. S20. TGA (black) and DTG (red) curves of TTPB under N₂.

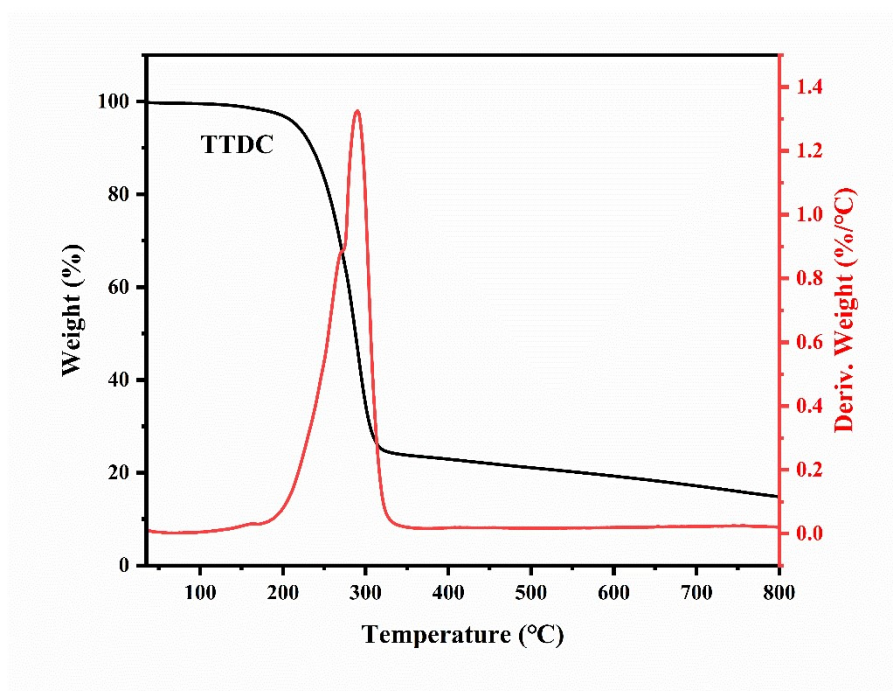


Fig. S21. TGA (black) and DTG (red) curves of TTDC under N₂.

S2.5 Stability test

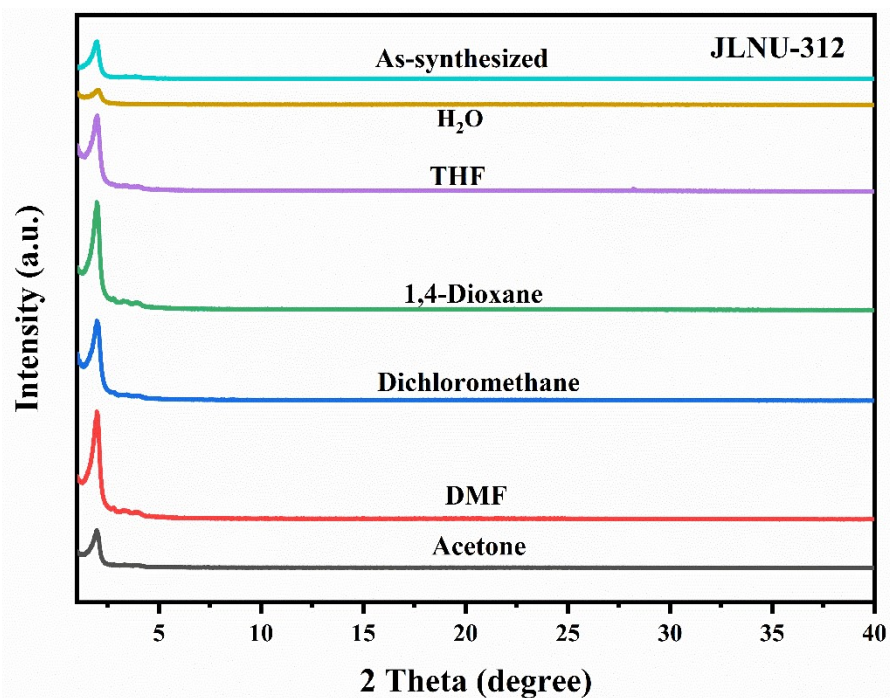


Fig. S22. PXRD patterns of JLNU-312 after 24 hours treatment in different organic solvents.

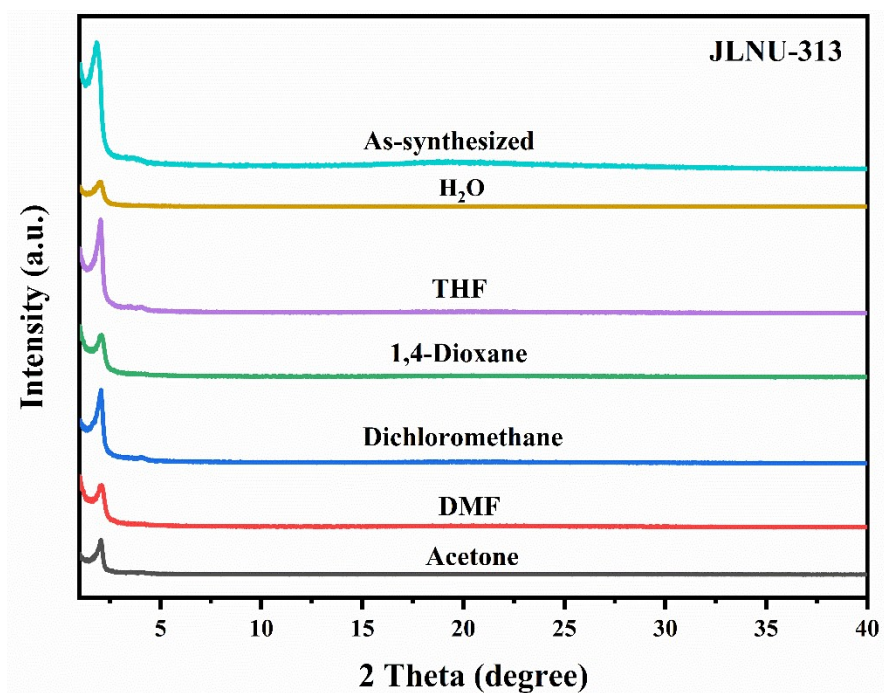


Fig. S23. PXRD patterns of JLNU-313 after 24 hours treatment in different organic solvents.

S2.6 Iodine uptake and release performance

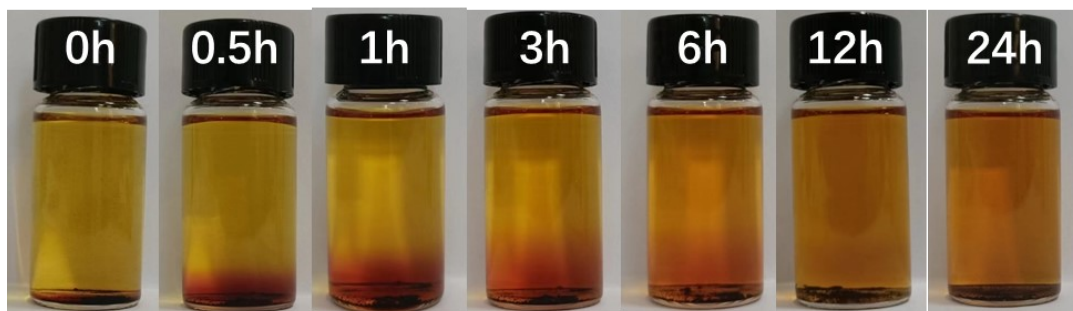


Figure S24. The iodine releasing process of $I_2@JLNU-312$ from ethanol solution.



Figure S25. The iodine releasing process of $I_2@JLNU-313$ from ethanol solution.

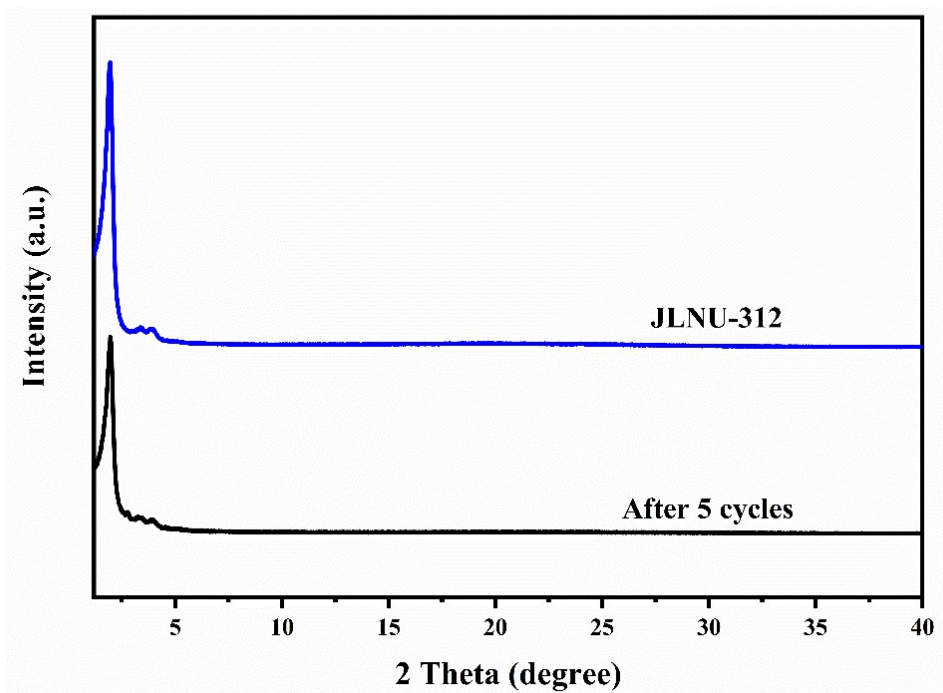


Fig. S26. PXRD of JLNU-312 before and after 5 cycles of iodine uptake.

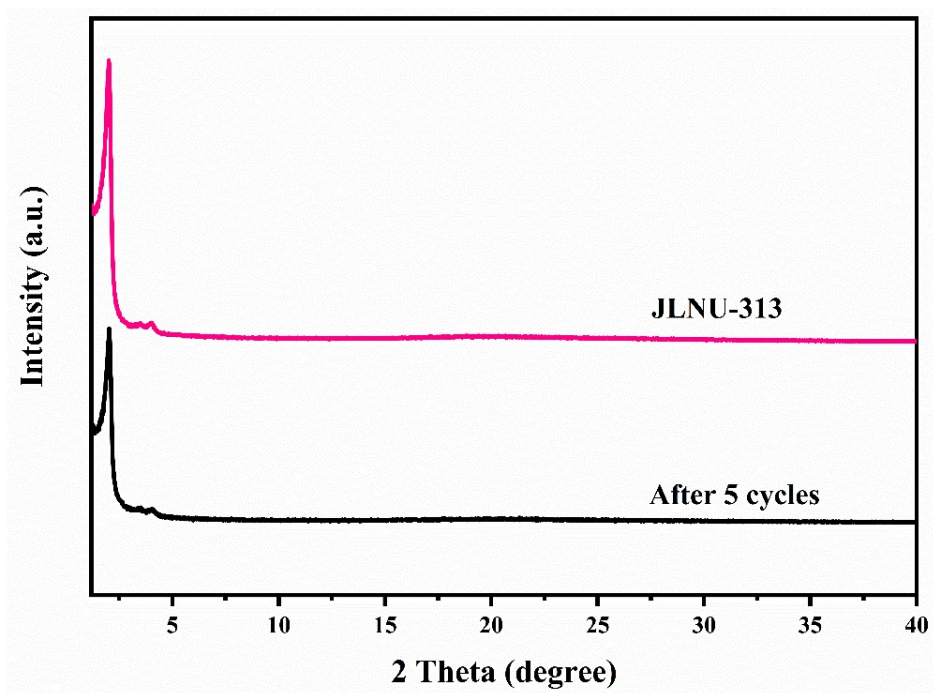


Fig. S27. PXRD of JLNU-313 before and after 5 cycles of iodine uptake.

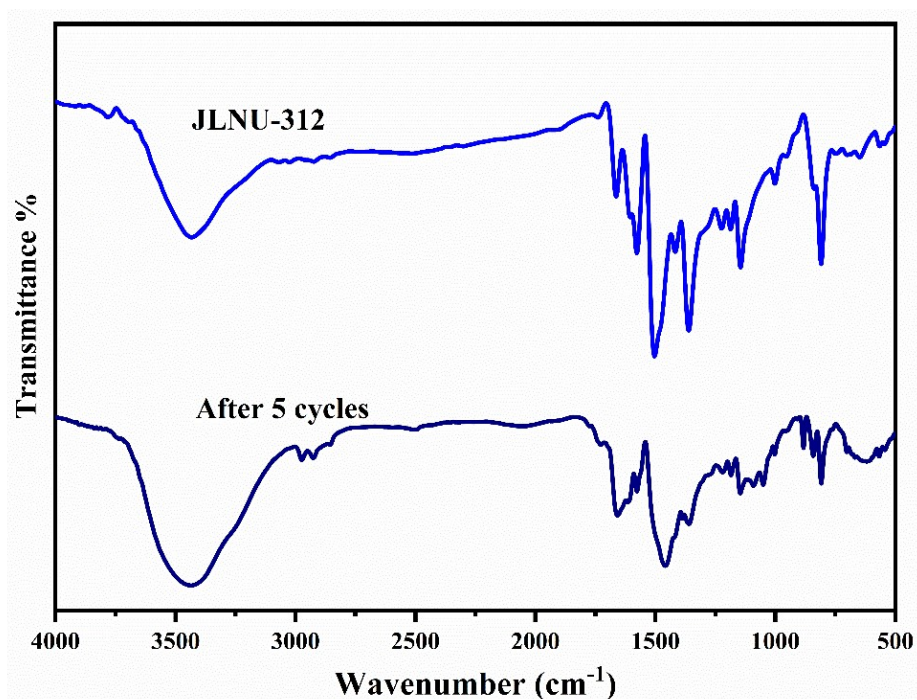


Fig. S28. FT-IR of JLNU-312 before and after 5 cycles of iodine uptake.

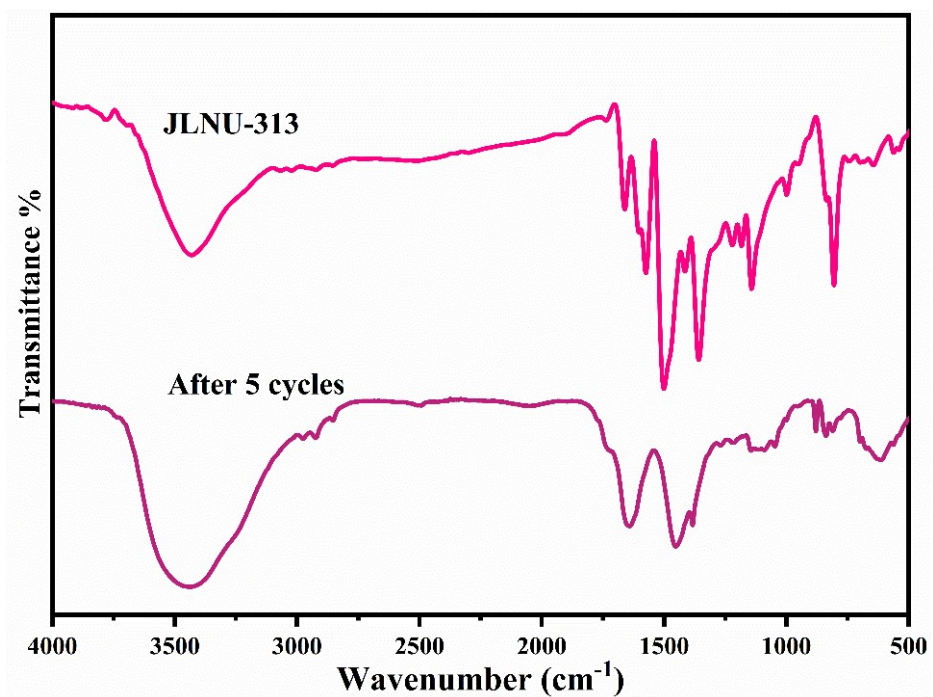


Fig. S29. FT-IR of JLNU-313 before and after 5 cycles of iodine uptake.

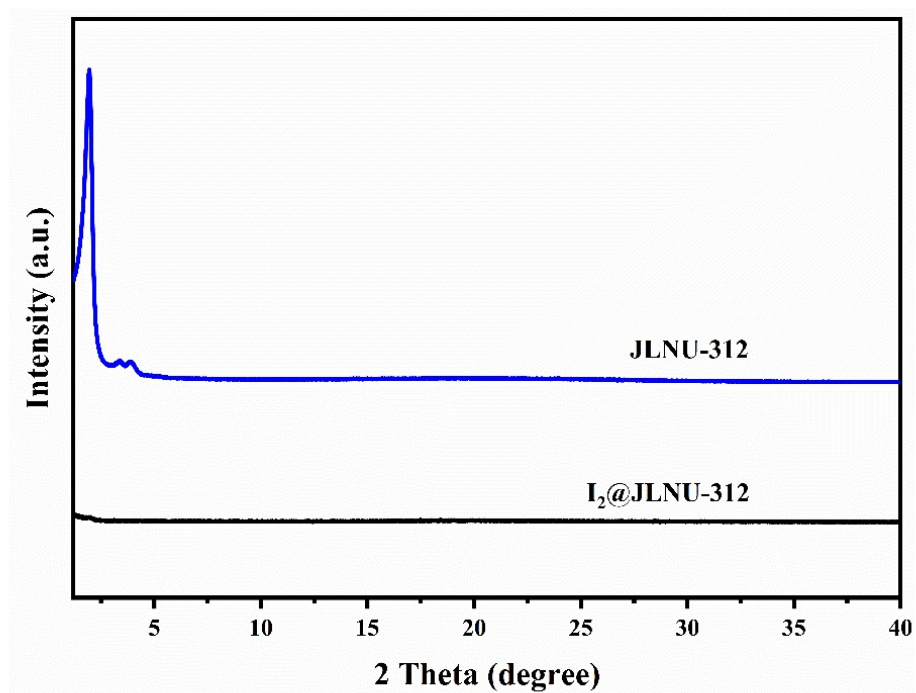


Fig. S30. PXRD patterns of JLNU-312 and I₂@JLNU-312.

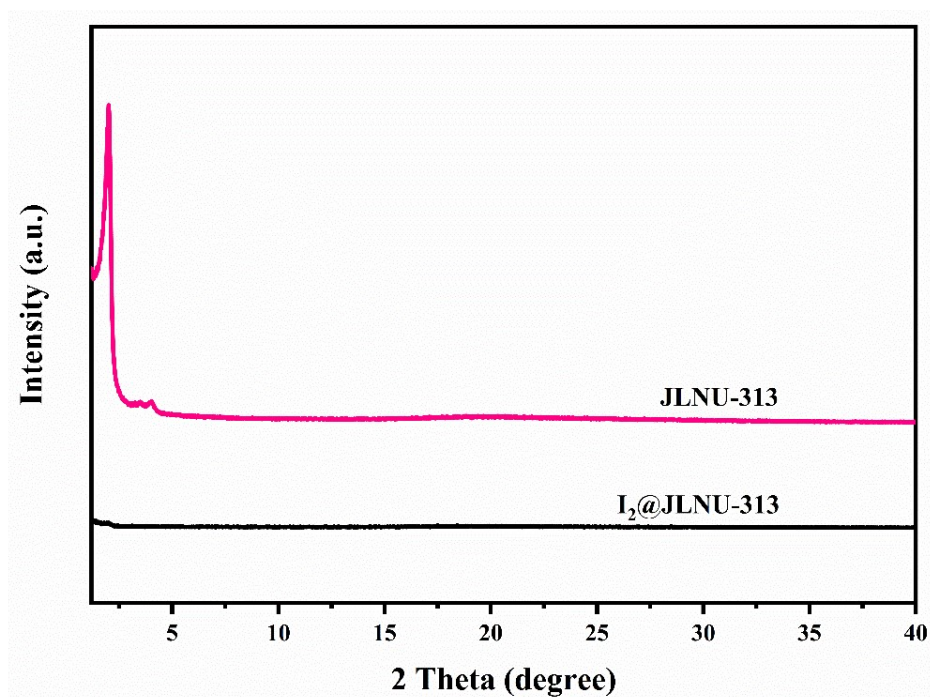


Fig. S31. PXRD patterns of JLNU-313 and I₂@JLNU-313.

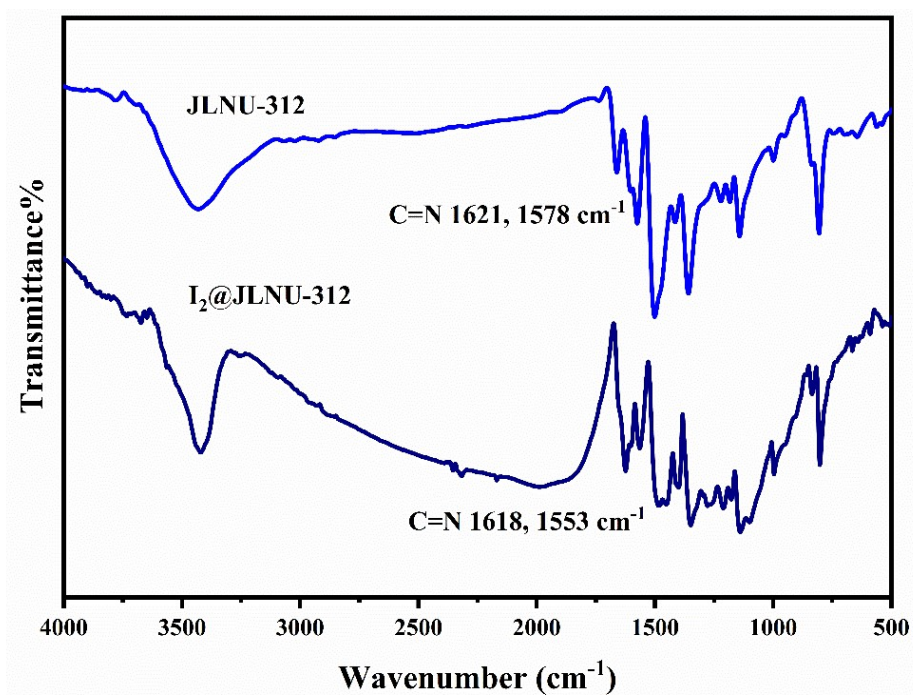


Fig. S32. FT-IR of JLNU-312 and I_2 @JLNU-312.

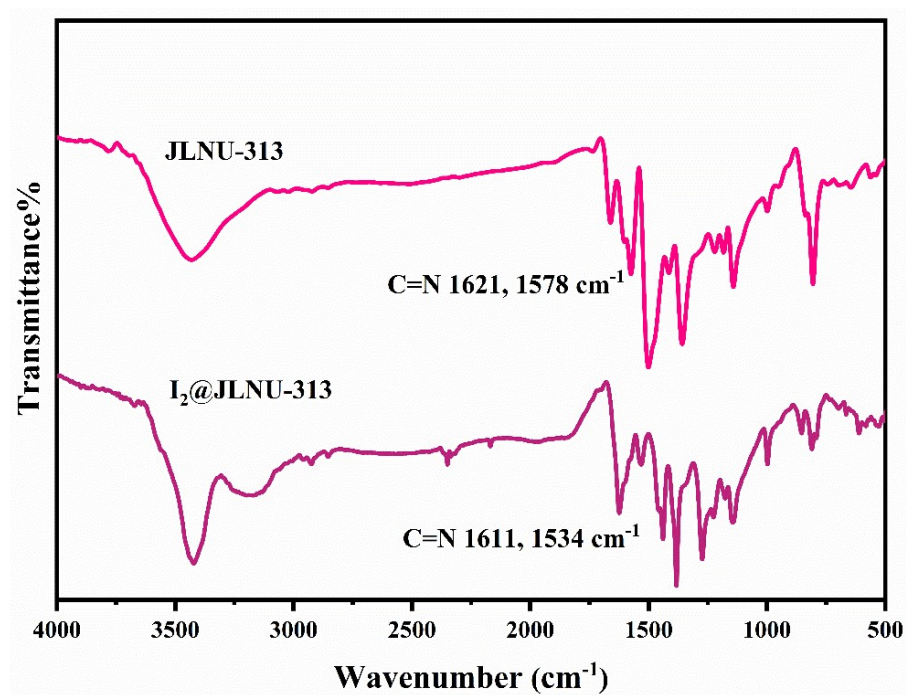


Fig. S33. FT-IR of JLNU-313 and I_2 @JLNU-313.

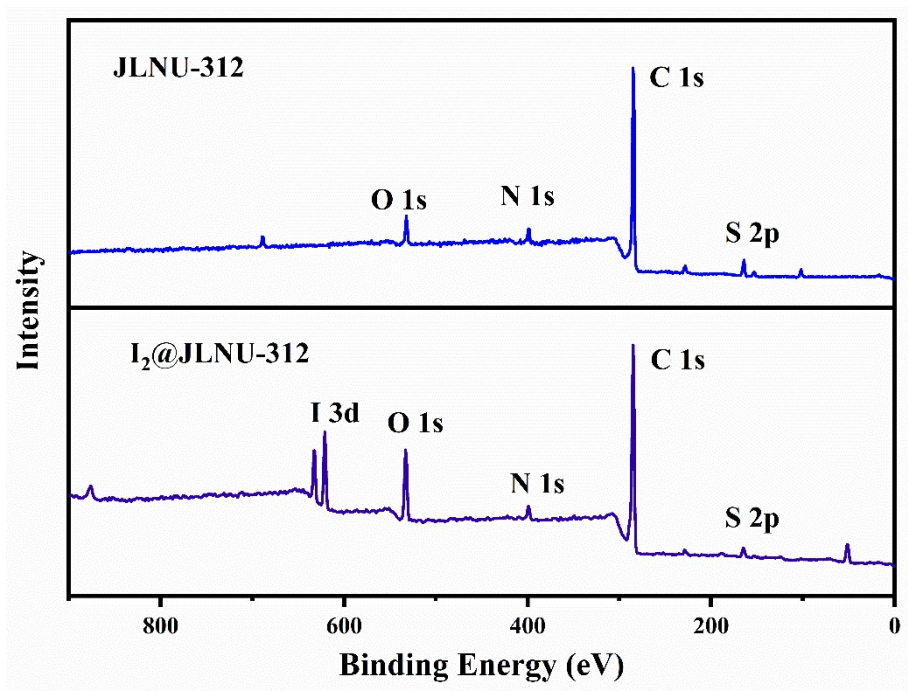


Fig. S34. XPS spectra of JLNU-312 and I₂@JLNU-312

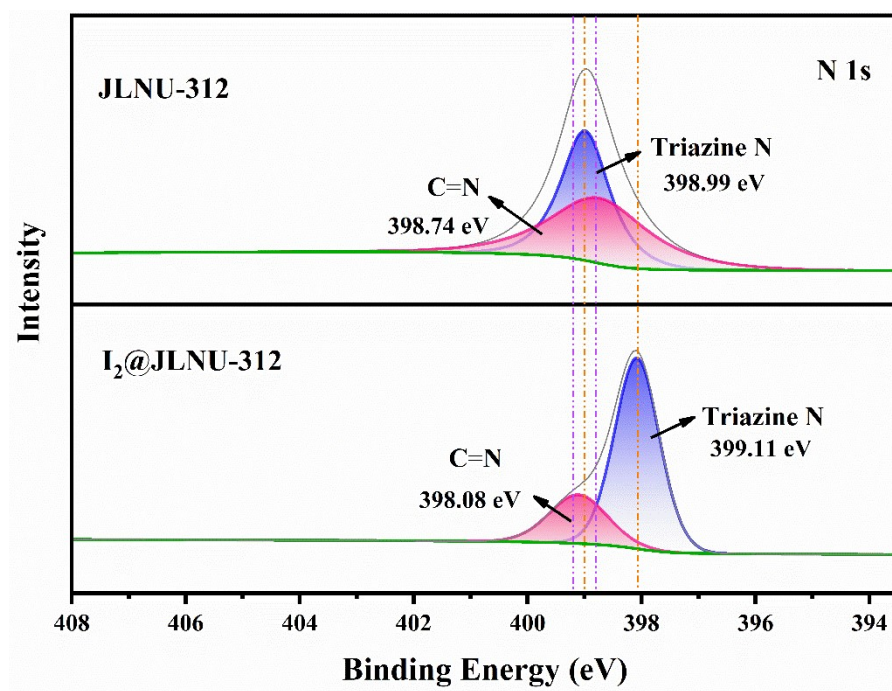


Fig. S35. XPS spectra of N 1s in JLNU-312 and I₂@JLNU-312.

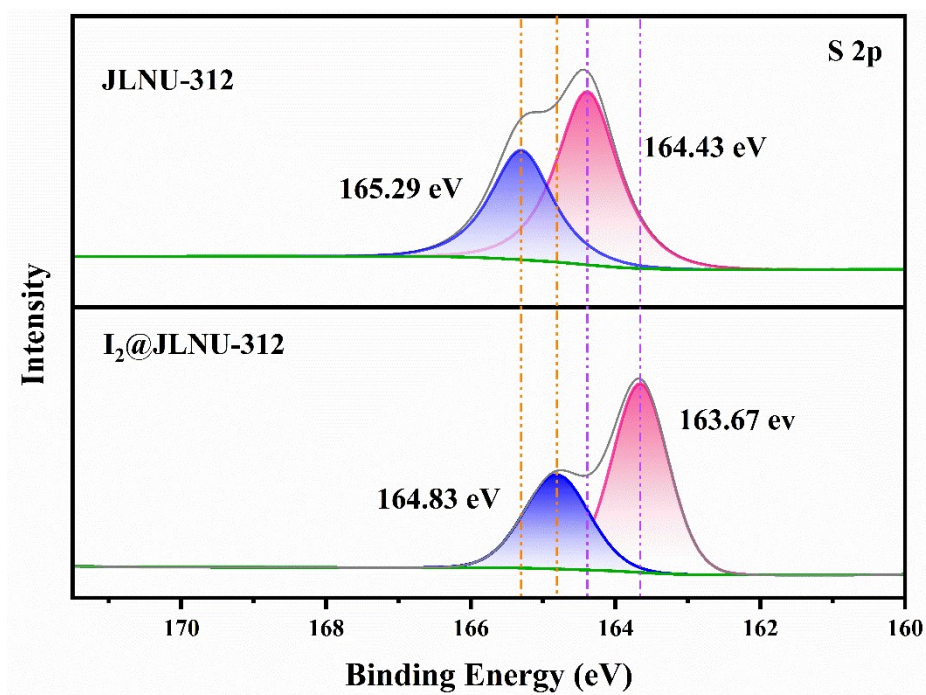


Fig. S36. XPS spectra of S 2p in JLNU-312 and I₂@JLNU-312

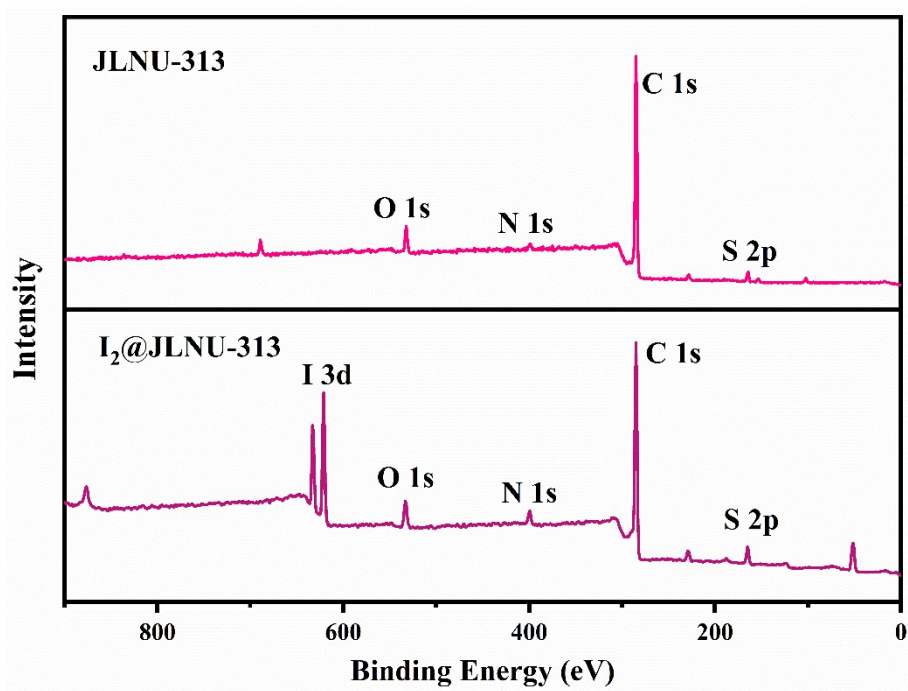


Fig. S37. XPS spectra of JLNU-313 and I₂@JLNU-313

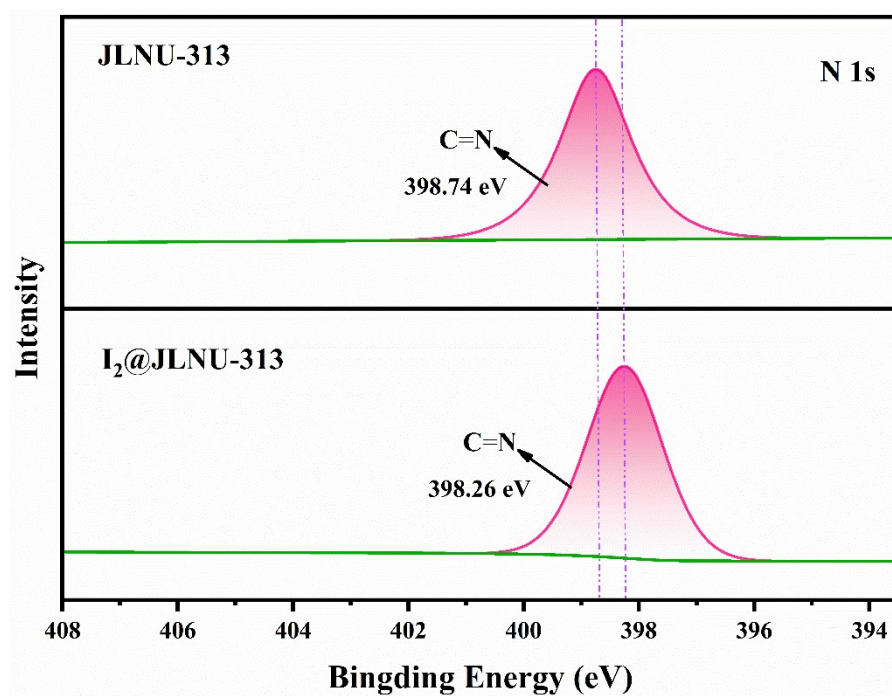


Fig. S38. XPS spectra of N 1s in JLNU-313 and I₂@JLNU-313.

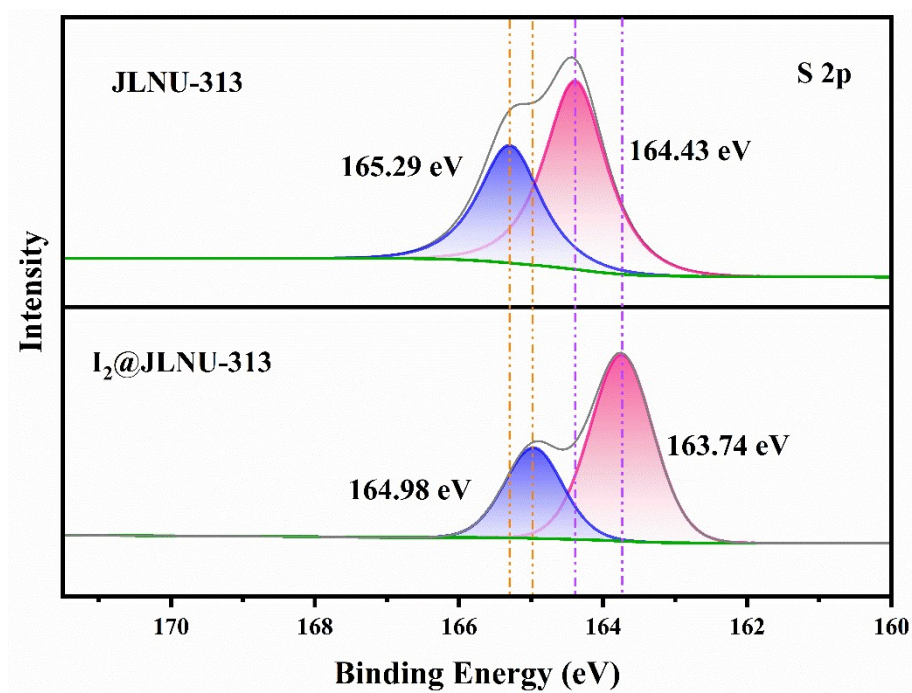


Fig. S39. XPS spectra of S 2p in JLNU-313 and I₂@JLNU-313.

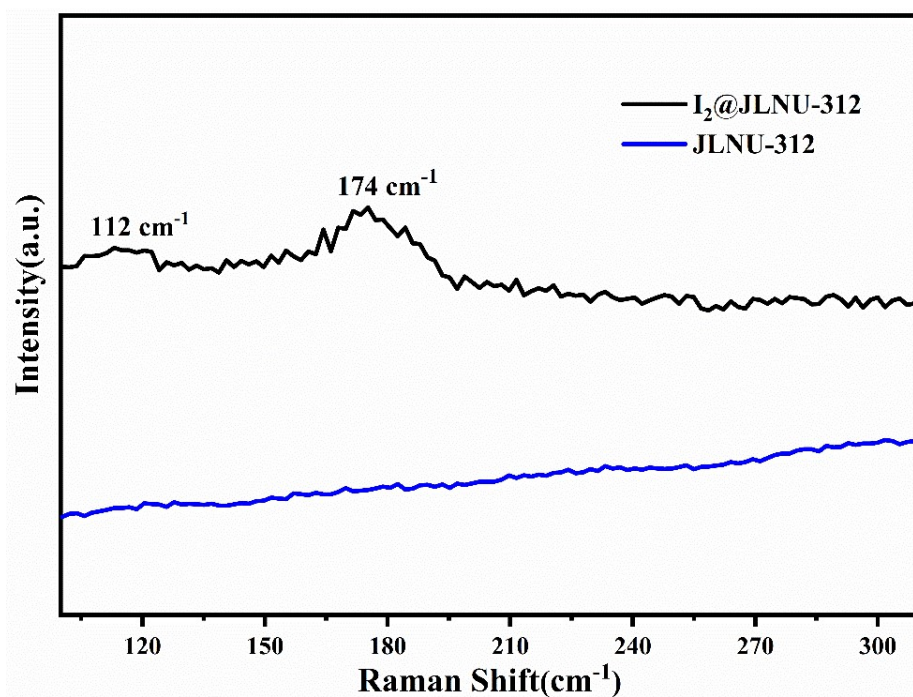


Fig. S40. Raman spectra of JLNU-312 and I₂@JLNU-312.

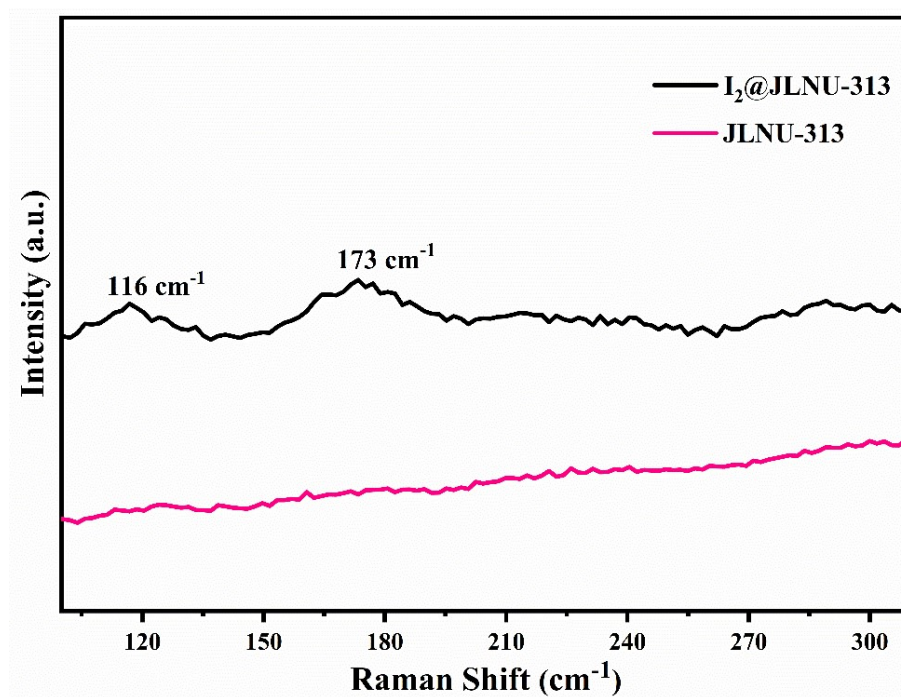


Fig. S41. Raman spectra of JLNU-313 and I₂@JLNU-313.

Section S3. Unit cell parameters and fractional atomic coordinates

Table S1. Unit cell parameters and fractional atomic coordinates for calculated JLNU-312

Space group		P6/m (No. 175)	
Calculated unit cell		a = b = 54.6173 Å, c = 3.5434 Å, $\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$	
Pawley refinement		$R_{\omega p} = 4.44\%$ and $R_p = 3.41\%$	
Atom	x	y	z
N1	0.01327	-0.01537	0.01049
C2	0.0288	0.01334	0.01049
C3	0.05995	0.02777	0.01049
C4	0.07602	0.05739	0.01049
C5	0.10555	0.07107	0.01049
C6	0.11957	0.0554	0.01049
C7	0.10339	0.02573	0.01049
C8	0.07386	0.01205	0.01049
C9	0.15089	0.06991	0.01049
C10	0.16492	0.05423	0.01049
C11	0.19446	0.0679	0.01049
C12	0.21048	0.09743	0.01049
C13	0.19661	0.11325	0.01049
C14	0.16708	0.09958	0.01049
N15	0.2407	0.11079	0.01049
C16	0.288	0.15074	0.01049
C17	0.37936	0.18294	0.01049
C18	0.45688	0.23625	0.01049
C19	0.47075	0.22043	0.01049

C20	0.50028	0.2341	0.01049
C21	0.51646	0.26377	0.01049
C22	0.50244	0.27944	0.01049
C23	0.4729	0.26578	0.01049
C24	0.54778	0.27828	0.01049
C25	0.5618	0.26261	0.01049
C26	0.59133	0.27629	0.01049
C27	0.60741	0.3059	0.01049
C28	0.5935	0.32163	0.01049
C29	0.56397	0.30795	0.01049
S30	0.30994	0.18701	0.01049
C31	0.33727	0.18053	0.01049
C32	0.33009	0.15315	0.01049
C33	0.30156	0.13486	0.01049
C34	0.3658	0.19882	0.01049
S35	0.35742	0.14667	0.01049
C36	0.25717	0.13801	0.01049
C37	0.41018	0.19567	1.00779
N38	0.42666	0.22289	1.00779
C39	0.63856	0.32034	0.01049
N40	0.65409	0.34905	0.01049

Table S2. Unit cell parameters and fractional atomic coordinates for calculated JLNU-313

Space group		P6/m (No. 175)	
Calculated unit cell		a = b = 54.1818 Å, c = 6.1385 Å, $\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$	
Pawley refinement		$R_{wp} = 5.90\%$ and $R_p = 4.21\%$	
Atom	x	y	z
C1	0.01359	-0.01573	0.00791
C2	0.02967	0.01375	0.00791
C3	0.06082	0.02819	0.00791
C4	0.07692	0.0577	0.00791
C5	0.10631	0.07131	0.00791
C6	0.12026	0.05573	0.00791
C7	0.10416	0.02622	0.00791
C8	0.07478	0.0126	0.00791
C9	0.15143	0.07018	0.00791
C10	0.16539	0.05458	0.00791
C11	0.19479	0.06819	0.00791
C12	0.21073	0.09758	0.00791
C13	0.19692	0.11332	0.00791
C14	0.16753	0.0997	0.00791
N15	0.24081	0.11087	0.00791
C16	0.28787	0.15064	0.00791
C17	0.37879	0.18269	0.00791
N18	0.42586	0.22246	0.00791
C19	0.45594	0.23576	0.00791
C20	0.46975	0.22002	0.00791
C21	0.49913	0.23363	0.00791
C22	0.51524	0.26316	0.00791

C23	0.50128	0.27875	0.00791
C24	0.47188	0.26515	0.00791
C25	0.54641	0.2776	0.00791
C26	0.56036	0.26202	0.00791
C27	0.58975	0.27564	0.00791
C28	0.60584	0.30515	0.00791
C29	0.59189	0.32073	0.00791
C30	0.56251	0.30711	0.00791
C31	0.637	0.31958	0.00791
C32	0.65093	0.30401	0.00791
S33	0.3097	0.18674	0.00791
C34	0.3369	0.18029	0.00791
C35	0.32976	0.15305	0.00791
C36	0.30137	0.13484	0.00791
C37	0.3653	0.19849	0.00791
S38	0.35697	0.1466	0.00791
C39	0.25719	0.13796	0.00791
C40	0.40947	0.19537	0.00791

Table S3. Iodine adsorption capacities of different adsorbents.

Porous Materials	I₂ uptake(g/g)	Temperature K	Pressure	S_{BET} m²/g	Cycle number	Ref.
ECUT-COF-13	10.81	75	1 bar	425	10	1
TJNU-201	5.63	77	1 bar	2510	5	2
T-COF-2	4.72	76	1 bar	781	5	3
JLNU-312	4.67	75	1 bar	540	5	This work
BTM	4.46	75	1 bar	/	4	4
Meso-COF-3	4.0	75	1 bar	982	/	5
CTF-CTTD-500	3.87	75	1 bar	1334	4	6
POP-2	3.82	80	1 bar	41	5	7
NH ₂ -TH-BTA COF	3.58	75	1 bar	10	6	8
Micro-COF-2	3.5	75	1 bar	1056	/	5
Meso-COF-4	3.3	75	1 bar	926	/	5
TFBT-1	3.15	75	1 bar	451	3	9
Micro-COF-1	2.9	75	1 bar	816	/	5
BDP-CPP-1	2.83	75	degassed	635	4	10
TF-TA-COF	2.74	75	1 bar	442	5	11
TFBT-2	2.60	75	1 bar	464	3	9
TTA-DMTP-COF	2.59	75	1 bar	2333	5	12
JLNU-313	2.47	75	1 bar	280	5	This work
COF-TpgBD	1.81	100	1 bar	217	/	13

NOP-53	1.77	75	1 bar	744	/	14
ZIF-8	1.20	75	1 bar	1630	/	15
COFs@ cotton	0.53	77	1 bar	124	5	16

Section S4. References

- [1] Y. W. Huang, Z. W. Yu, Q. Y. Zhang and F. Luo, *Sci. China-Mater.*, 2023, **66**, 2339-2345.
- [2] J. H. Li, H. X. Zhang, L. Y. Zhang, K. Wang, Z. K. Wang, G. Y. Liu, Y. L. Zhao and Y. F. Zeng, *J. Mater. Chem. A*, 2020, **8**, 9523-9527.
- [3] Q. Y. Niu, Q. X. Cui, X. T. Meng, P. Zhang, Y. N. Zhou, H. Fu, B. W. Ma, N. Qin and L. P. Zhai, *New J. Chem.*, 2023, **47**, 7642-7647.
- [4] Y. Zhu, Y. Qi, X. Guo, M. Zhang, Z. Jia, C. Xia, N. Liu, C. Bai, L. Ma and Q. Wang, *J. Mater. Chem. A*, 2021, **9**, 16961-16966.
- [5] S. An, X. Zhu, Y. He, L. Yang, H. Wang, S. Jin, J. Hu and H. Liu, *Ind. Eng. Chem. Res.*, 2019, **58**, 10495-10502.
- [6] Q. Jiang, H. L. Huang, Y. Z. Tang, Y. X. Zhang and C. L. Zhong, *Ind. Eng. Chem. Res.*, 2018, **57**, 15114-15121.
- [7] X. Qian, B. Wang, Z. Q. Zhu, H. X. Sun, F. Ren, P. Mu, C. H. Ma, W. D. Liang and A. Li, *J. Hazard. Mater.*, 2017, **338**, 224-232.
- [8] S. Y. Zhang, X. H. Tang, Y. L. Yan, S. Q. Li, S. R. Zheng, J. Fan, X. L. Li, W. G. Zhang and S. L. Cai, *ACS Macro Lett.*, 2021, **10**, 1590-1596.
- [9] H. Li, D. Zhang, K. Cheng, Z. Li and P.-Z. Li, *ACS Appl. Nano Mater.*, 2023, **6**, 1295-1302.
- [10] Y. L. Zhu, Y. J. Ji, D. G. Wang, Y. Zhang, H. Tang, X. R. Jia, M. Song, G. P. Yu and

- G. C. Kuang, *J. Mater. Chem. A*, 2017, **5**, 6622-6629.
- [11] Y. Li, G. Cui, X. Cai, G. Yun, Y. Zhao, L. Jiang, S. Cui, J. Zhang, M. Liu, W. Zeng, Z. Wang and J. Jiang, *Chem-Eur. J.*, 2024, **30**.
- [12] W. Z. She, Q. L. Wen, H. C. Zhang, J. Z. Liu, R. S. Li, J. Ling and Q. E. Cao, *ACS Appl. Nano Mater.*, 2023, **6**, 18177-18187.
- [13] Y. H. Sun, S. A. Song, D. H. Xiao, L. F. Gan and Y. R. Wang, *ACS Omega*, 2020, **5**, 24262-24271.
- [14] D. Y. Chen, Y. Fu, W. G. Yu, G. P. Yu and C. Y. Pan, *Chem. Eng. J.*, 2018, **334**, 900-906.
- [15] D. F. Sava, T. J. Garino and T. M. Nenoff, *Ind. Eng Chem Res.*, 2012, **51**, 614-620.
- [16] Y. Q. Li, Y. R. Li, Q. H. Zhao, L. Li, R. Chen and C. Y. He, *Cellulose*, 2020, **27**, 1517-1529.