A Ni(II) metal-organic framework with helical channels for the capture of iodine via guest exchange induced amorphization

Jie-Fen Huang,[†] Shu-Qi Deng,[‡] Hao-Chen Hu,[§] Song-Liang Cai,* [†] Wei-Guang Zhang,* [†] Jun Fan,[†] Sheng-Run Zheng*, [†]

[†]School of Chemistry, South China Normal University, Guangzhou, 510006, China.

[‡] Institute for Sustainable Energy/College of Sciences, Shanghai University, Shanghai, 200444, China

[§]School of Chemistry and Chemical Engineering, Shanghai University of Engineering Science, Shanghai, 201620, China

School of Chemistry, South China Normal University, Guangzhou, 510006, P. R. China

* Corresponding author: Prof. Sheng-Run, Zheng; Prof. Wei-Guang Zhang; Dr. Song-Liang Cai

E-mail address: zhengsr@scnu.edu.cn; wgzhang@scnu.edu.cn; songliangcai@m.scnu.edu.cn

Tel./Fax.: +86-20-39310187

Supporting Information

Table S1 Crystallographic data and structure refinement summary for SCNU-Z5

Complex	SCNU-Z5
Empirical formula	$C_{91}H_{90}N_{31}Ni_2O_4$
Formula weight	1799.35
Crystal system	Trigonal
Space group	*R*3 :H
a / Å	22.7024(11)
b / Å	22.7024(11)
c / Å	24.4575(13)
α / °	90
β / °	90
γ / °	120
V / Å^3	10916.6(12)
Z	3
D / g cm^{-3}	0.821
μ / mm^{-1}	1.670
T / K	193(2)
R^a / wR^b	0.0363 / 0.1003
Total / unique	17166 / 8814

[a] $R_1 = \Sigma||F_o| - |F_c||/|F_o|$, [b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)_2 + bP]$. $P = (F_o^2 + 2F_c^2)/3$.

*The refinement results were obtained from squeeze data.

Table S2 Selected bond lengths [Å] and angles [°] for SCNU-Z5

SCNU-Z5

Ni(1)-N(1A)#1	2.050(18)	Ni(2)-N(7)#1	2.120(6)
Ni(1)-N(1A)	2.050(7)	Ni(2)-N(7)#2	2.120(6)
Ni(1)-N(1A)#2	2.050(17)	Ni(2)-N(7)	2.120(6)
Ni(1)-N(1B)	2.052(6)	Ni(2)-N(5)#1	2.145(12)
Ni(1)-N(1B)#2	2.052(12)	Ni(2)-N(5)	2.145(12)
Ni(1)-N(1B)#1	2.052(16)	Ni(2)-N(5)#2	2.145(12)
Ni(1)-N(8)#2	2.054(6)	Ni(2)-N(5A)#1	2.229(10)
Ni(1)-N(8)	2.054(6)	Ni(2)-N(5A)	2.230(10)
Ni(1)-N(8)#1	2.055(6)	Ni(2)-N(5A)#2	2.230(10)
N(1A)#1-Ni(1)-N(1A)	81.1(8)	N(7)#1-Ni(2)-N(7)	89.8(2)
N(1A)#1-Ni(1)-N(1A)#2	81.1(9)	N(7)#2-Ni(2)-N(7)	89.8(2)
N(1A)-Ni(1)-N(1A)#2	81.1(9)	N(7)#1-Ni(2)-N(5)#1	93.9(5)
N(1A)#1-Ni(1)-N(1B)#2	85.9(8)	N(7)#2-Ni(2)-N(5)#1	83.0(5)
N(1A)-Ni(1)-N(1B)#2	93.2(8)	N(7)-Ni(2)-N(5)#1	171.9(5)
N(1A)#2-Ni(1)-N(1B)#2	12.5(11)	N(7)#1-Ni(2)-N(5)	83.0(5)
N(1A)#1-Ni(1)-N(1B)#1	12.5(10)	N(7)#2-Ni(2)-N(5)	171.9(5)
N(1A)-Ni(1)-N(1B)#1	85.9(8)	N(7)-Ni(2)-N(5)	93.9(5)
N(1A)#2-Ni(1)-N(1B)#1	93.2(9)	N(5)#1-Ni(2)-N(5)	93.7(7)
N(1B)-Ni(1)-N(1B)#1	97.1(8)	N(7)#1-Ni(2)-N(5)#2	171.9(5)
N(1B)#2-Ni(1)-N(1B)#1	97.1(7)	N(7)#2-Ni(2)-N(5)#2	93.9(5)
N(1A)#1-Ni(1)-N(8)#2	173.8(7)	N(7)-Ni(2)-N(5)#2	83.0(5)
N(1A)-Ni(1)-N(8)#2	93.6(3)	N(5)#1-Ni(2)-N(5)#2	93.7(7)
N(1A)#2-Ni(1)-N(8)#2	95.0(6)	N(5)-Ni(2)-N(5)#2	93.7(7)
N(1A)#1-Ni(1)-N(8)	93.6(6)	N(7)#1-Ni(2)-N(5A)#1	87.6(4)
N(1A)-Ni(1)-N(8)	95.0(3)	N(7)#2-Ni(2)-N(5A)#1	89.2(4)
N(1A)#2-Ni(1)-N(8)	173.8(7)	N(7)-Ni(2)-N(5A)#1	177.3(4)
N(1B)-Ni(1)-N(8)	91.3(3)	N(5)#1-Ni(2)-N(5A)#1	8.9(7)
N(1B)#2-Ni(1)-N(8)	171.6(8)	N(5)-Ni(2)-N(5A)#1	86.7(6)
N(1B)#1-Ni(1)-N(8)	81.7(7)	N(5)#2-Ni(2)-N(5A)#1	99.7(5)
N(8)#2-Ni(1)-N(8)	90.0(2)	N(7)#1-Ni(2)-N(5A)	89.2(4)
N(1A)#1-Ni(1)-N(8)#1	95.0(8)	N(7)#2-Ni(2)-N(5A)	177.3(4)
N(1A)-Ni(1)-N(8)#1	173.8(3)	N(7)-Ni(2)-N(5A)	87.6(4)
N(1A)#2-Ni(1)-N(8)#1	93.6(9)	N(5A)#1-Ni(2)-N(5A)	93.3(6)
N(1B)-Ni(1)-N(8)#1	171.6(3)	N(7)#1-Ni(2)-N(5A)#2	177.3(4)
N(1B)#2-Ni(1)-N(8)#1	81.7(8)	N(7)#2-Ni(2)-N(5A)#2	87.6(4)
N(1B)#1-Ni(1)-N(8)#1	91.3(7)	N(7)-Ni(2)-N(5A)#2	89.2(4)
N(8)#2-Ni(1)-N(8)#1	90.0(2)	N(5)#1-Ni(2)-N(5A)#2	86.7(6)
N(8)-Ni(1)-N(8)#1	90.0(2)	N(5)-Ni(2)-N(5A)#2	99.7(5)
N(7)#1-Ni(2)-N(7)#2	89.8(2)	N(5)#2-Ni(2)-N(5A)#2	8.9(7)

Symmetry transformations used to generate equivalent atoms: #1 -y + 1, x - y, z; #2 -x + y + 1, -x + 1, z; #3 x - 2/3, y - 1/3, z - 1/3; #4 x + 1/3, y + 2/3, z + 2/3; #5 x - 1/3, y - 2/3, z - 2/3; #6 x + 2/3, y + 1/3, z + 1/3.
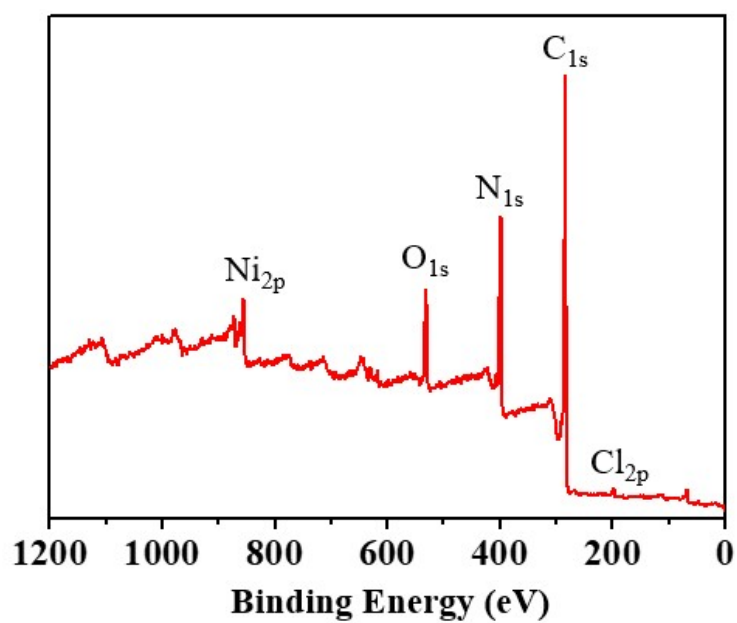
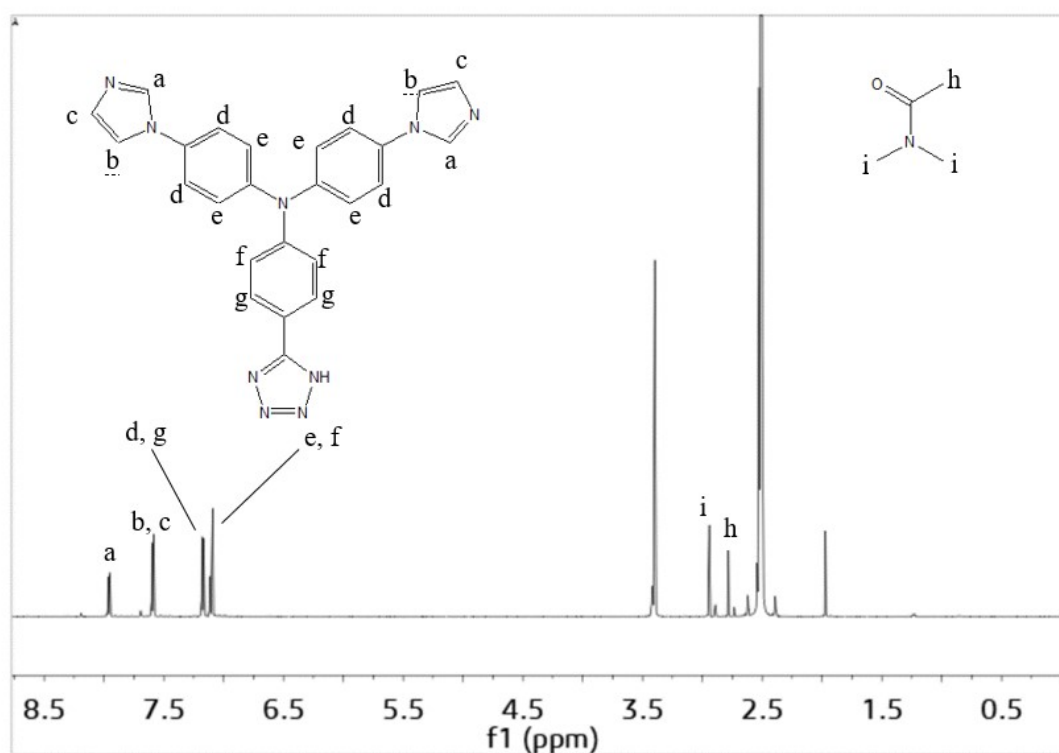**Fig. S1** XPS full-survey scan spectrum of as-synthesized SCNU-Z5.

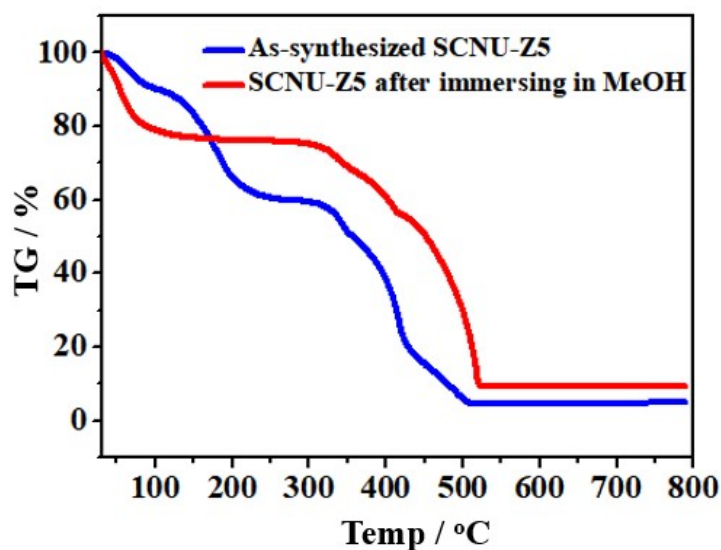**Fig. S2** ^{1}HNMR of the solution after digestion of SCNU-Z5 with NaOH.

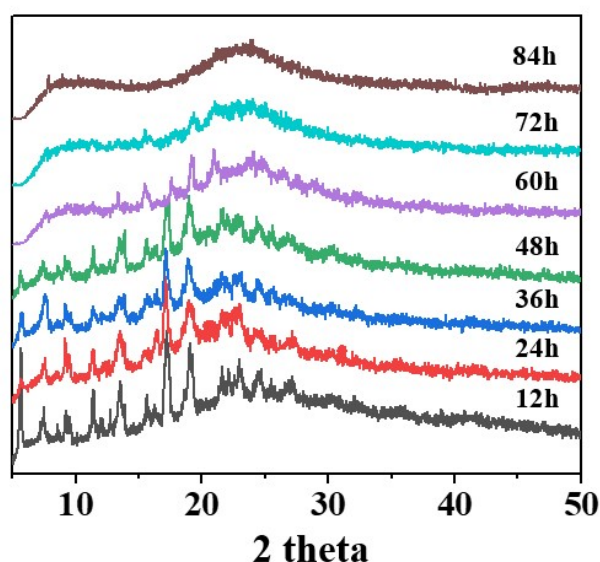**Fig. S3** The TG curves of SCNU-Z5 and SCNU-Z5 that after immersing in MeOH.

Fig. S4 The PXRD of SCNU-Z5 after immersing in water with different time.

Adsorption kinetics study.

The adsorption data were studied using pseudo-first-order and pseudo-second-order equation equations.

The pseudo-first-order equation is shown below:

$$Ln(Q_e-Q_t) = lnQ_e-k_1t$$

where k_1 is the pseudo-first-order rate constant (min^{-1}), Q_e and Q_t are the adsorption capacity at equilibrium and at the time of t, respectively.

The pseudo-second-order equation is shown below:

$t/Q_t = 1/(k_2 Q_e^2) + t/Q_e$

where k_2 is the pseudo-second-order rate constant (mg/g·min), Q_e and Q_t are the adsorption capacity at equilibrium and at the time of t, respectively.

Adsorption isotherms study.

The Langmuir, Freundlich and Themkin equations were selected to fit the data**.**

Langmuir model is the most widely used model based on the assumption of a monolayer adsorption on a homogeneous surface. It can be given by:

$$\frac{c_e}{Q_e} = \frac{1}{Q_m b} + \frac{c_e}{Q_m}$$

where c_e (mg L^{-1}) is the equilibrium concentration of MB in solution, Q_e (mg g^{-1}) is the adsorption capacity at equilibrium, Q_m (mg g^{-1}) and b (L mg^{-1}) represent the maximum adsorption capacity of adsorbents and the energy of adsorption, respectively.

Freundlich model is another widely applied isothermal model based on the assumption that adsorption energy decays exponentially with coverage rise. The Freundlich equation is given as:

$$lnqQ_e = lnk_F + \frac{1}{n}lnc_e$$

where k_F [(mg g^{-1})(L mg^{-1})$^{1/n}$] is a constant indicative of the adsorption capacity of the adsorbent and (1/n) of the adsorption intensity.

Tempkin model is a widely used isothermal model based on the assumption that adsorption energy decreases linearly with coverage rise. The Tempkin equation is given as:

$$Q_e = Bln(A) + BlnC_e$$

where B = *(RT/b)* is related to the heat of adsorption, A is the equilibrium binding constant, T (K) is the absolute temperature and R is the universal gas constant.
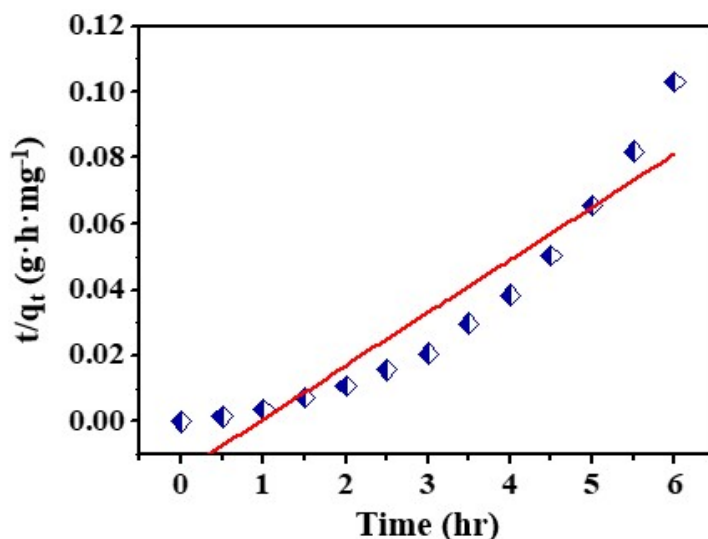
Fig. S5 Plot of the pseudo-second order kinetic model for the adsorption of I_2 on SCNU-Z5.

Table S3. The equilibrium capacities, pseudo-first order and pseudo-second order rate constants and correlation coefficient R^2 of SCNU-Z5 adsorbing I_2.

	Pseudo-first order			Pseudo-second order		
$q_{e, Exp}$ (mg/g)	$q_{e, Cal}$ (mg·g^{-1})	K_1 (min^{-1})	R^2	$q_{e, Cal}$ (mg·g^{-1})	K_2 (g·mg^{-1}·min^{-1})	R^2
	347.9	0.302	0.9960	62.11	-1.03×10^{-9}	0.881

Table S4. A summary of some representative MOFs for the iodine capture in various media and their uptake capacities.

MOFs	Sorption medium	Maximum q_m (mg·g)	Ref
UiO-66-PYDC	cyclohexane	1250	S1
UiO-66	cyclohexane	401	S1
JLNU-4	cyclohexane	680	S2
Th-TATAB	cyclohexane	750	S3
Th-SINAP-7	cyclohexane	107	S4
Th-SINAP-8	cyclohexane	258	S4
Th-TTHA	cyclohexane	562	S5
AgNPs@UiO-66	cyclohexane	1260	S6
SCNU-Z4	cyclohexane	237	S7
SCNU-Z5	cyclohexane	442	This work
Mn-MOF	water	1.1	S8
SCNU-Z4	water	332	S7
SCNU-Z5	water	351	This work
$Zr_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4(ITTC)_4$	I_2 vapor	2.92	S9
UPC-158	I_2 vapor	1.77	S9
Continued			

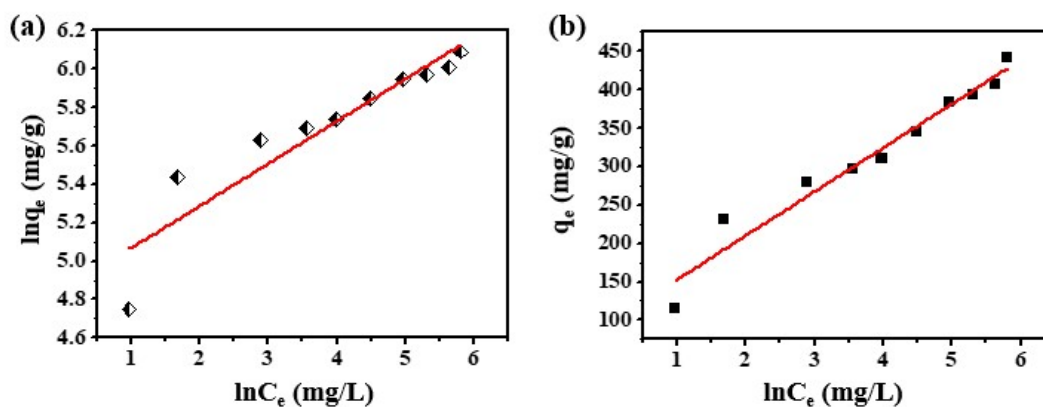| Th-SINAP-7 | I_2 vapor | 0.352 | S4 |
Th-SINAP-8	I_2 vapor	0.473	S4
MOF-808	I_2 vapor	2.18	S10
HKUST-1	I_2 vapor	1.75	S11
NU-1000	I_2 vapor	1.45	S10
ZIF-8	I_2 vapor	1.25	S12
MFM-300(In)	I_2 vapor	1.16	S13
UiO-67	I_2 vapor	0.53	S10
AlOC-28-NC	I_2 vapor	0.621	S14
JNU-200	I_2 vapor	1.08	S15
SCNU-Z5	I_2 vapor	1.68	This work

Fig. S6 Plots of the fitting of the I_2 adsorption on SCNU-Z5 experimental data with (a) Freundlich and (b) Themkin isotherm models.

Table S5. Parameters of the adsorption of I_2 on SCNU-Z5.

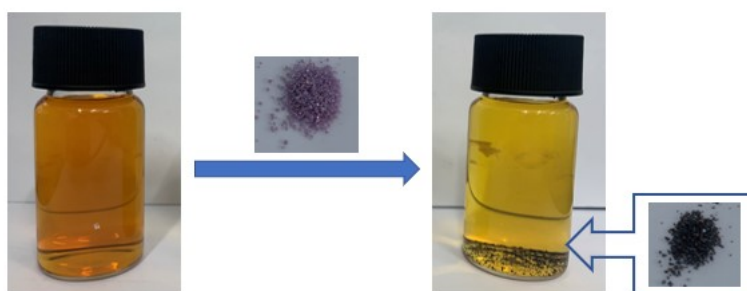| Models	Parameters	
Langmuir	q_m (mg·g^{-1})	438.6
	b (L·mg^{-1})	0.067
	R^2	0.9933
Freundlich	n	4.54
	k_F (mg·g^{-1}(L·mg^{-1})$^{1/n}$)	127.5
	R^2	0.8513
Tempkin	A (L·g^{-1})	5.36
	B	57.18
	R^2	0.9508

Fig. S7 The color change of the solutions and solids before and after iodine capture in water.

Details for I_2 titration

Step 1. Preparation of 0.01000 M $Na_2S_2O_3$ standard solution

Pipette 10.00 ml of 0.1000 M $Na_2S_2O_3$ standard solution, put it into a 100 ml volumetric flask, dilute it with water, and fix the volume after cooling.

Step 2. Determination of iodine in aqueous solution by titration

Take 10 ml of iodine aqueous solution. Then, the concentrations were determined by titrating against $Na_2S_2O_3$ standard solution (0.01000 M). The experiments were performed three times and the average value is used for following calculation.

Step 3. Calculation of amount of iodine removed from aqueous iodine solution

The data is below:

Readings	Volume of I_2 (mL)	Volume of $Na_2S_2O_3$ (mL)	M_{I_2} (mg/L)
Before	20.00	6.97	447.6
After immersing for 36 h	10.00	1.50	96.38

The mass of I_2 adsorbed by SCNU-Z5 is

m_{I_2} = （447.6-96.38）×10×10^{-3}= 3.512 mg

The mass of I_2 adsorbed by per gram of SCNU-Z5 is
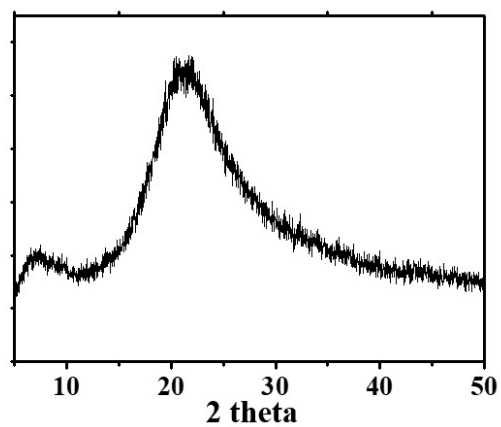
m = 3.512/10*1000 = 351.2 mg/g

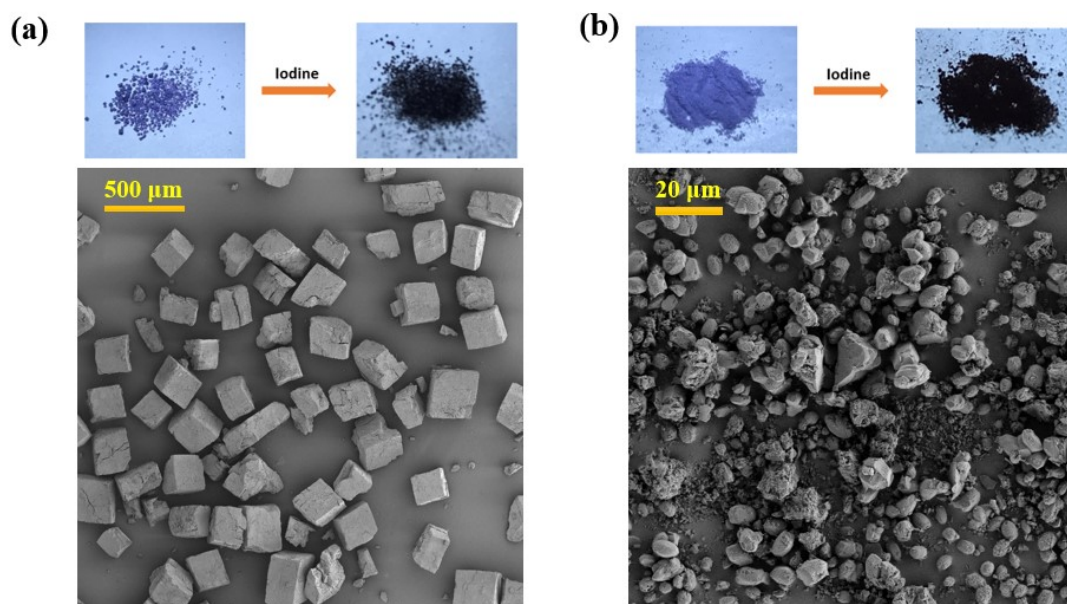**Fig. S8** PXRD data of I_2 loaded SCNU-Z5 sample that after iodine adsorption in water for 12 h.

Fig. S9 The pictures of (a) non-ground and (b) ground samples before and after iodine adsorption in water and their corresponding SEM image before iodine adsopion.
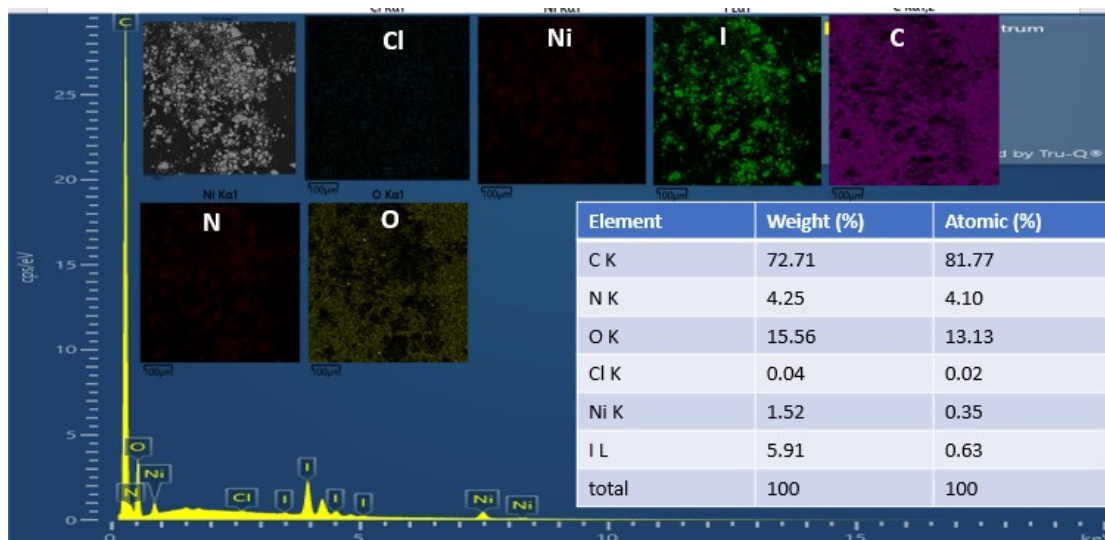
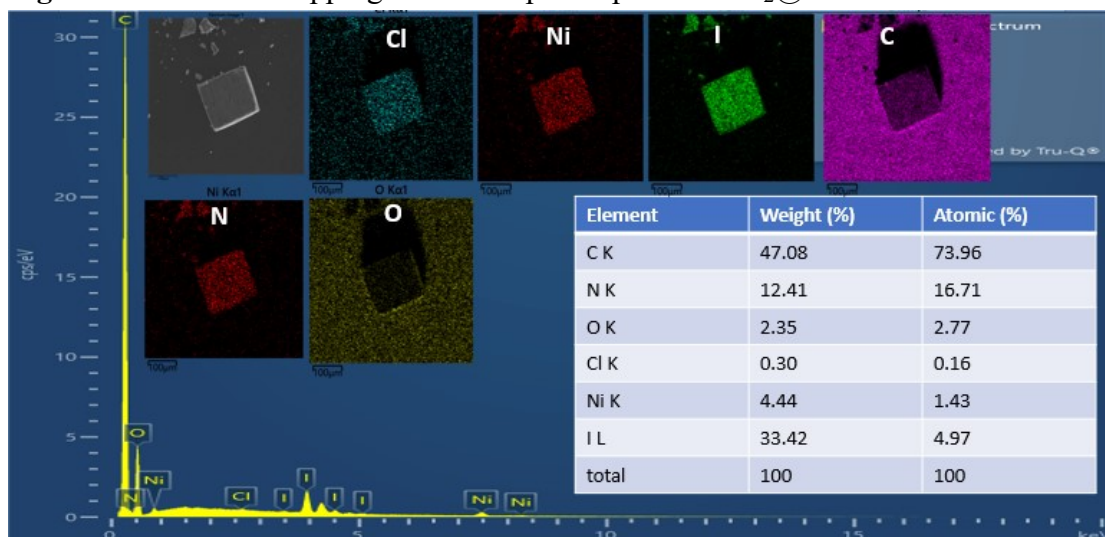**Fig. S10** SEM-EDS mapping and EDS spectra profiles of I_2@SCNU-Z5-water.

Element	Weight (%)	Atomic (%)
C K	72.71	81.77
N K	4.25	4.10
O K	15.56	13.13
Cl K	0.04	0.02
Ni K	1.52	0.35
I L	5.91	0.63
total	100	100

Fig. S11 SEM-EDS mapping and EDS spectra profiles of I_2@SCNU-Z5-cyclohexane.

Element	Weight (%)	Atomic (%)
C K	47.08	73.96
N K	12.41	16.71
O K	2.35	2.77
Cl K	0.30	0.16
Ni K	4.44	1.43
I L	33.42	4.97
total	100	100

Fig. S12 SEM-EDS mapping and EDS spectra profiles of I_2@SCNU-Z5-vapor.

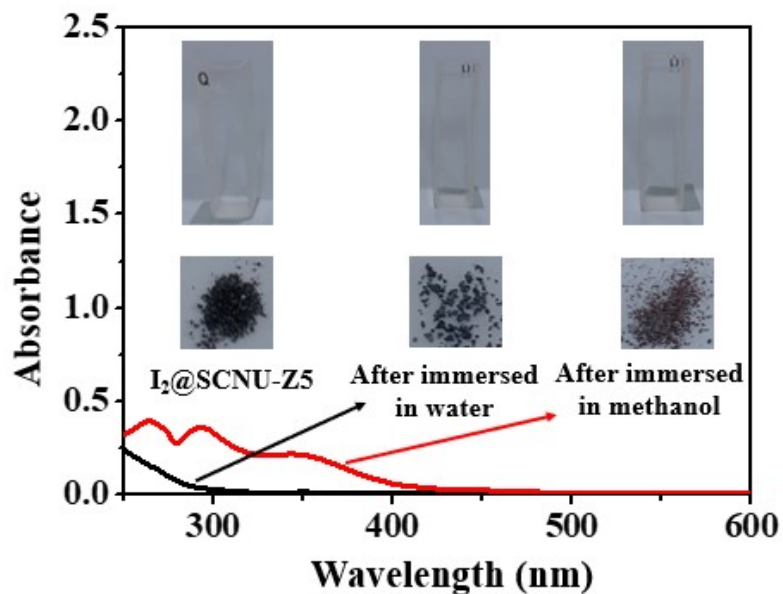| Element	Weight (%)	Atomic (%)
C K	71.44	84.21
N K	0.10	0.10
O K	16.02	14.18
Cl K	0.15	0.06
Ni K	0.63	0.15
I L	11.68	1.3
total	100	100

Fig. S13 The UV-Vis spectra of the water and methanol solution after immersing with I_2@SCNU-Z5 for 7 days. (Inserted are the figures for the color change of the solutions and the solids)
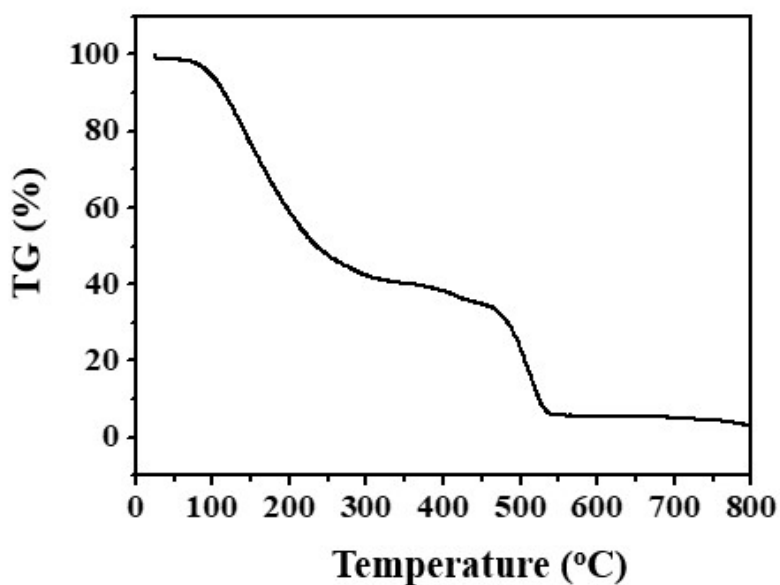

Fig. S14 The TG curve of I_2@SCNU-Z5.

Reference

(1) Wang, Z.; Huang, Y.; Yang, J.; Li, Y.; Zhuang, Q.; Gu, J. *Dalton Trans.* **2017**, *46*, 7412–7420.

(2) Yao, C.; Wang, W.; Zhang, S. R.; Li, H. Y.; Xu, Y. H.; Su, Z. M.; Che, G. B. *RSC. Adv.* **2018**, *8*. 36400–36406.

(3) Zhang, N.; Sun, L.X.; Xing, Y. H.; Bai, F. Y. *Cryst. Growth Des.* **2019**, *19*, 5686–5695.

(4) Li, Z. J.; Yue, Z.; Wu, X.; Ren, Y.; Wang, S.; Li, Y.; Zhang, Z. H.; Guo, X.; Lin, J.; Wang, J. Q. *Inorg. Chem.* **2020**, *59*, 4435–4442.

(5) Zhang, N.; Sun, L. X.; Bai, F. Y.; Xing, Y. H. *Inorg. Chem.* **2020**, *59*, 3964–3973.

(6) Feng, Y.; Yang, P.; Li, Y.; Gu J. *J. Chem. Eng. Data* **2020**, *65*, 1986–1992.

(7) S7 ICF Wang, G. Q.; Huang, J. F.; Huang, X. F.; Deng, S. Q.; Zheng, S. R.; Cai, S. L.; Fan, J.; Zhang, W. G. *Inorg. Chem. Front.* **2021**, *8*,1083–1092.

(8) Gogia, A.; Das, P.; Mandal, S. K. *ACS Appl. Mater. Interfaces* **2020**, *12*, 46107–46118.

(9) Guo, B.; Li, F.; Wang, C.; Zhang, L.; Sun, D. *J. Mater. Chem. A.* **2019**, *7*, 13173–13179.

(10) Chen, P.; He, X. H.; Pang, M. B.; Dong, X. T.; Zhao, S.; Zhang, W. *ACS Appl. Mater. Interfaces* **2020**, *12*, 20429–20439.

(11) Sava, D. F.; Chapman, K. W.; Rodriguez, M. A.; J. Greathouse, A.; Crozier, P. S.; Zhao, H.; Chupas P. J.; Nenoff, T. M. *Chem. Mater.* **2013**, *25*, 2591–2596.

(12) Sava, D. F.; Rodriguez, M. A.; Chapman, K. W.; Chupas, P. J.; Greathouse, J. A.; Crozier, P. S.; Nenoff, T. M. *J. Am. Chem. Soc.* **2011**, *133*, 12398–12401.

(13) Zhang, X.; da Silva, I.; Godfrey, H. G. W.; Callear, S. K.; Sapchenko, S. A.; Cheng, Y.; Vitorica-Yrezabal, I.; Frogley, M. D.; Cinque, G.; Tang, C. C.; Giacobbe, C.; Dejoie, C.; Rudic, S.; Ramirez-Cuesta, A. J.; Denecke, M. A.; Yang, S.; Schroder, M. *J. Am. Chem. Soc.* **2017,** *139*,16289–16296.

(14) Yao, S.; Fang, W. H.; Sun, Y.; S. Wang, T.; Zhang, J. *J. Am. Chem. Soc.* **2021**, DOI: 10.1021/jacs.0c11778.

(15) Wu, K.; Huang, Y.-L.; Zheng, J.; Luo, D.; Xie, M.; Li, Y. Y.; Lu, W.; Li, D. *Mater. Chem. Front.* **2021**, *5*, 4300–4309.