Supporting Information

Cu(II) and Zn(II) frameworks constructed by directional tuning of diverse substituted groups on triazine skeleton and supermassive adsorption behavior about iodine and dyes

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Supplementary Index

1. Materials and methods

All other chemicals purchased were of reagent grade or better and used without further purification. The elemental analyses for C, H, and N were carried out on a Perkin Elmer 240C automatic analyzer. The ^{1}H-NMR spectra were measured on Nuclear Magnetic Resonance Spectrometer (Bruker Avance II 400). The chlorine content was analyzed using an HPLC instrument of the LC-6A series (Shimadzu Company, Japan). The N_2 adsorption measurements were conducted using a Autosorb-IQ-XR. Infrared spectra were measured on a Bruker AXS TENSOR-27 FT-IR spectrometer with pressed KBr pellets in the range of 4000-400 cm^{-1}. UV-vis absorption spectra were recorded with a JASCO V570 UV/VIS/NIR spectrophotometer (200-2500 nm, in the form of the solid sample) and with a UV-1000 spectrometer (200-800 nm, in the form of the liquid sample). Centrifugal precipitation is operated with a Netherlands PGSTAT302N centrifugal machine. X-ray powder diffraction (PXRD) patterns were obtained on a Bruker Advance-D8 equipped with Cu-Kα radiation, in the range of $5° < 2\theta < 60°$, with a step size of 0.02° (2θ) and a count time of 2s per step. Thermogravimetric analyses (TG) were performed under a nitrogen atmosphere with a heating rate of 10°C/min on a Perkin Elmer Diamond TG/DTA. The fluorescence spectra were determined with a FP-4600 spectrofluorimeter (JASCO, Tokyo, Japan) (200-800 nm).

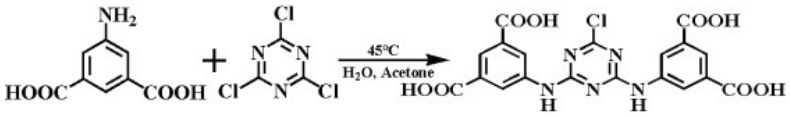
2. X-ray Crystallographic Determination

Suitable single crystals of the complexes were mounted on glass fibers for X-ray measurement. Reflection data were collected at room temperature on a Bruker AXS SMART APEX II CCD diffractometer with graphite monochromatized Mo-Kα radiation ($\lambda = 0.71073$ Å)[1]. All the measure independent reflections ($I > 2\sigma(I)$) were used in the structural analyses, and semi-empirical absorption corrections were applied by the SADABS program[2-3]. Crystal structures were solved by the direct method using OLEX 2. For complexes **1** and **2**, all non-hydrogen atoms were refined anisotropically. The DFIX, SADI, FLAT, SIMU and other commands were used to help to restrain the bond length in a target value with an estimated standard deviation. The "SHEL 999 0.84" and OMIT commands were also added for making crystallographic data more reasonable. Among, in the structure of the complex **1**, C6, C7, N3 and Cl1 were disordered. The PLATON/SQUEEZE method was applied to delete the contributions from solvent molecules and counter cations[4-5]. The solvent-free structure of **1** and **2** were obtained by the SQUEEZE routine. Based on the squeeze electrons, the guest molecule consisted of 10 DMF molecules and 30 H_2O molecules for complex **1** and four dimethylamine cations for complex **2**. Crystal data of complexes **1** and **2** were both listed in Table S6 and the characteristic bond lengths were summarized in Table S7. For the complex **1**, there was a B level alert: "D-H Bond Without Acceptor O1--H1C". This was due to that the lattice solvent molecules were squeezed out which should form H-bond with H1C potentially.

3. Synthesis

3.1 Synthesis of 5, 5'-((6-chloro-1, 3, 5-triazine-2, 4-diyl) bis (azanediyl)) diisophthalic acid (H_4TBDA)

Firstly, 5-aminoisophthalic acid 9.13 g (50.0 mmol), 100 mL deionized water, and 20 mL NaOH (5 M) were put into a 250 mL flask. After stirring, 4.60 g (55.0 mmol of $NaHCO_3$ was added. After cooling to below 10 ℃, 4.7 g (25.0 mmol) of cyanuric chloride powder was dissolved in 25 mL acetone, and dropwise again added to the above-cooled solution. Then stirred at room temperature, water bath at 45 ℃ and stirred for 4 h, stirred at normal temperature for 18 h, rotary evaporated, added 150 mL EtOH, filtered, washed solid part several times with water and ethanol, and the last dried. The white powder was obtained (Scheme S1). Molecular Formula: $C_{19}H_8N_5O_8H_4Cl$ (473.78), Elemental analysis (%): Calcd. for (%) C, 47.57; H, 2.45; N, 15.38; Found (%) C, 47.92; H, 2.40; N, 15.30. ^{1}H-NMR (400 MHZ, DMSO-d6): δ 13.13 (s, 2H), 10.71 (s, 1H), 8.41 (s, 2H), 8.18 (s, 1H) (Figure S1). IR data (KBr, cm^{-1}): 3406, 1628, 1570, 1364, 1252, 1108, 1077, 1023, 904, 787, 721, 649, 610, 511 (Figure S4).



Scheme S1 Synthesis of H_4TBDA.

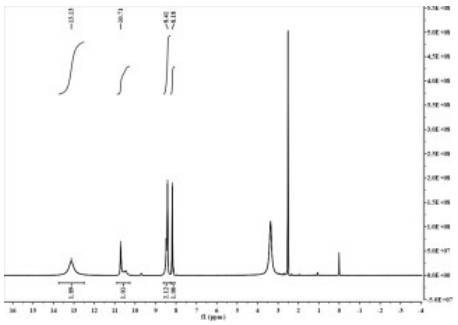


Figure. S1 The ^{1}H-NMR spectrum of H_4TBDA.

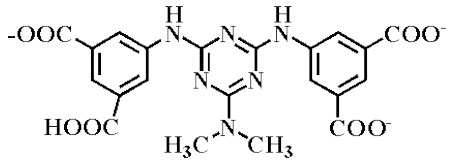


Figure S2 The molecular structure of HTBDA-N.

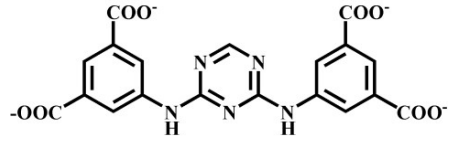


Figure S3 The molecular structure of TBDA-H.

4. IR spectra

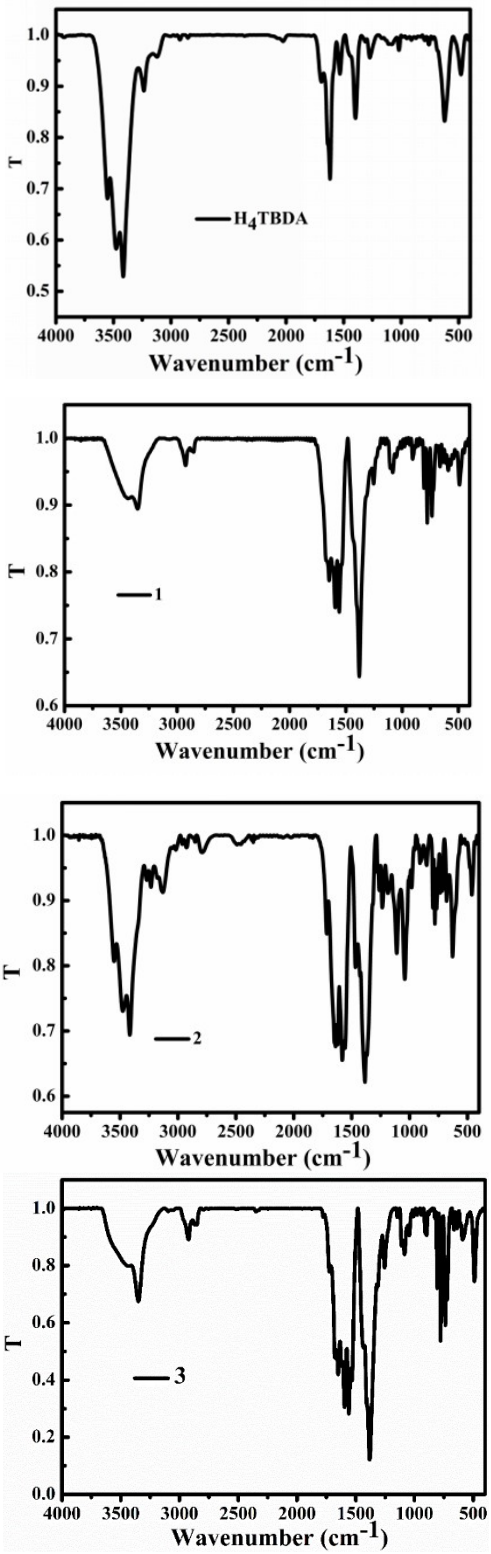


Figure S4 The IR spectra of H_4TBDA ligand and complexes **1**-**3**.

Table S1 The attribution of IR (cm^{-1}) for ligand and complexes **1**-**3**.

Complexes	H_4TBDA	**1**	**2**	**3**
ν_{O-H}	3406	3443	3410	3451
ν_{C-H}	-	2926	2926	2929
	-	2863	2787	2864
$\nu_{as(COO)-}$	1623	1600	1612	1597
$\nu_{s(COO)-}$	1543	1370	1475	1385
ν_{C-N}	1108	1096	1100	1110
ν_{C-O}	1023	1037	1039	1044
ν_{C-Cl}	570	567	-	-

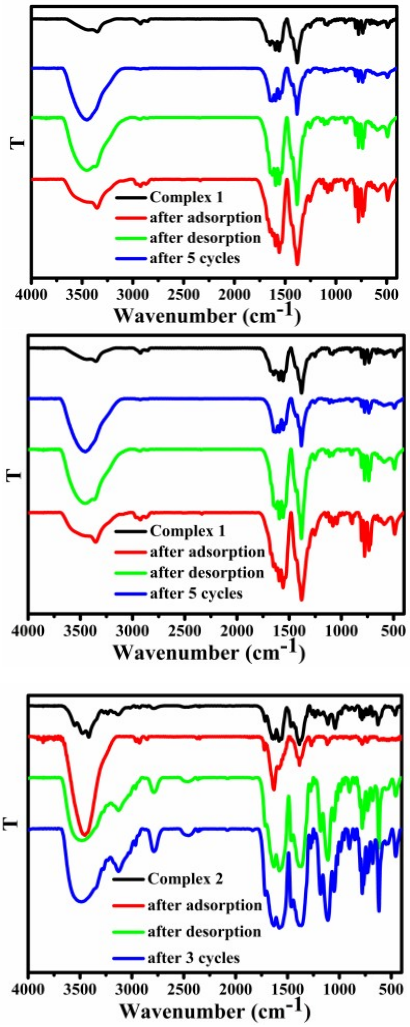


Figure S5 The IR spectra of before adsorption, after adsorption, after desorption, and after cycle experiments (a) of the dyes of complex **1**; (b) of I_2 in the water of complex **1**; (c) of I_2 in cyclohexane solution **o**f complex **2**.

5. UV-Vis spectra

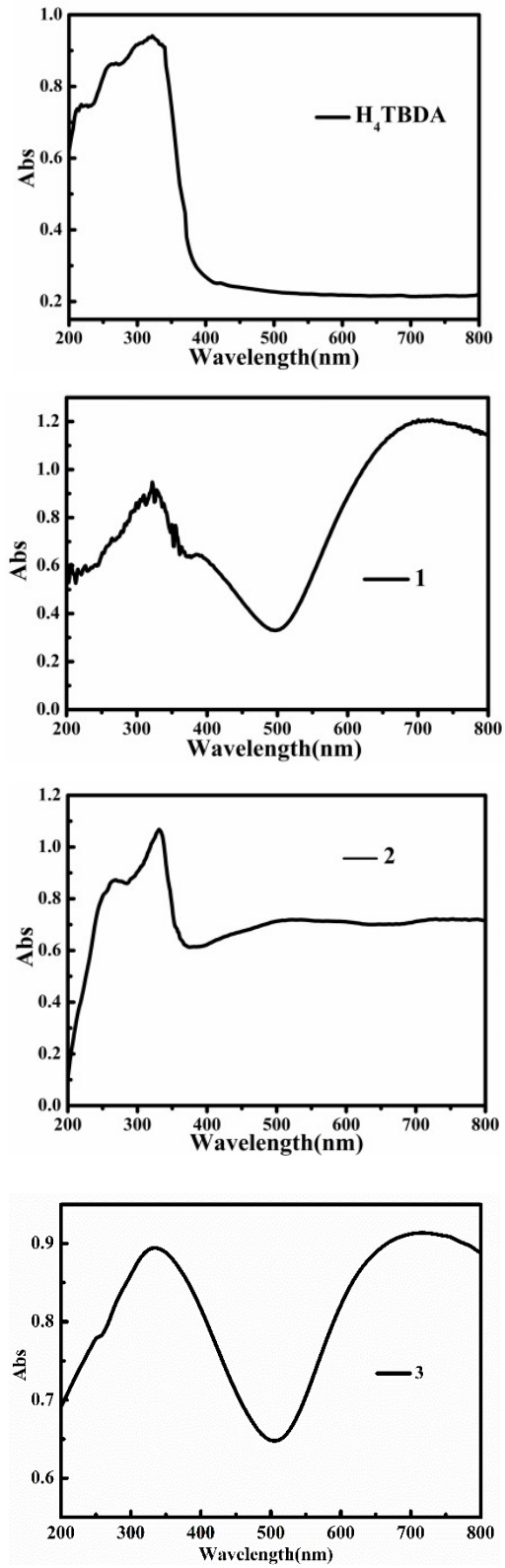


Figure S6 The UV spectra of H_4TBDA ligand and complexes **1**-**3**.

Table S2 UV-vis spectra identifications of complexes **1-3**.

	LLCT		LMCT	d-d*
	π–π*	n–π*		
H_4TBDA	218, 256	320	-	-
1	323	353	386	701
2	254	266	331	-
3	252	281	333	718

6. TG curves

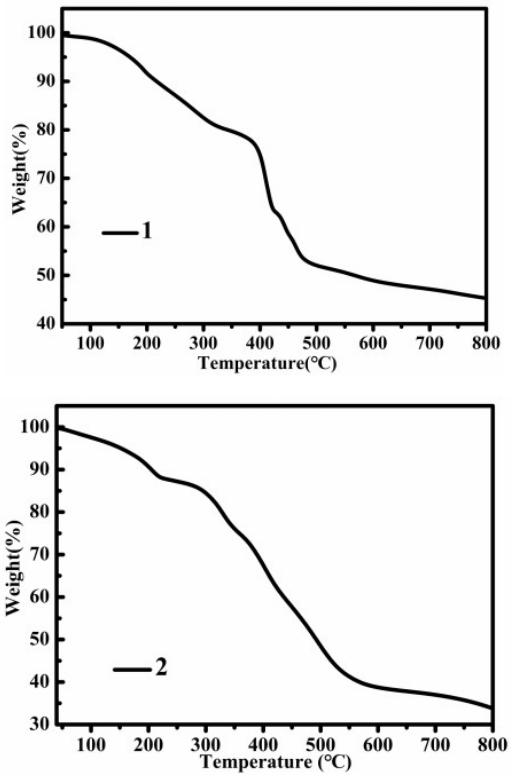


Figure S7 The TG curves of complexes **1**-**3**.

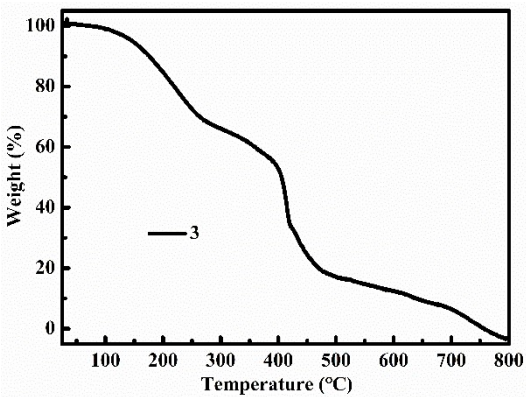
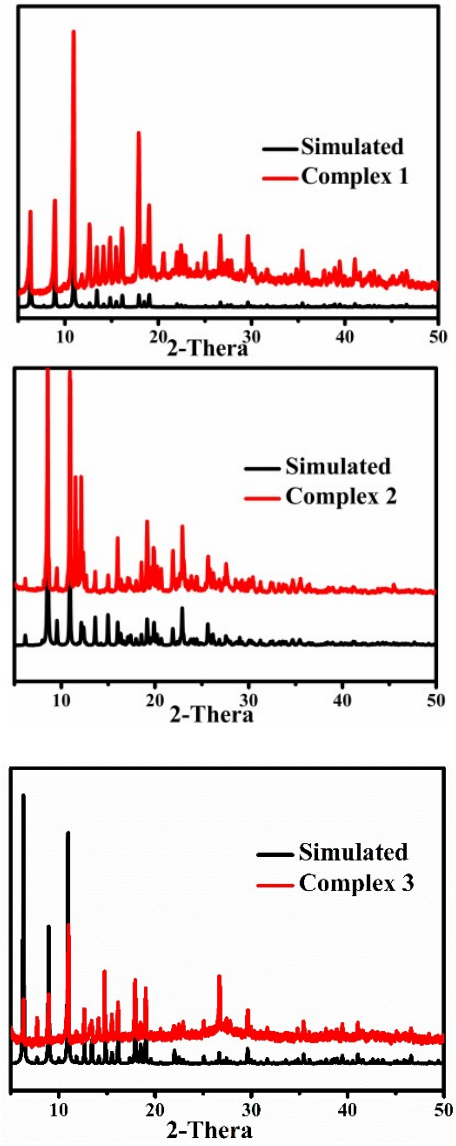


Table S3 TG analysis of complexes **1-2**.

Complexes / Weight loss range	**1**	**2**	**3**
I	96-210 ℃ (ten free H_2O molecules)	146-180 ℃ (four free dimethylamine cations)	122-275 ℃ (two free H_2O molecules and three -COOH)
II	210-350 ℃ (ten free DMF molecules)	210-320 ℃ (two sulfate radical cations)	385-410 ℃ (one -COOH and two -NH)
III	350-400 ℃ (a coordinated H_2O molecule)	420-800 ℃ (the collapse of the skeleton)	450-800 ℃ (the collapse of the skeleton)
IV	388-423 ℃ (a carboxyl and Cl)		
V	480-800 ℃ (the collapse of the skeleton)		

7. PXRD patterns



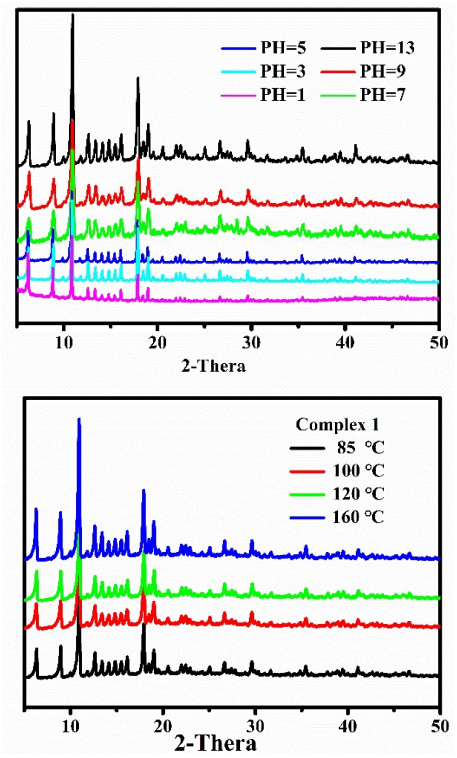
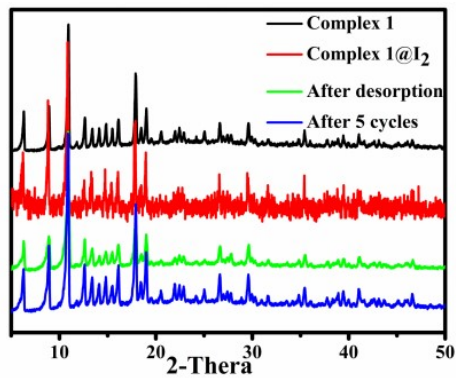


Figure S8 The PXRD spectra of complexes **1**-**3**, and in the different PH systems.



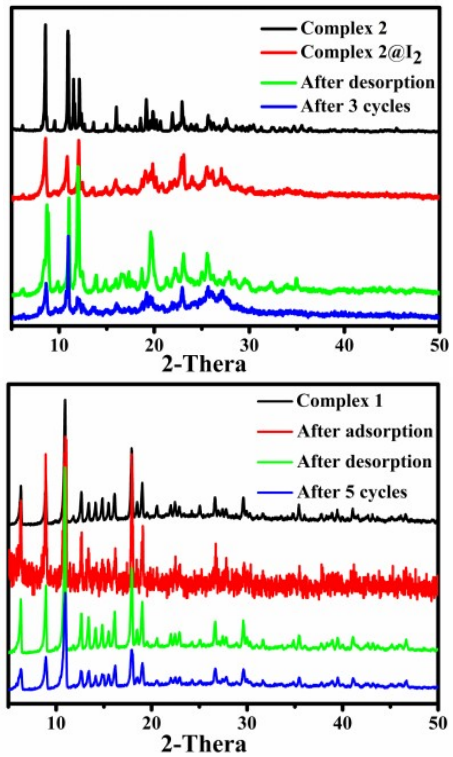


Figure S9 The PXRD spectra of before and after adsorption (a) of I_2 in the water of complex **1**; (b) of I_2 in cyclohexane solution of complex **2**. (c) of the dyes of complex **1**.

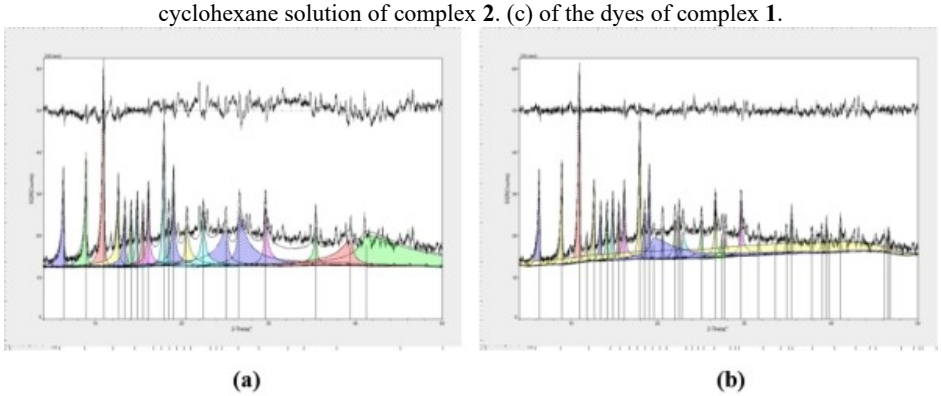


Figure S10 The crystallinity rate: (a) complex **1**; (b) complex **2**.

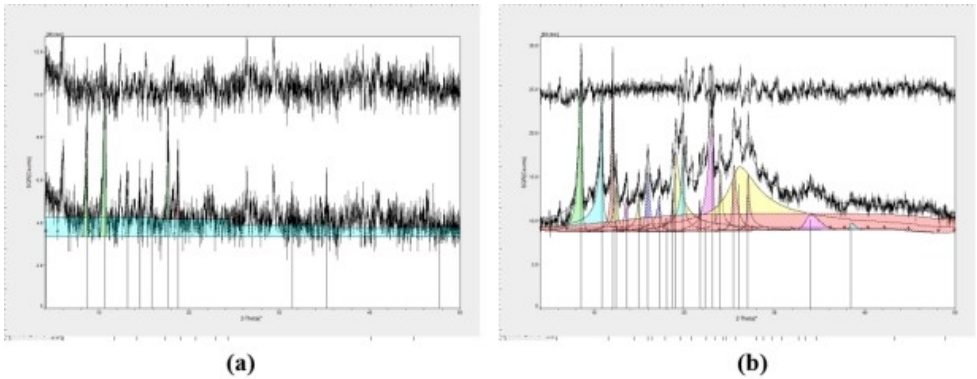


Figure S11 The crystallinity rate after adsorption: (a) complex **1**; (b) complex **2**.

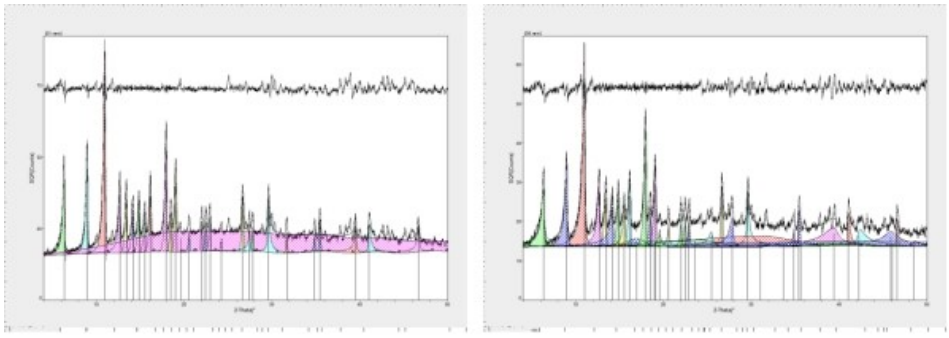


Figure S12 The crystallinity rate after desorption: (a) complex **1**; (b) complex **2**.

8. Photoluminescence Property

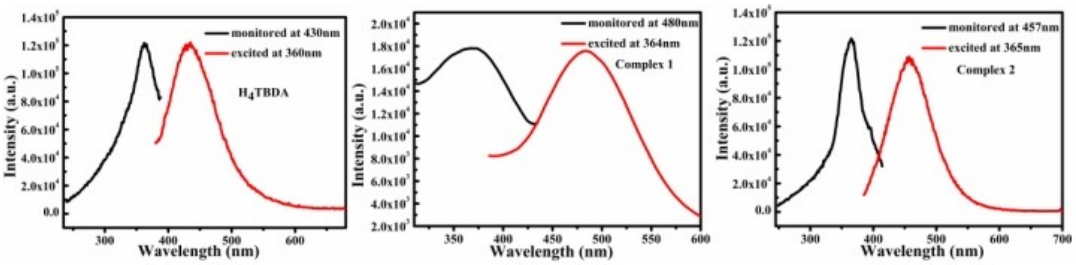


Figure S13 Fluorescent behavior: (a) ligand H_4TBDA (b) complex **1**; (c) complex **2.**

9. Adsorption Experiments

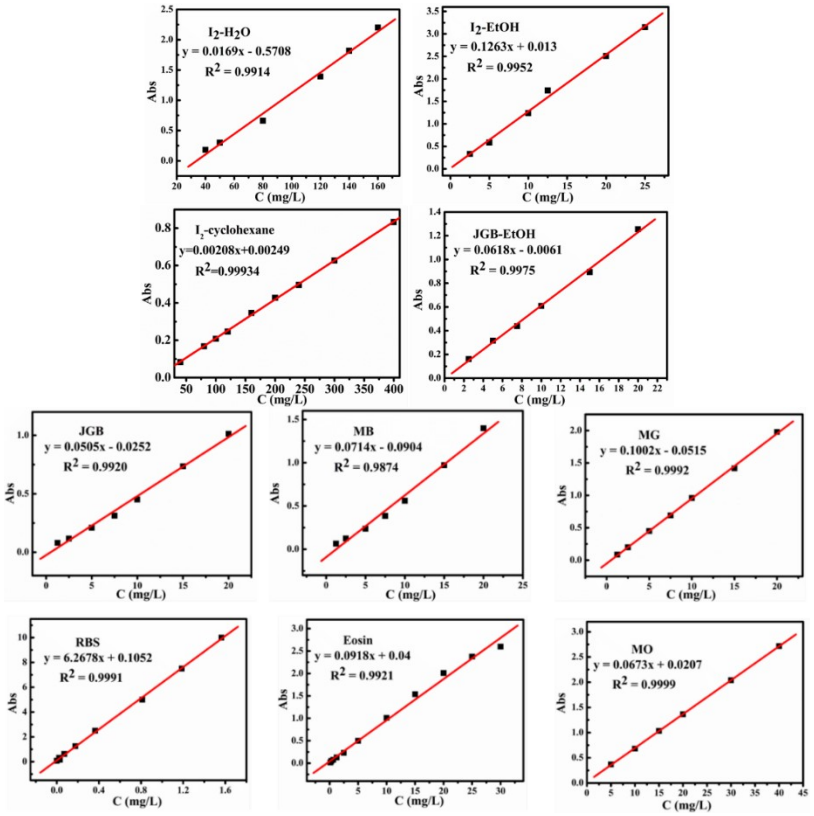


Figure S14 The standard curve used in the experiment.

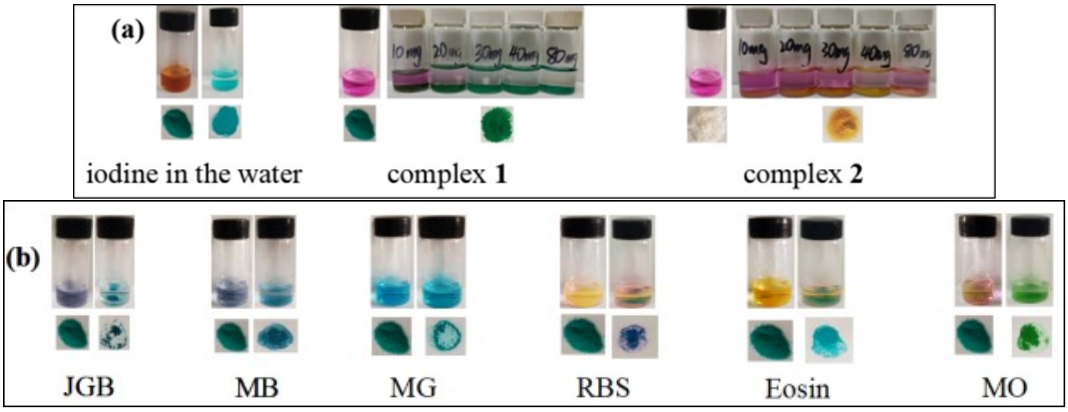


Figure S15 The color changes of solution and solid- before (left) and after (right) the adsorption (a) from left to right: iodine adsorption in the water, iodine adsorption in the cyclohexane of complex **1** and iodine adsorption in the cyclohexane of complex **2** (b) dyes adsorption of complex **1**.

Table S4 The Relevant data of complex **1** in the iodine adsorption.

Dose (mg)	Adsorption equilibrium time (h)	Adsorption rate (%)	Equilibrium absorption capacity (mg/g)
5	26	93.6	163.96
10	34	92.8	82.83
15	31	92.3	55.47

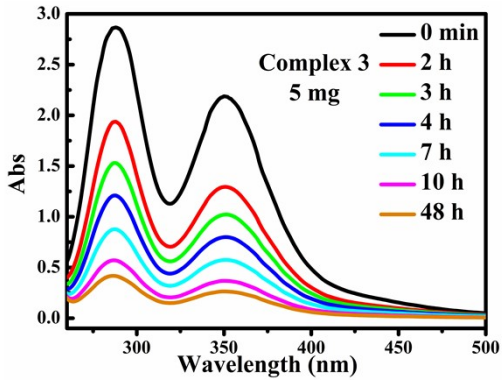


Figure S16 The adsorption rates of 5mg of complex **3**.

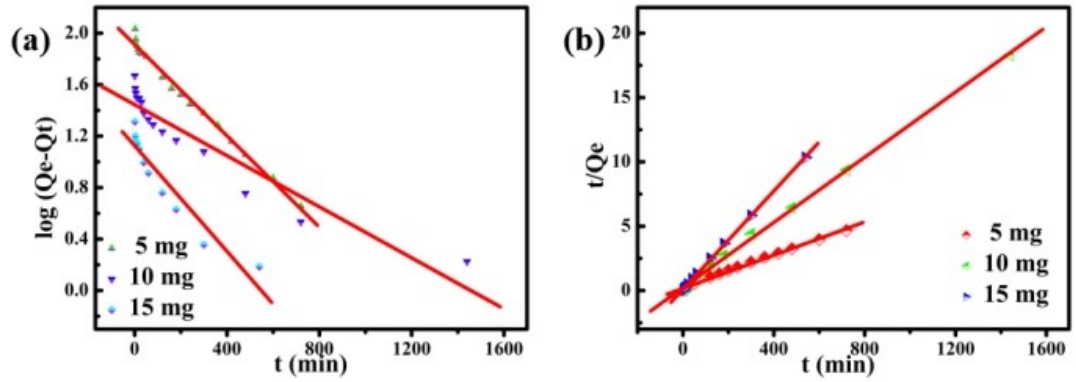


Figure S17 (a) Quasi-first-order kinetic curve; (b) quasi-second-order kinetic curve when different doses complex **1** were added.

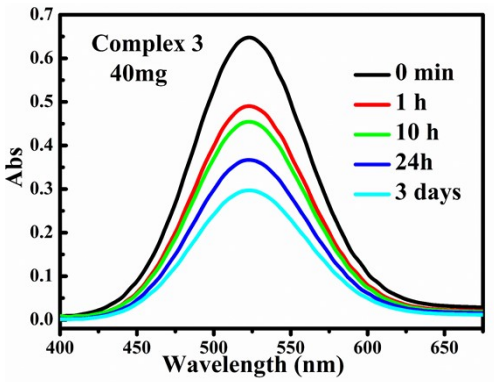


Figure S18 The adsorption rate of iodine in the cyclohexane when added 40mg of complex **3**.

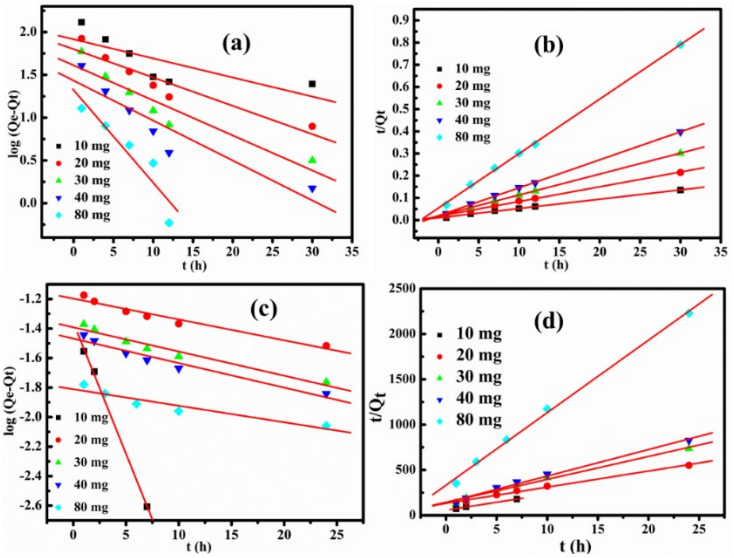


Figure S19 Complex 1: (a) Quasi-first-order kinetic curve; (b) quasi-second-order kinetic curve; Complex 2: (c) Quasi-first-order kinetic curve; (d) quasi-second-order kinetic curve

Table S5 Compared with the amount of iodine adsorbed by other reported materials

Adsorbents	Adsorption capacity (mg/g)	Refs
P-DPDA	289.5	49
Th-UiO-66	292.4	50
TPFM	292.3	51
TALPOP	400	52
H-C-CTPs	293	53
Complex 1	**548.2**	**this work**
Complex 2	**529.0**	

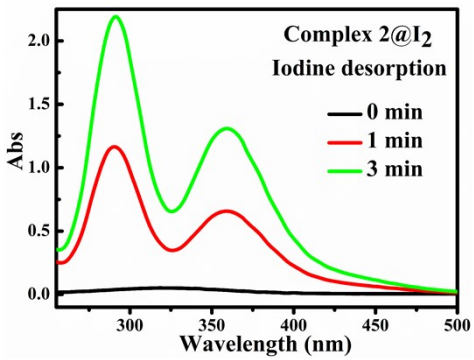


Figure S20 Desorption curve of the complex **2**.

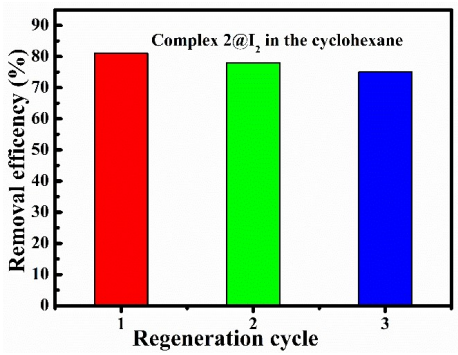


Figure S21 Complex **2**: cyclic experiment of iodine adsorption in the cyclohexane solution.

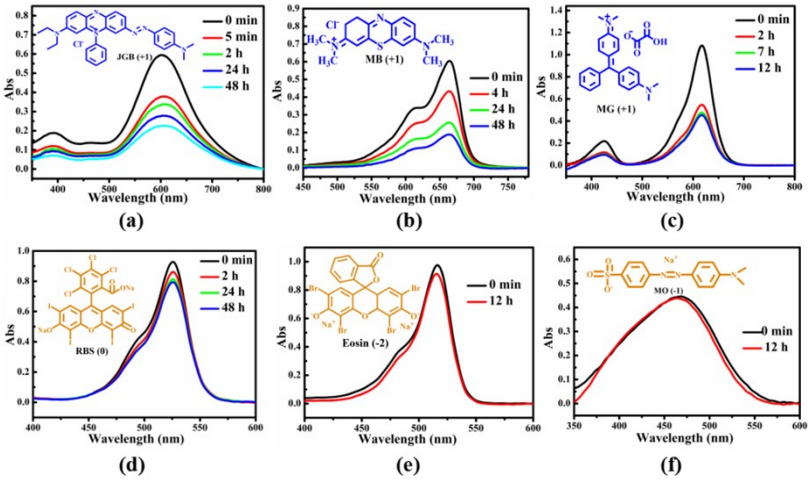


Figure S22 The removal rate of (a) JGB (b) MB (c) MG (d) RBS (d) RBS (e) Eosin (e) MO of 5mg complex **3**.

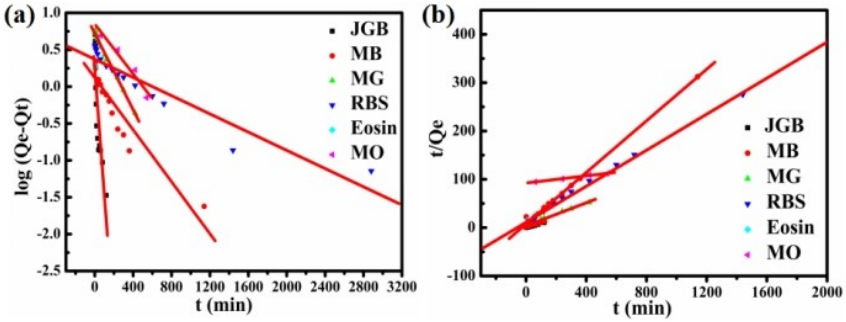


Figure S23 (a) Quasi-first-order kinetic curve; (b) quasi-second-order kinetic curve when 5mg complex 1 was added in different dyes adsorption.

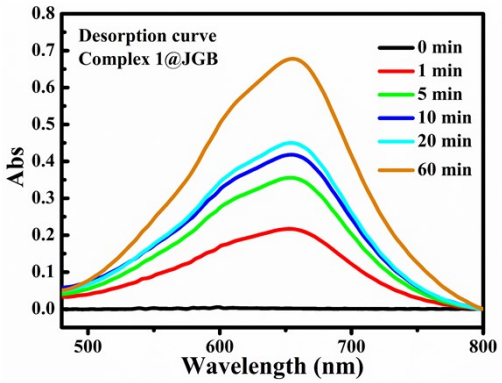


Figure S24 Desorption curve of the complex **1** after adsorption.

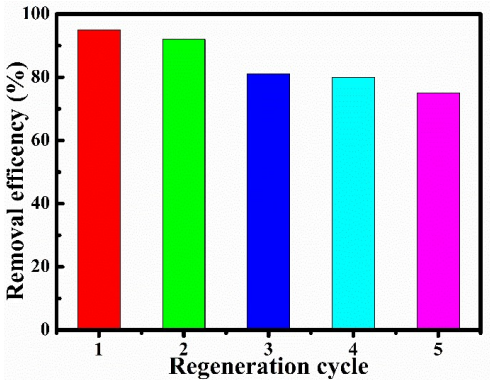


Figure S25 Complex **1**: the cycle experiments of the JGB adsorption.

10. SEM

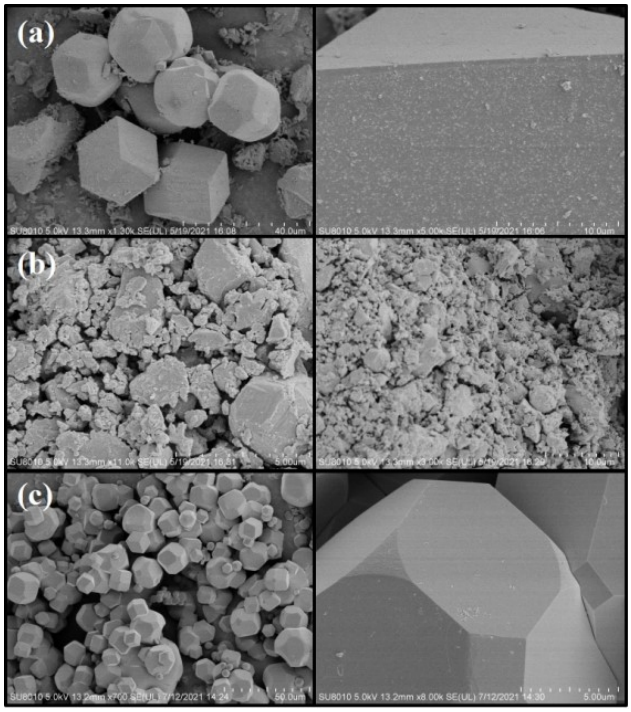


Figure S26 SEM images of complex **1**: (a) Crystal morphology (b) after iodine absorption in the water (c) after iodine desorption.

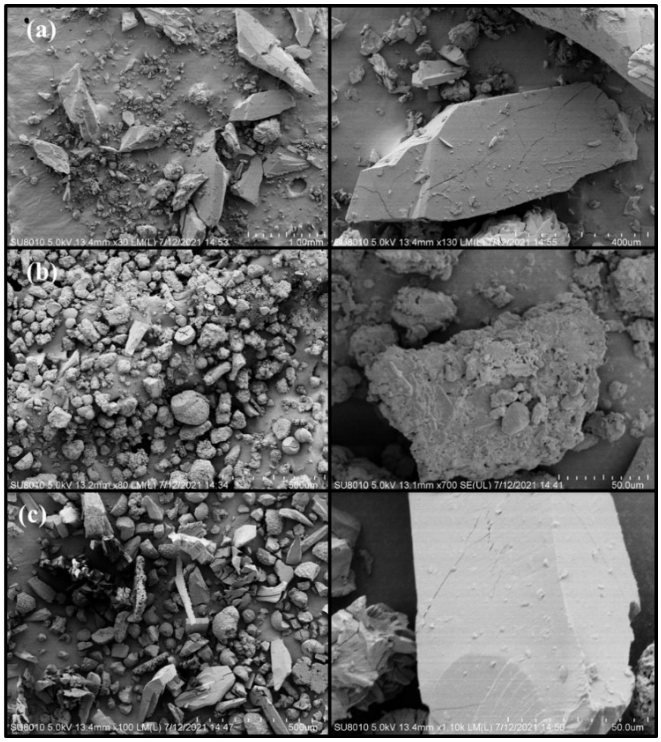


Figure S27 SEM images of complex **2** (a) Crystal morphology (b) after iodine absorption in the cyclohexane and (c) after iodine desorption.

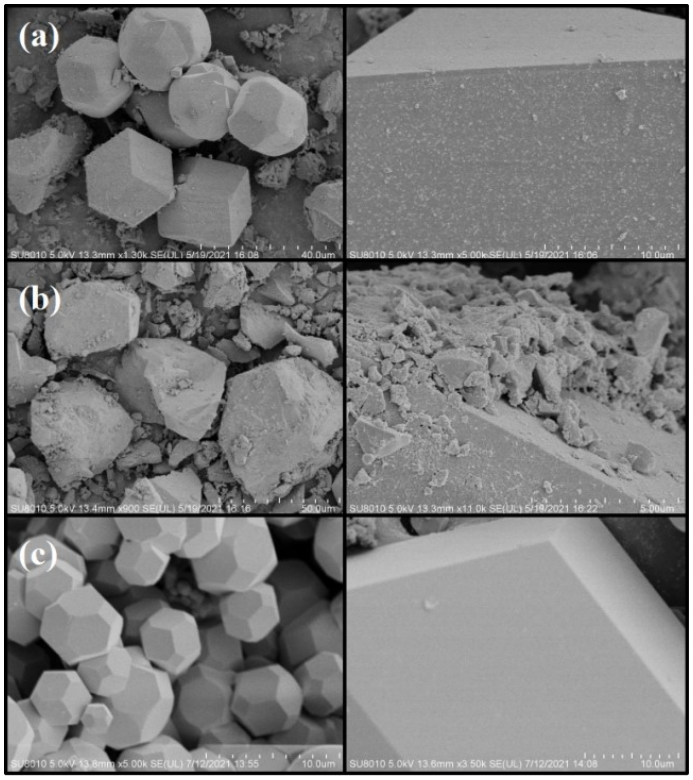


Figure S28 SEM images of complex **1**: (a) Crystal morphology (b) after dyes absorption (c) after dyes desorption.

11. Crystal data

Table S6 Crystallographic data for the complexes **1** and **2***.

Coordination polymers	**1**	**2**
Chemical formula	$C_{49}H_{140}N_{15}O_{49}ClCu_2$	$C_{48}H_{52}N_{16}O_{24}S_2Zn_3$
M ($g \cdot mol^{-1}$)	1886.3	1495.6
Crystal system	cubic	monoclinic
Space group	$Im\bar{3}m$	*C2/c*
a (*Å*)	27.9557(9)	30.492(2)
b (*Å*)	27.9557(9)	11.9895(9)
c (*Å*)	27.9557(9)	21.9612(17)
α (°)	90	90
β (°)	90	109.883(1)
γ (°)	90	90
V ($Å^3$)	21848(12)	7550.1(10)
Z	24	4
D_c ($g \cdot cm^{-3}$)	1.122	1.476
F(000)	7370.2	3479.6
M(Mo Ka) (mm^{-1})	1.280	1.088
θ (°)	1.03-25.01	1.84-28.23
Reflections collected	70839	23565
Independent reflections (I>2σ(*I*))	1886	9171
Parameters	131	407
Δ(*ρ*) ($e Å^{-3}$)	-9.19	-0.74
Goodness of fit on F^2	1.080	0.962
R^{α}	0.0957 (0.1072)[b]	0.0428 (0.0837)b
wR_2^{α}	0.2372 (0.2517)[b]	0.0910 (0.1065)b

*[a]$R=\Sigma||Fo|-|Fc||/\Sigma|Fo|$, $wR_2=[\Sigma w(Fo^2-Fc^2)^2/\Sigma w(Fo^2)^2]^{1/2}$; [*Fo*>4σ(*Fo*)]. [b]Based on all data.

Table S7 Selected bond lengths (Å) for complexes **1** and **2***.

Complex **1**			
Cu(1)-O(3)	1.987(5)	Cu(2)-O(2)$^{\#2}$	1.939(5)
Cu(1)-N(2)$^{\#4}$	2.184(12)	Cu(2)-O(1)	2.161(14)
Complex **2**			
Zn(1)-O(5)$^{\#1}$	1.953(19)	Zn(1)-O(1)$^{\#2}$	1.970(2)
Zn(2)-O(9)	1.947(18)	Zn(2)-O(8)	1.945(19)
Zn(2)-O(12)$^{\#4}$	1.975(18)	Zn(2)-N(2)$^{\#5}$	2.062(2)

*Symmetry codes: Complex **1**: #2, +x, -y, +z; #4, 1/2-x, 1/2-z, 1/2-y; Complex **2**: #1, 2-x, +y, 3/2-z; #2, 3/2-x, 3/2-y, 1-z; #4, 3/2-x, 1/2-y, 2-z; #5, 3/2-x, -1/2+y, 3/2-z.

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