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A hydrolytically stable cage-based metal-organic framework containing two types of building blocks for the adsorption of iodine and dyes

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Supporting Information

Table S1 Crystallographic data and structure refinement summary for SCNU-Z4

Complex	SCNU-Z4*
Empirical formula	$C_{104}H_{62}Cl_3Cu_{10}N_{72}O_6$
Formula weight	3158.00
Crystal system	Tetragonal
Space group	*P*-4m2
a / Å	20.2414(3)
b / Å	20.2414(3)
c / Å	17.2343(10)
α / °	90
β / °	90
γ / °	90
V / Å^3	7061.1(5)
Z	1
D / g cm^{-3}	0.743
μ / mm^{-1}	1.375
T / K	293(2)
R^a / wR^b	0.0523/0.1422
Total / unique	16224/7227
Rint	0.0550

^{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-Z4

SCNU-Z4			
Cu(1)-N(2)	2.023(5)	Cu(1)-N(2)#1	2.023(5)
Cu(1)-N(3)#2	2.027(5)	Cu(1)-N(3)#3	2.027(5)
Cu(1)-O(2)	2.292(7)	Cu(1)-Cl(2)	2.5121(9)
Cu(2)-N(7)#4	1.981(5)	Cu(2)-N(7)	1.982(5)
Cu(2)-N(9)#5	2.006(5)	Cu(2)-N(9)#6	2.006(5)
Cu(2)-Cl(1)	2.5256(12)	Cu(3)-N(6)	2.019(5)
Cu(3)-N(6)#4	2.019(5)	Cu(3)-N(6)#7	2.019(5)
Cu(3)-N(6)#8	2.019(5)	Cu(3)-O(1)	2.252(11)
N(2)-Cu(1)-N(2)#1	96.1(3)	N(2)-Cu(1)-N(3)#2	174.80(17)
N(2)#1-Cu(1)-N(3)#2	85.96(16)	N(2)-Cu(1)-N(3)#3	85.96(16)
N(2)#1-Cu(1)-N(3)#3	174.79(17)	N(3)#2-Cu(1)-N(3)#3	91.6(3)
N(2)-Cu(1)-O(2)	94.2(3)	N(2)#1-Cu(1)-O(2)	94.2(3)
N(3)#2-Cu(1)-O(2)	90.5(3)	N(3)#3-Cu(1)-O(2)	90.5(3)
N(2)-Cu(1)-Cl(2)	88.00(12)	N(2)#1-Cu(1)-Cl(2)	88.00(12)
N(3)#2-Cu(1)-Cl(2)	87.28(13)	N(3)#3-Cu(1)-Cl(2)	87.28(13)
O(2)-Cu(1)-Cl(2)	176.8(3)	N(7)#4-Cu(2)-N(7)	89.0(3)
N(7)#4-Cu(2)-N(9)#5	88.58(19)	N(7)-Cu(2)-N(9)#5	169.3(2)
N(7)#4-Cu(2)-N(9)#6	169.3(2)	N(7)-Cu(2)-N(9)#6	88.57(19)
N(9)#5-Cu(2)-N(9)#6	91.9(3)	N(7)#4-Cu(2)-Cl(1)	91.92(16)
N(7)-Cu(2)-Cl(1)	91.92(16)	N(9)#5-Cu(2)-Cl(1)	98.57(17)
N(9)#6-Cu(2)-Cl(1)	98.57(17)	N(6)-Cu(3)-N(6)#4	89.0(2)
N(6)-Cu(3)-N(6)#7	89.8(3)	N(6)#4-Cu(3)-N(6)#7	168.1(3)
N(6)-Cu(3)-N(6)#8	168.2(3)	N(6)#4-Cu(3)-N(6)#8	89.8(3)
N(6)#7-Cu(3)-N(6)#8	89.0(2)	N(6)-Cu(3)-O(1)	95.92(14)
N(6)#4-Cu(3)-O(1)	95.93(14)	N(6)#7-Cu(3)-O(1)	95.93(14)
N(6)#8-Cu(3)-O(1)	95.93(14)		

Symmetry transformations used to generate equivalent atoms: #1 -x + 1, y, z; #2 -y + 1, x, -z + 1; #3 y, x, -z + 1; #4 -x, y, z; #5 -y, x, -z; #6 y, x, -z; #7 x, -y + 1, z; #8 -x, -y + 1, z; #9 -x + 1, -y + 1, z; #10 y, -x + 1, -z + 1; #11 y, -x, -z.

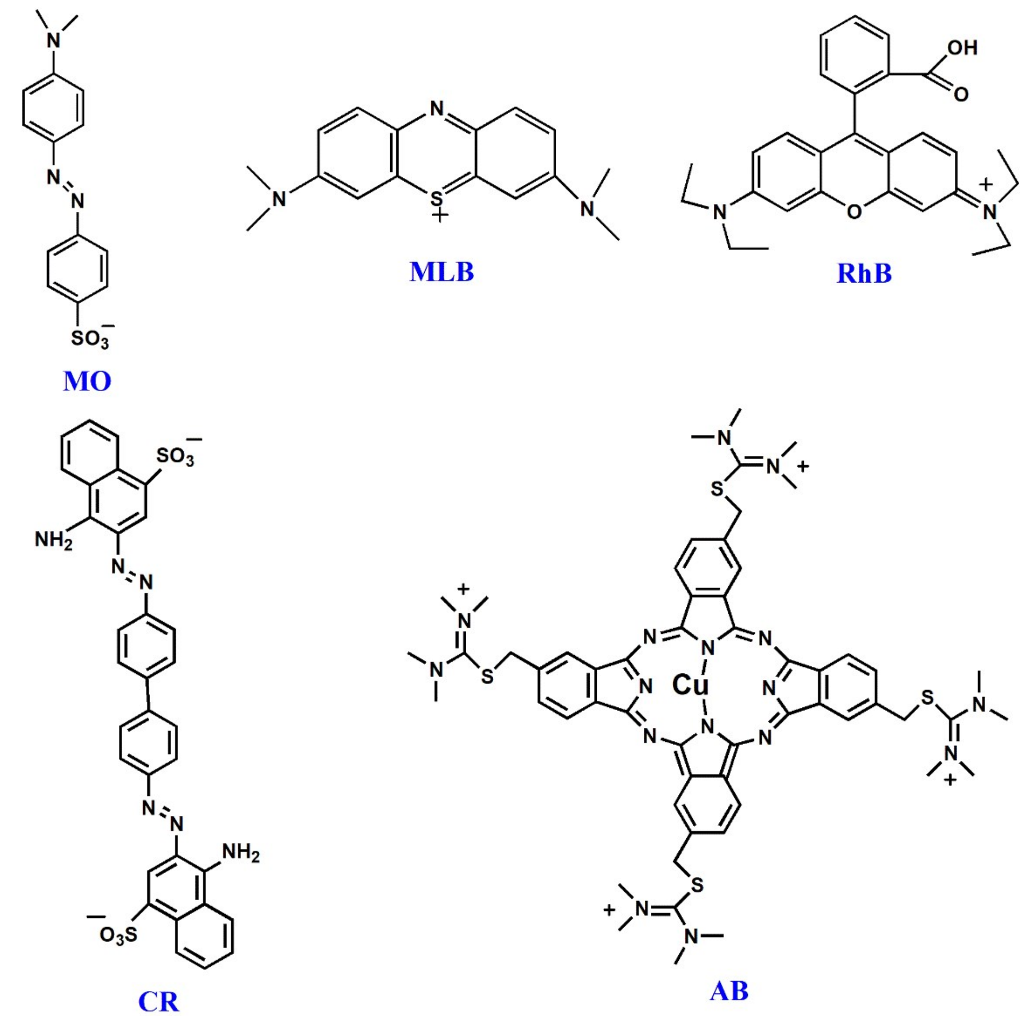
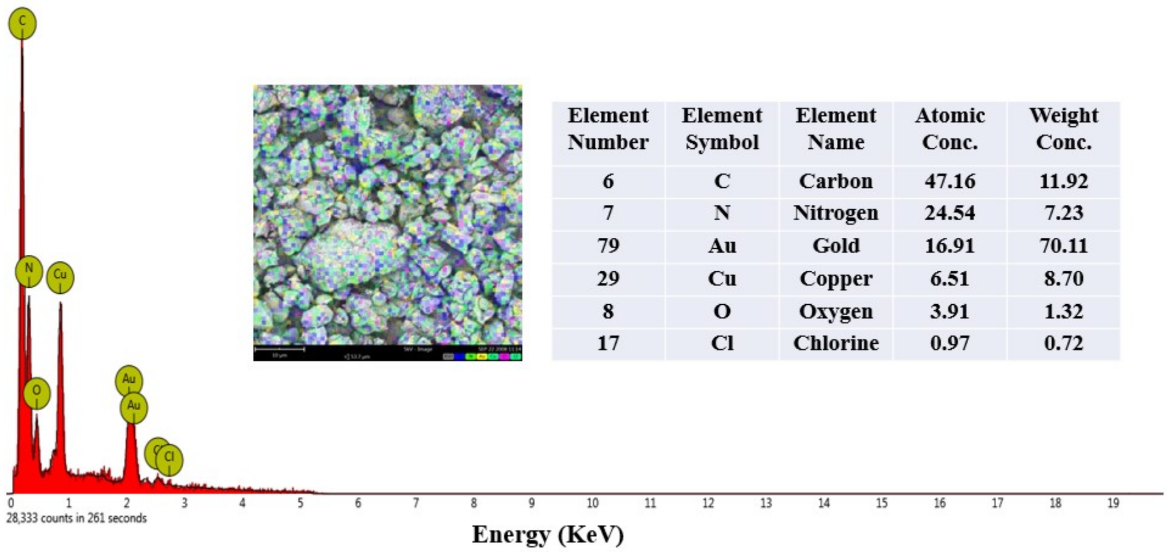


Fig. S1 The structures of the selected dye molecules.



Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
6	C	Carbon	47.16	11.92
7	N	Nitrogen	24.54	7.23
79	Au	Gold	16.91	70.11
29	Cu	Copper	6.51	8.70
8	O	Oxygen	3.91	1.32
17	Cl	Chlorine	0.97	0.72

Fig. S2 EDX analysis of SCNU-Z4.

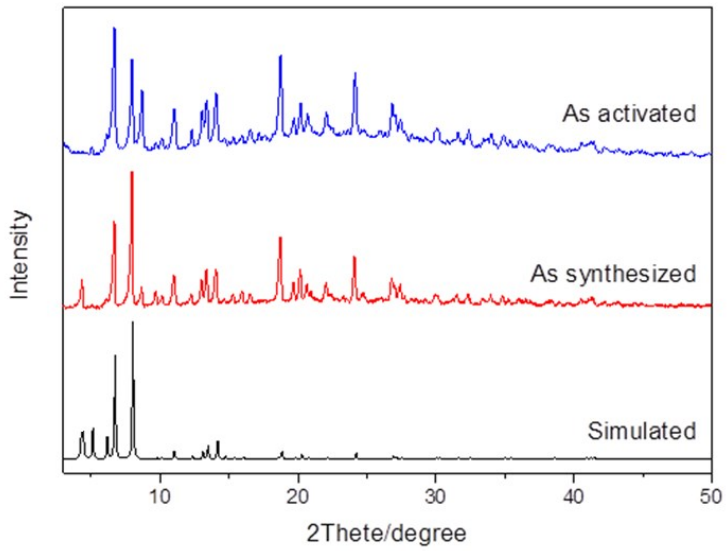


Fig. S3 The PXRD of simulated, as-synthesized and activated SCNU-Z4.

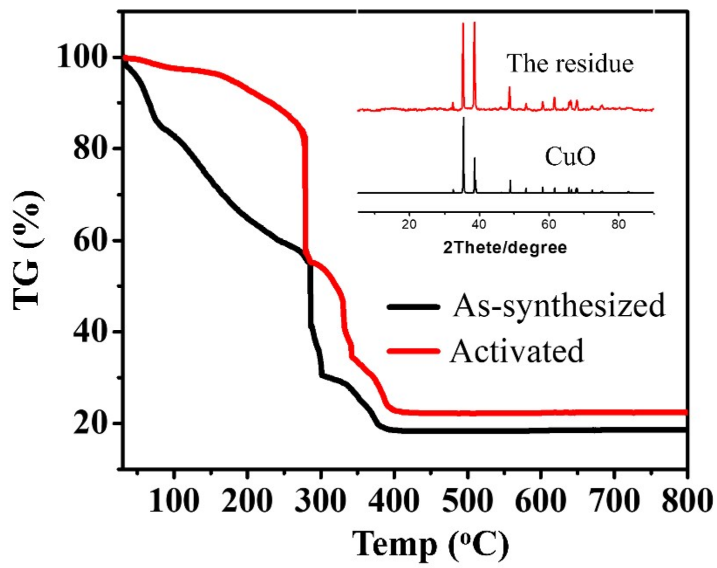


Fig. S4 The TG curves as-synthesized and activated SCNU-Z4 (Insert: The PXRD of the residue and CuO).

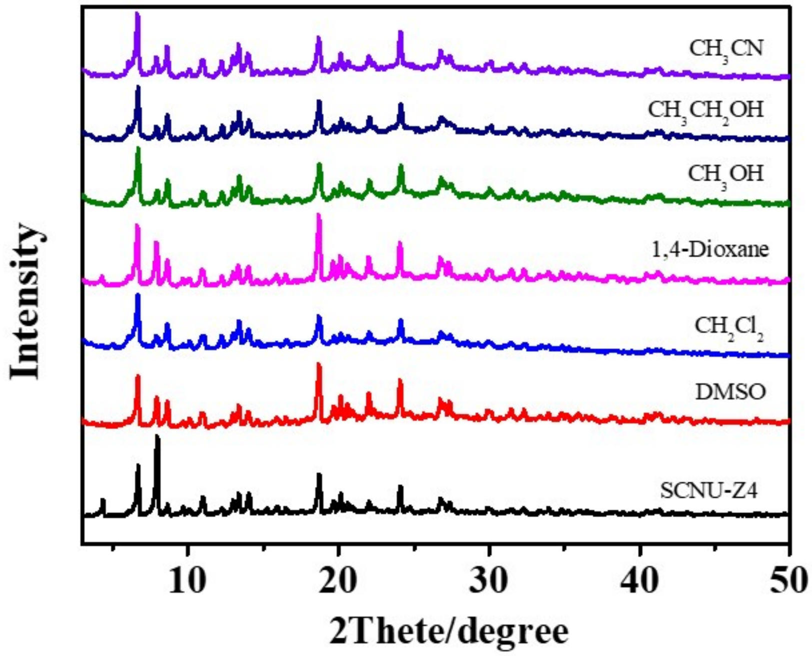


Fig. S5 The PXRD SCNU-Z4 crystals immersed in different organic solvents after 72 h.

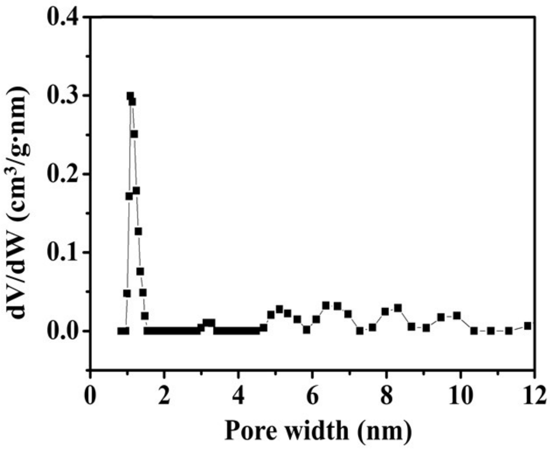


Fig. S6 The pore size distributions of SCNU-Z4.

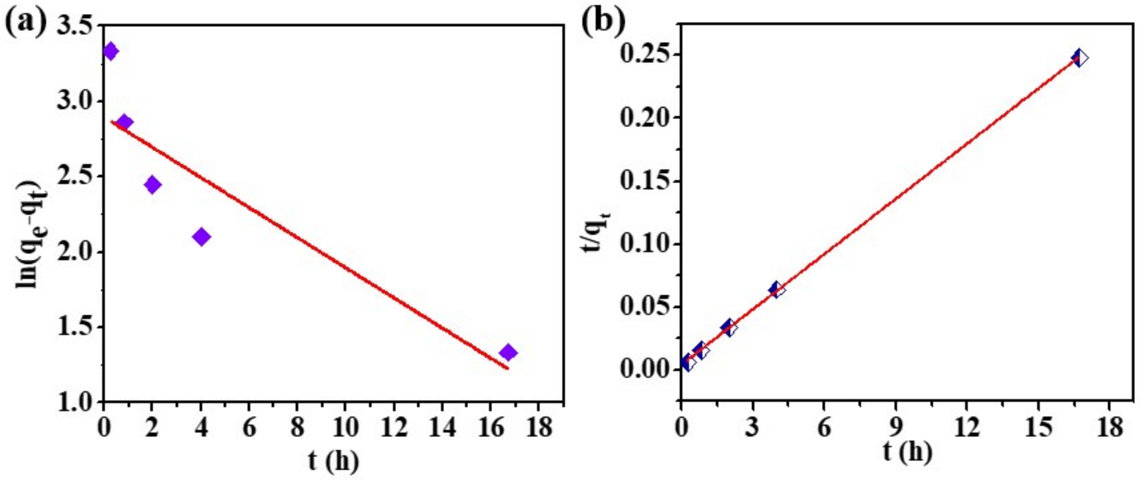


Fig. S7 Plot of (a) the pseudo-first order kinetic model and (b) the pseudo-second order kinetic model for the adsorption of I_2 on SCNU-Z4.

Table S3 The equilibrium capacities, pseudo-first order and pseudo-second order rate constants and correlation coefficient R^2 of SCNU-Z4 adsorbing I_2.

	Pseudo-first-order			Pseudo-second-order		
$q_{e,Exp}$(mg.g^{-1})	$q_{e,Cal}$ (mg.g^{-1})	K_1 (min^{-1})	R^2	$q_{e,Cal}$ (mg.g^{-1})	k_2 (g·mg^{-1}·min^{-1})	R^2
70.90	18.057	0.1001	0.7439	68.306	0.0537	0.9998

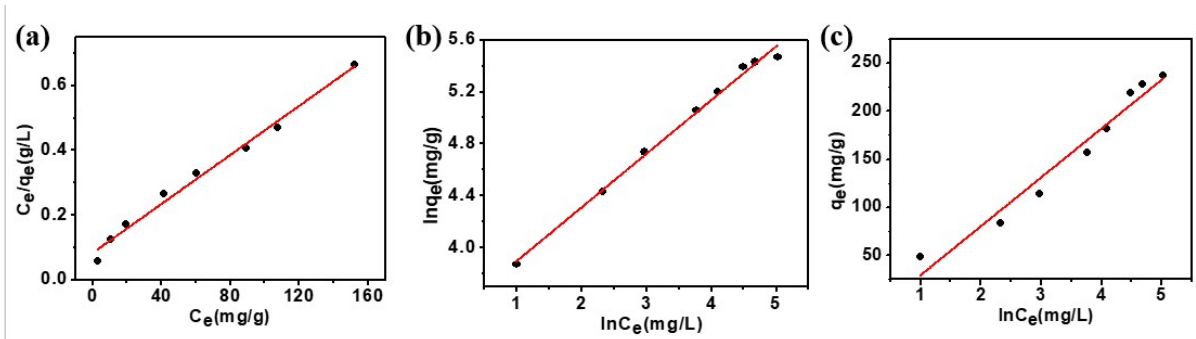


Fig. S8 Plots of the fitting of the I_2 adsorption on SCNU-Z4 experimental data with (a) Langmuir isotherm, (b) Freundlich and (c) Themkin isotherm models.

Table S4 Parameters of the adsorption of I_2 on SCNU-Z4.

Models	Parameters	I_2
Langmuir	q_m (mg·g^{-1})	263.852
	b (L·mg^{-1})	0.046
	R^2	0.9870
Freundlich	n	2.4210
	kF (mg g^{-1} (L mg^{-1})$^{1/n}$)	32.57
	R^2	0.9925
Tempkin	A (L g^{-1})	0.66
	B	50.78
	R^2	0.9574

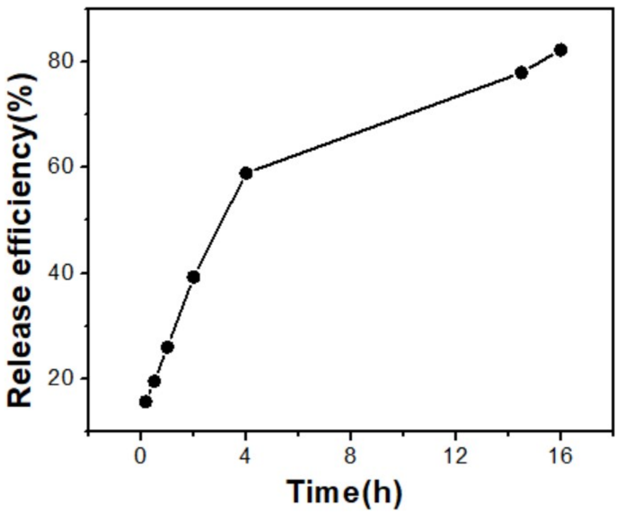


Fig. S9 The release efficiency of I_2 from I_2@SCNU-Z4 in EtOH.

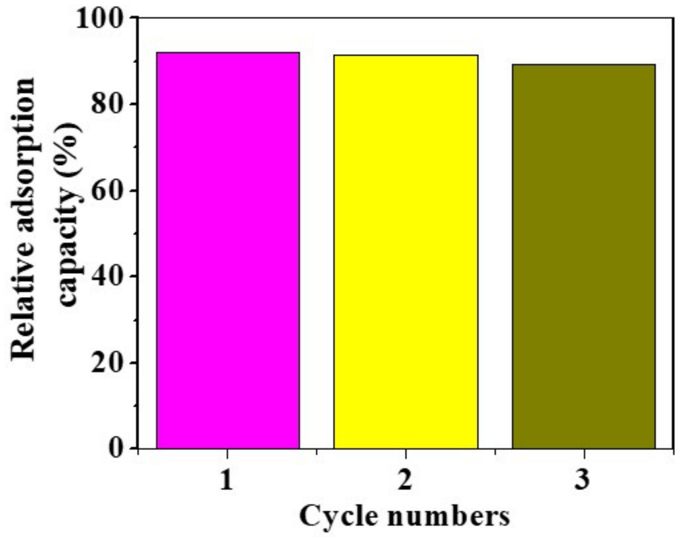


Fig. S10 The relative adsorption capacity on I_2 for three adsorption-desorption cycles.

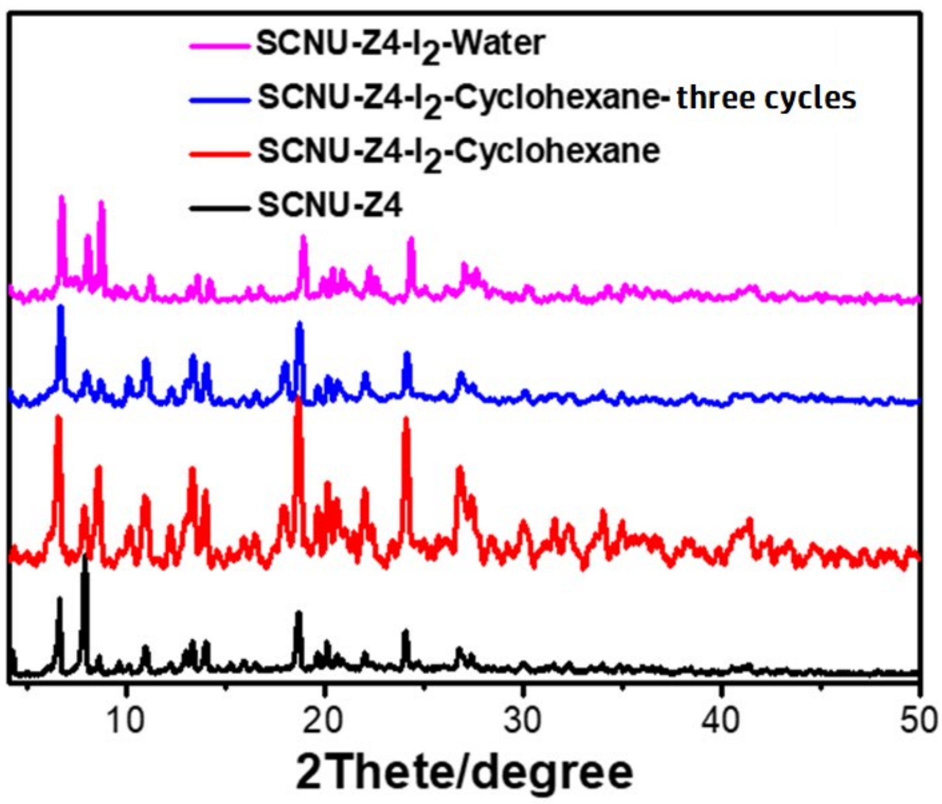
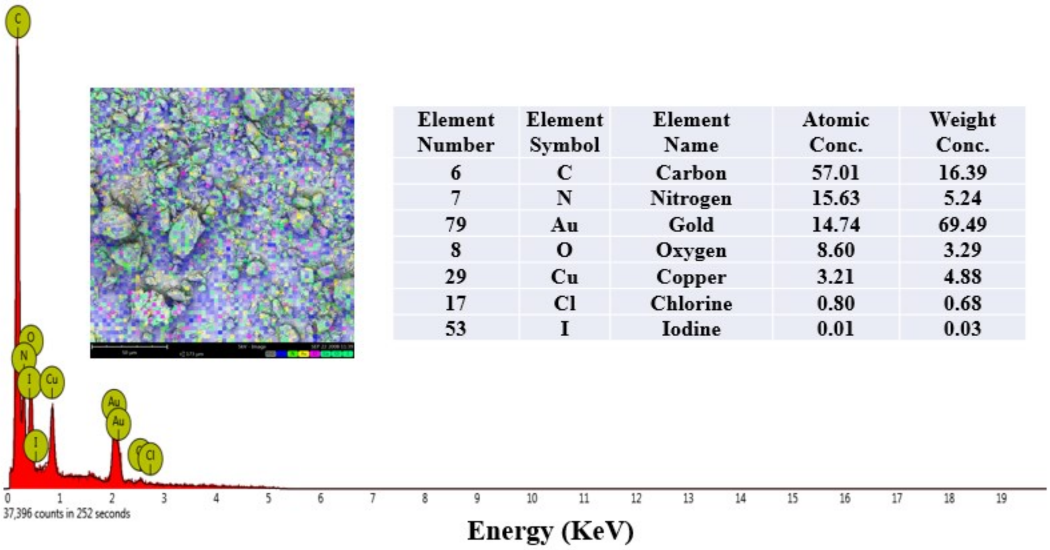


Fig. S11 The PXRD of SCNU-Z4 and I_2@SCNU-Z4.



Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
6	C	Carbon	57.01	16.39
7	N	Nitrogen	15.63	5.24
79	Au	Gold	14.74	69.49
8	O	Oxygen	8.60	3.29
29	Cu	Copper	3.21	4.88
17	Cl	Chlorine	0.80	0.68
53	I	Iodine	0.01	0.03

Fig. S12 EDX analysis of I_2@SCNU-Z4.

Details for I_2 titration

Step 1. Preparation of 0.008000 M $Na_2S_2O_3$ standard solution

Pipette 8 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 and was added with 10 ml of water. The solution was stand for several seconds. Then, the concentrations were determined by titrating against $Na_2S_2O_3$ standard solution (0.008000 M).

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 $_{I_2}$ (M)
Before	10.00	9.50	0.00380
After immersing for 36 h	10.00	4.60	0.00184

The mass of I_2 adsorbed by SCNU-Z4 is

$m_{I_2} = (0.00380-0.00184) \times 20\times10^{-3}\times253.8 = 9.95mg$

The mass of I_2 adsorbed by per gram of SCNU-Z4 is

m = 9.95/30*1000 = 331.7 mg/g

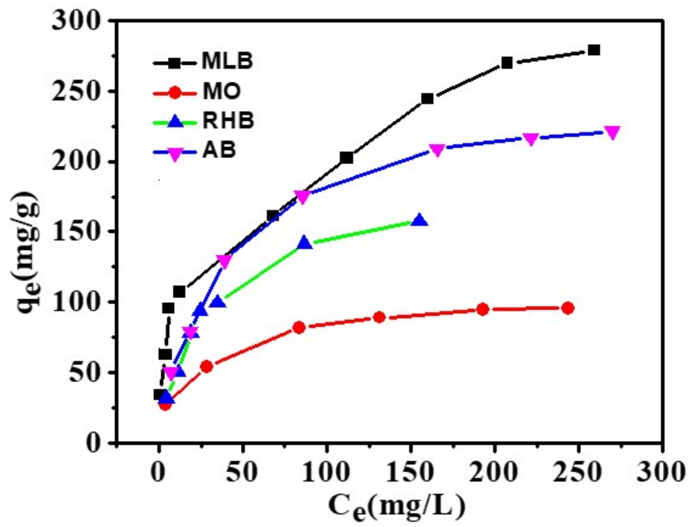


Fig. S13 Adsorption isotherms of MLB, RhB, MO and AB to SCNU-Z4 (t = 24 h, T = 30 °C).

Tab. S5 A comparison table of CR capture with some well-studied examples in the literature.

Adsorbents	Q_e (mg/g)	Ref
Cu-MOF	656.0	S1
MIL-68 (In)-MOF	1204.0	S2
Zn-MOF	60.2	S3
Ni-MOF	585.0	S4
Sn-BDC MOF	95.2	S5
In-MOF	299.0	S6
Zn-MOF	2348.0	S7
Ce-MOF	799.6	S8
Ag-MOF	823.3	S9
SCNU-Z4	1200.0	this work

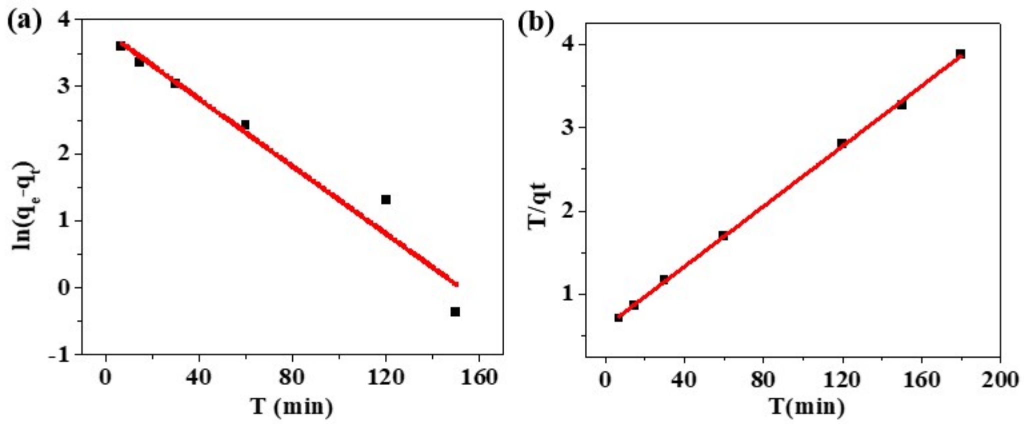


Fig. S14 Plot of (a) the pseudo-first order kinetic model and (b) the pseudo-second order kinetic model for the adsorption of MLB on SCNU-Z4.

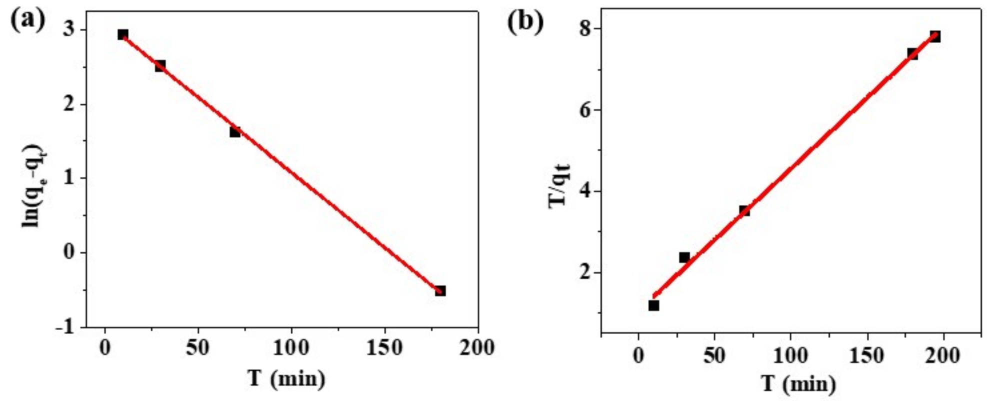


Fig. S15 Plot of (a) the pseudo-first order kinetic model and (b) the pseudo-second order kinetic model for the adsorption of RhB on SCNU-Z4.

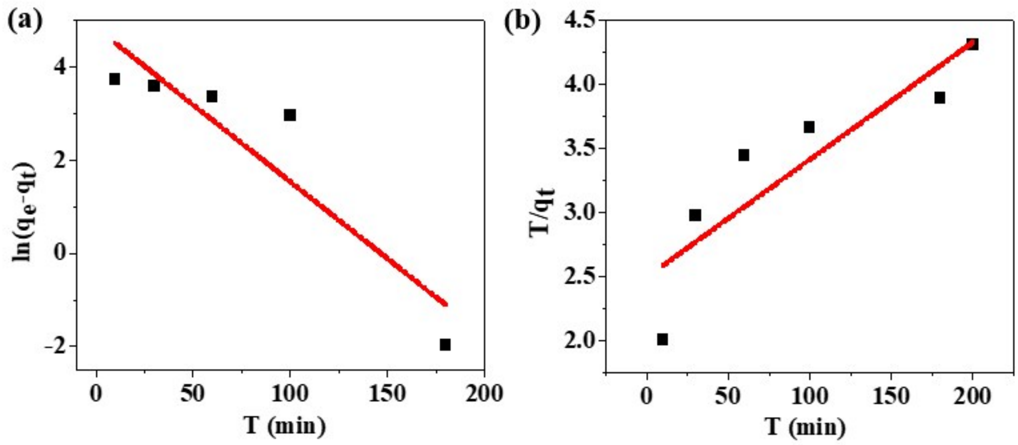


Fig. S16 Plot of (a) the pseudo-first order kinetic model and (b) the pseudo-second order kinetic model for the adsorption of AB on SCNU-Z4.

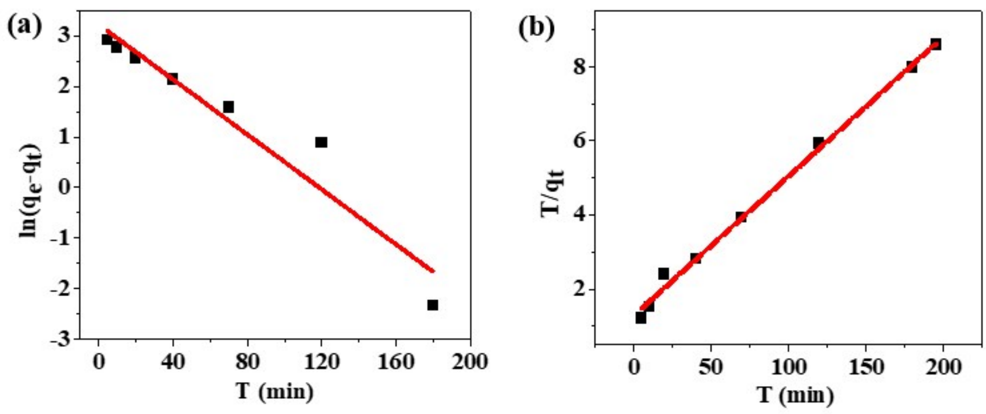


Fig. S17 Plot of (a) the pseudo-first order kinetic model and (b) the pseudo-second order kinetic model for the adsorption of MO on SCNU-Z4.

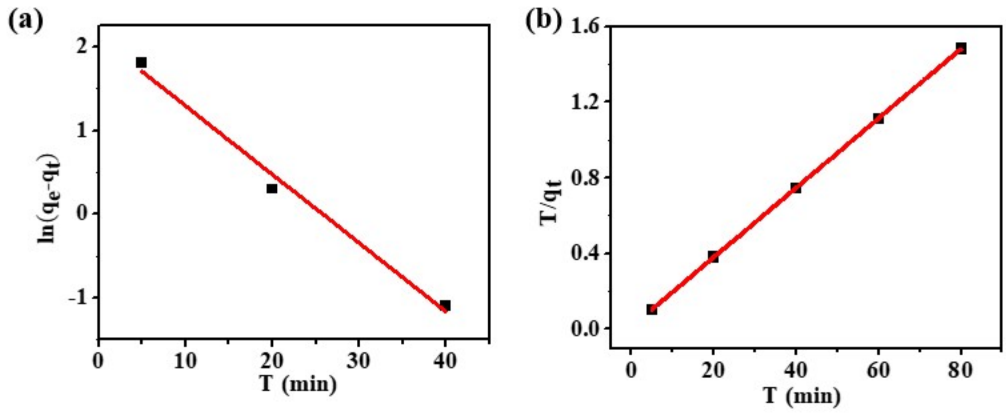


Fig. S18 Plot of (a) the pseudo- first order kinetic model and (b) the pseudo-second order kinetic model for the adsorption of CR on SCNU-Z4.

Tab. S6 The equilibrium capacities, pseudo-first order and pseudo-second order rate constants and correlation coefficient R^2 of SCNU-Z4 adsorbing different dyes.

Dyes		Pseudo-first-order			Pseudo-second-order		
	$q_{e,Exp}$ (mg.g^{-1})	$q_{e,Cal}$ (mg.g^{-1})	K_1 (min^{-1})	R^2	$q_{e,Cal}$ (mg.g^{-1})	k_2 (g·mg^{-1}·min^{-1})	R^2
MO	20.65	15.06	0.0437	0.9671	22.31	0.0048	0.9994
MLB	46.48	46.17	0.0252	0.9606	55.25	0.0001	0.9997
CR	53.93	8.27	0.0819	0.9778	54.44	0.0284	0.9999
RHB	24.99	22.22	0.0203	0.9990	28.60	0.0012	0.9964
AB	46.36	114.30	0.0292	0.7455	114.94	0.0000	0.7203

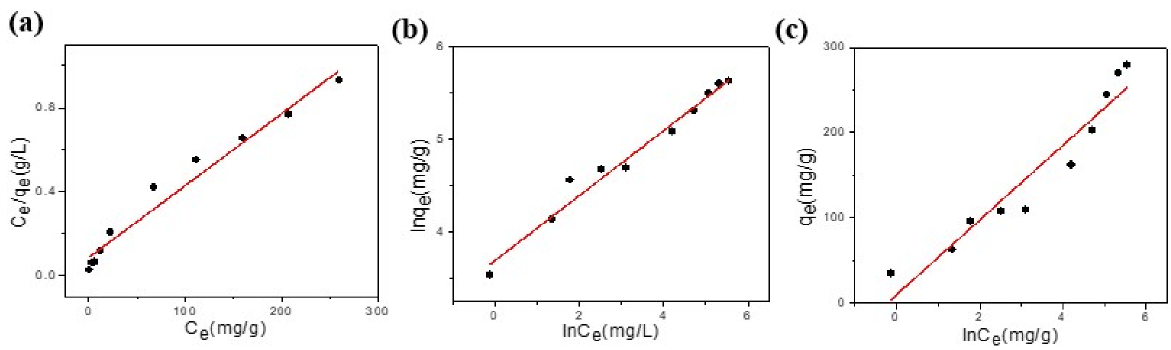


Fig. S19 Plots of the fitting of the MLB adsorption on SCNU-Z4 experimental data with (a) Langmuir isotherm, (b) Freundlich and (c) Themkin isotherm models.

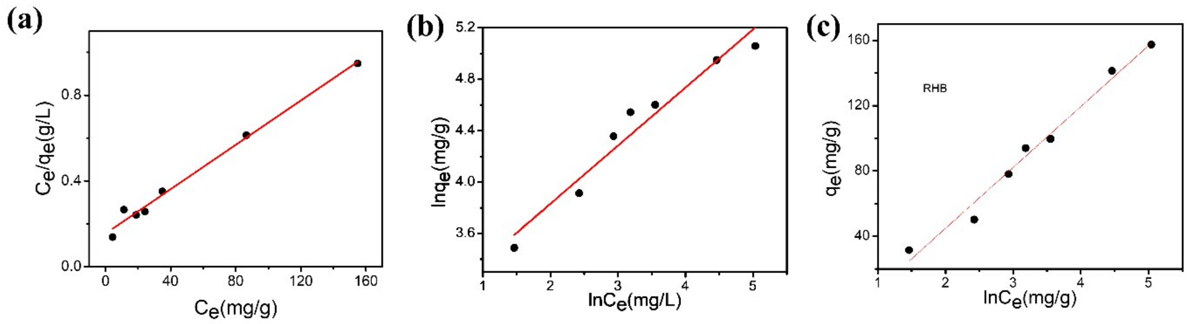


Fig. S20 Plots of the fitting of the RhB adsorption on SCNU-Z4 experimental data with (a) Langmuir isotherm, (b) Freundlich and (c) Themkin isotherm models.

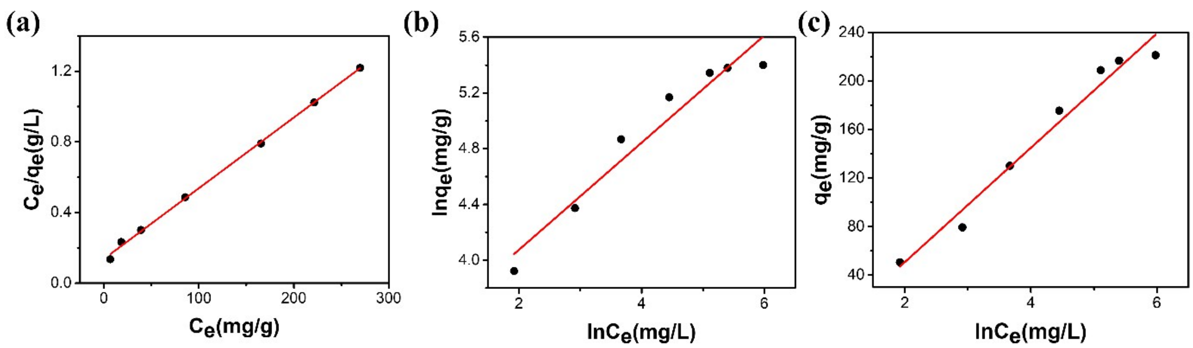


Fig. S21 Plots of the fitting of the AB adsorption on SCNU-Z4 experimental data with (a) Langmuir isotherm, (b) Freundlich and (c) Themkin isotherm models.

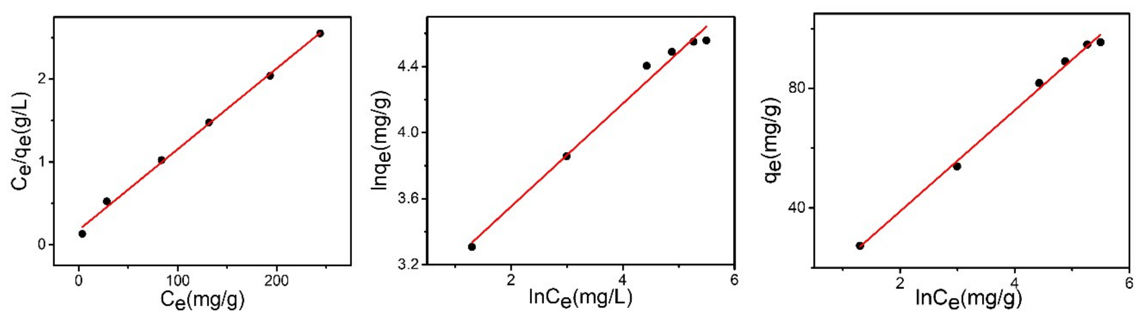


Fig. S22 Plots of the fitting of the MO adsorption on SCNU-Z4 experimental data with (a) Langmuir isotherm, (b) Freundlich and (c) Themkin isotherm models.

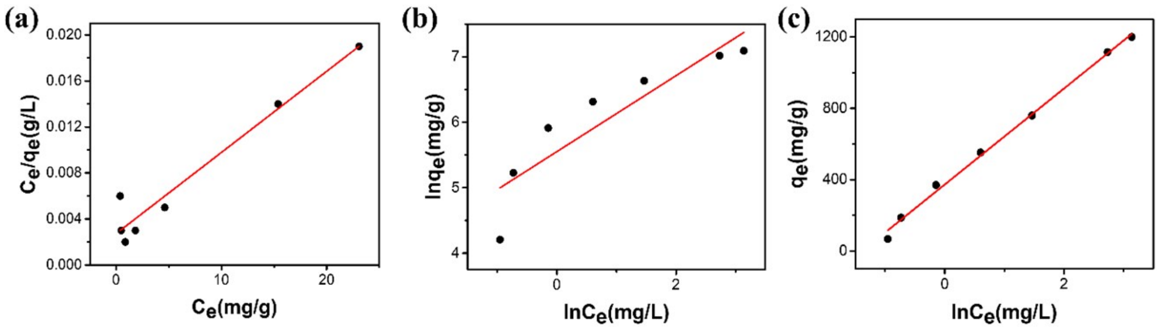


Fig. S23 Plots of the fitting of the CR adsorption on SCNU-Z4 experimental data with (a) Langmuir isotherm, (b) Freundlich and (c) Themkin isotherm models.

Tab. S7 Parameters of the adsorption of different dyes on SCNU-Z4.

Models	Parameters	Dyes				
		MLB	RHB	MO	CR	AB
Langmuir	q_m (mg·g^{-1})	290.70	193.42	102.46	1418.38	250.00
	b (L·mg^{-1})	0.0396	0.0335	0.0543	0.2583	0.0292
	R^2	0.9664	0.9866	0.9961	0.9386	0.9983
Freundlich	n	2.8511	18.6973	3.2086	1.7262	2.6009
	kF (mg g^{-1} (L mg^{-1})$^{1/n}$)	40.24	12.45	18.71	257.81	27.25
	R^2	0.9733	0.9424	0.9818	0.7883	0.9328
Tempkin	A (L g^{-1})	1.25	0.45	1.35	3.38	0.40
	B	43.79	37.29	16.90	269.07	47.15
	R^2	0.9146	0.9791	0.9948	0.9954	0.9680

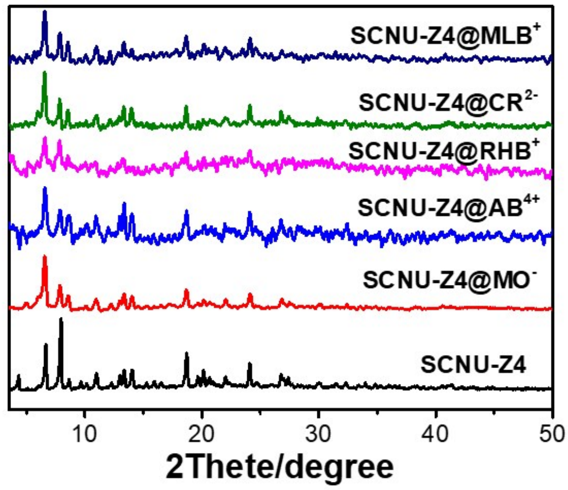
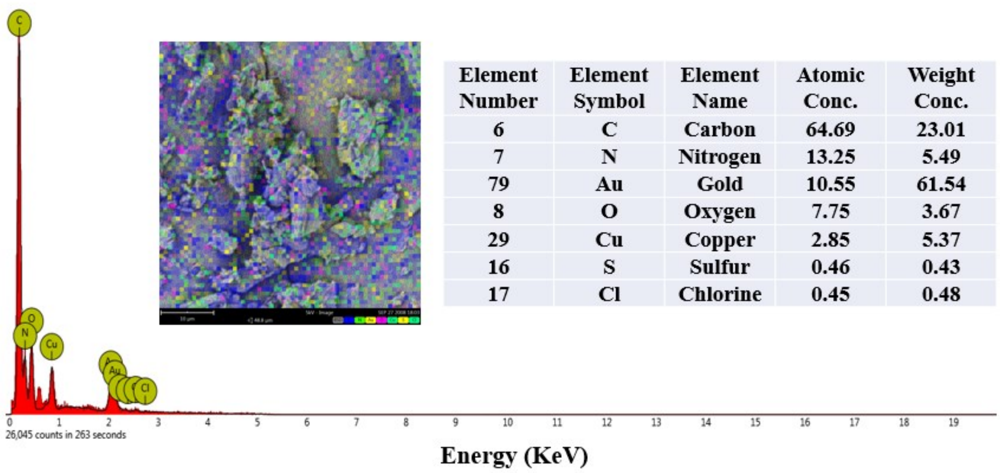
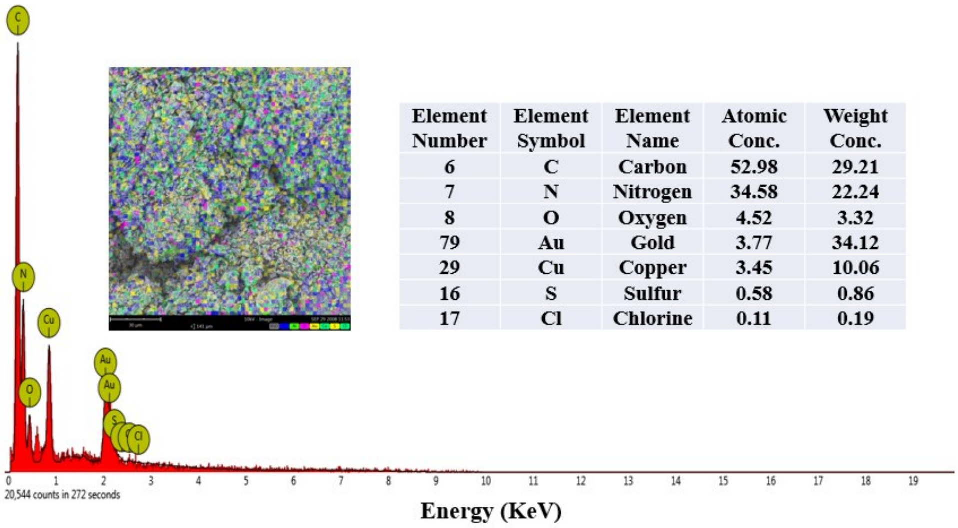


Fig. S24 PXRD of SCNU-Z4 before and after dye adsorption.



Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
6	C	Carbon	64.69	23.01
7	N	Nitrogen	13.25	5.49
79	Au	Gold	10.55	61.54
8	O	Oxygen	7.75	3.67
29	Cu	Copper	2.85	5.37
16	S	Sulfur	0.46	0.43
17	Cl	Chlorine	0.45	0.48

Fig. S25 EDX analysis of CR@SCNU-Z4.



Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
6	C	Carbon	52.98	29.21
7	N	Nitrogen	34.58	22.24
8	O	Oxygen	4.52	3.32
79	Au	Gold	3.77	34.12
29	Cu	Copper	3.45	10.06
16	S	Sulfur	0.58	0.86
17	Cl	Chlorine	0.11	0.19

Fig. S26 EDX analysis of AB@SCNU-Z4.

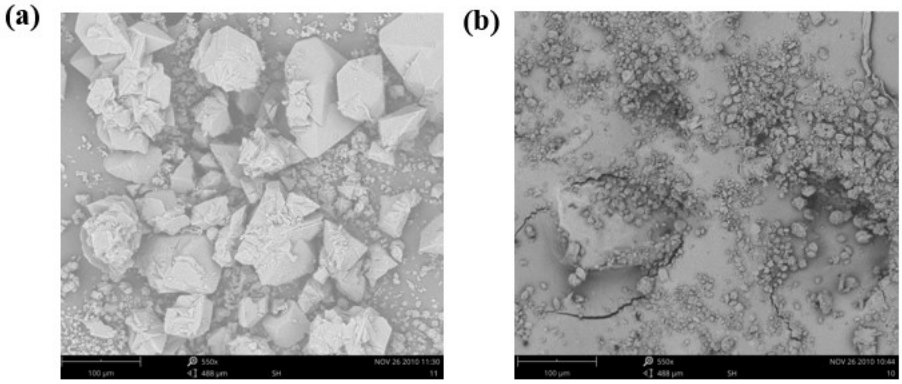


Fig. S27 The SEM of the (a) bigger and (b) smaller particles.

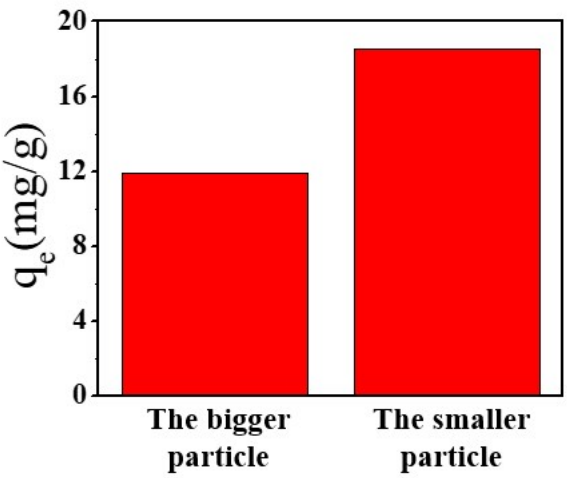


Fig. S28 The adsorption capacities on AB (20 ppm) for the bigger and smaller particles.

Reference

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