A Multifunctional MOFs as Recyclable Catalyst for Fixation of CO_2 with Aziridines or Epoxides and Luminescent Probe of Cr(VI)

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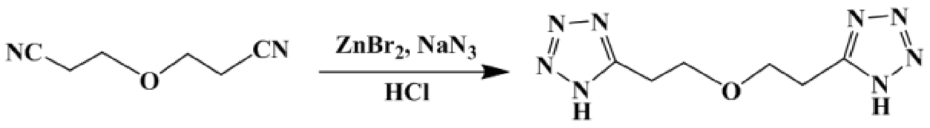
Experimental Section

Preparation of H_2btz ligand. The 1,5-bis(5-tetrazolo)-3-oxapentane (H_2btz in **Scheme S1**) ligand was in advance synthesized according to literature.[1] The mixture of 2.48 g 2-cyanoethyl ether (20 mmol) and 9 g zinc bromide (40 mmol) were added in 30 mL water with stirring constantly. Then 3 g sodium azide (46 mmol) were added in the solution and was heated to reflux and stirred 12h. The mixture was cooled and 15 mL of 4 mol/L HCl was added. The solution was stirred for 2 h without heating. The solids were then filtered off and recrystallized from acetonitrile to give 1.26 g (30%) white crystalline solid.

Caution! Owing to the potentially explosive nature of NaN_3 compounds, only a small amount of material should be used and handled with care!



Scheme S1 The H_2btz ligand was generated by 2-cyanoethyl ether.

Preparation of the compound 1. The compound **1** was synthesized according to the literature.[2] $Zn(NO_3)_2 \cdot 6H_2O$ (0.0297 g, 0.2 mmol) was dissolved in 3 mL methanol to form a solution. A solution of H_2btz (0.0105 g, 0.10 mmol) in 3 mL N,N' -dimethylacetamide (DMF) was added to the above solution. An aqueous solution of HCl (0.1 mL, 1 M) was added into the mixture while stirring, the mixture was allowed to stand at room temperature. After several days, pure colorless cubic crystals of **1** formed.

The Powder X-Ray Diffraction analysis

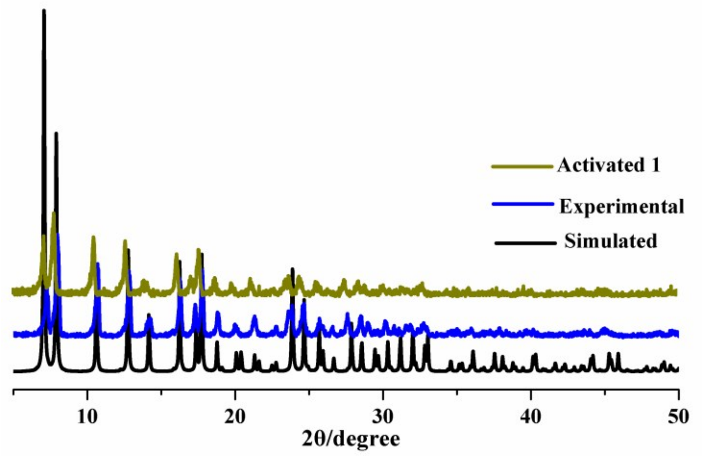


Fig. S1 Powder XRD patterns of the compound **1** and activated **1**.

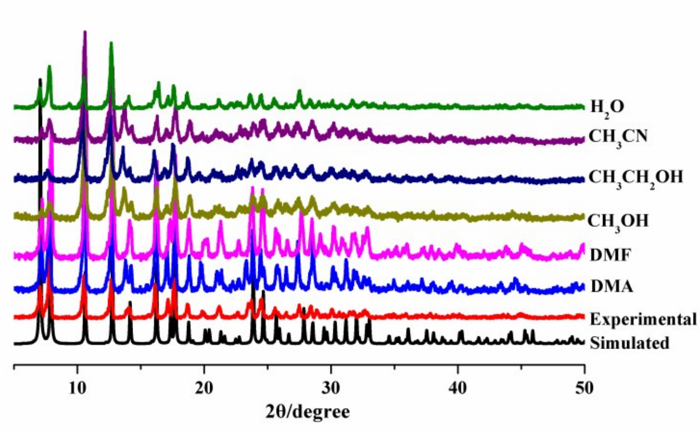


Fig. S2 The powder XRD diffraction of the compound **1** after immersing in various organic solvents.

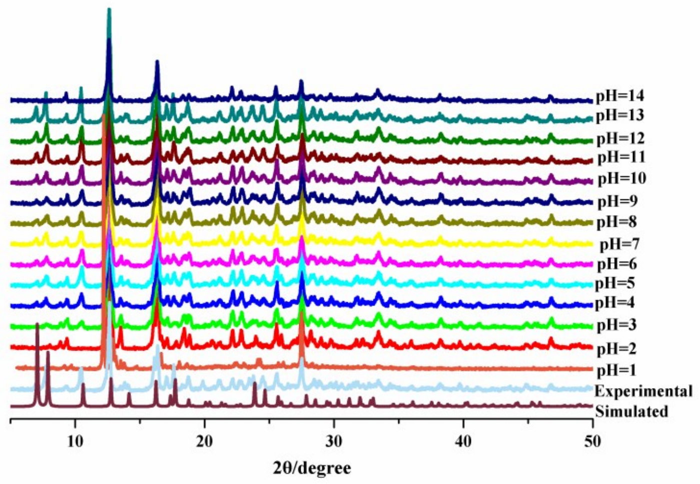
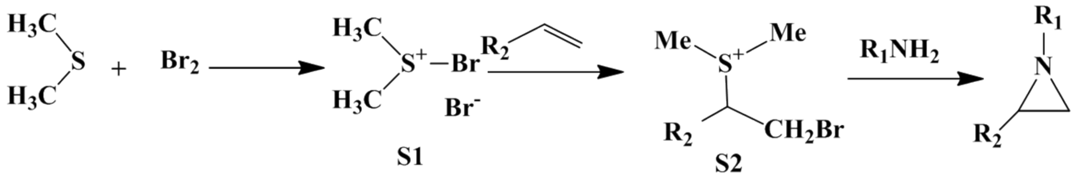


Fig. S3 The powder XRD diffraction of the compound **1** after immersing in various solvents with pH values from 1.0 to 14.0.

Catalyze cycloaddition of CO_2 with aziridines.

Preparation of aziridines. [3]



Scheme S2 Preparation of aziridines.

Typical procedure for the synthesis of aziridines was described as following (**Scheme S2**): Firstly, bromine (0.2 mol, 32.0 g) in dry CH_2Cl_2 (40 mL) was slowly dropped over 30 min to 40 mL CH_2Cl_2 solution of dimethyl sulfide (0.2 mol, 12.4 g) in ice-salt baths. Light orange crystals of bromodimethyl sulfonium bromide gradually generated during the process, and the orange crystals **S1** were completely obtained and collected by filtration. Yield: 80%.

Secondly, olefin (160 mmol) was slowly dropped to 160 mL CH_3CN solution of **S1** (160 mmol, 35.56 g) in ice-salt baths. The solution was stirred for 2h after the addition of olefin was completed. The white solid **S2** gradually generated during the process. The crystals **S2** was collected by filtration, dried under vacuum. Yield: 30-38.6 %.

Thirdly, a solution of amine (20-50 mmol) was slowly added into a stirred solution of compound **S2** (10 mmol) in 20 mL water at r.t., and the resulting mixture was stirred overnight. Then the mixture was slowly dropped into 20 mL of saturated brine, extracted with diethyl ether (3×20 mL), dried with anhydrous Na_2SO_4 overnight and the solvent evaporated under reduced pressure. Aziridines were obtained by distillation under reduced pressure. Yield: 85-100 %.

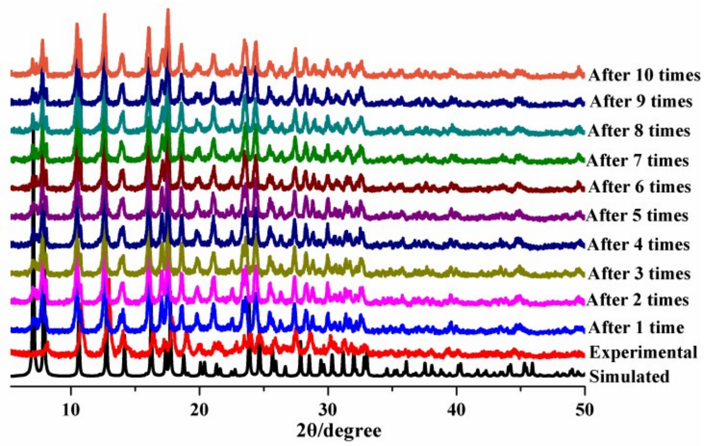


Fig. S4 The PXRD patterns of **1** after ten cyclic cycloaddition reaction of 1-ethyl-2-phenylaziridine and CO_2.

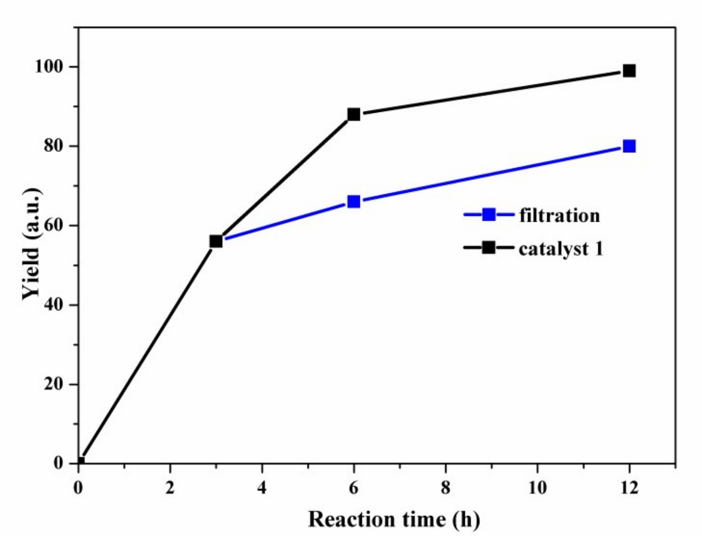


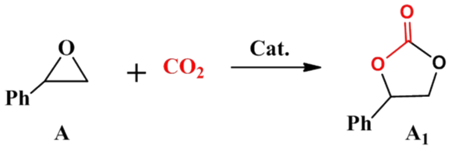
Fig. S5 Catalyst filtration test experiment for the cycloaddition of 1-ethyl-2-phenylaziridine and CO_2.

Sample	Zn (ppm) (after the first time)	Zn (ppm) (after the tenth time)
1	7.628	8.630

Table S1 The ICP results of **1** after cyclic cycloaddition reaction of 1-ethyl-2-phenylaziridine and CO_2.

Catalyze cycloaddition of CO_2 with epoxides.

Table S2. Cycloaddition reaction of CO_2 with phenylethylene oxide under various conditions.$^{(a)}$



Entry	Catalyst 1(mg)	TBAB(mg)	T(°C)	Yield$^{(b)}$ [%]
1	40	32.4	30	39
2	40	32.4	40	69
3	40	32.4	50	90
4	40	32.4	60	94
5	40	32.4	70	>99
6	40	32.4	80	>99
7	40	32.4	90	98
8	40	32.4	100	97
9	0	32.4	70	56
10	0	32.4	80	69
11	40	0	70	0
12	40	16.2	70	84
13	40	64.8	70	>99
14	20	32.4	70	95
15$^{(c)}$	0	32.4	70	82
16$^{(d)}$	0	32.4	70	50
17$^{(e)}$	0	32.4	70	78
18$^{(f)}$	0	32.4	70	45

$^{(a)}$Reaction conditions: Phenylethylene Oxide (240.0 mg, 2.0 mmol), solvent-free, TBAB, CO_2 (0.1 MPa), 12 h, 40 mg catalyst **1** (loading based on metal center Zn, about 5.6 mol%); $^{(b)}$Total yield of $\mathbf{A_1}$ determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard; $^{(c)}$TBAB (32.4 mg, 0.1 mmol) and $Zn(OAc)_2$ (24.6 mg, 0.112 mmol); $^{(d)}$TBAB (32.4 mg, 0.1 mmol) and $Zn(NO_3)_2$ (33.3 mg, 0.112 mmol); $^{(e)}$TBAB (32.4 mg, 0.1 mmol) and $ZnSO_4$ (32.2 mg, 0.112 mmol); $^{(f)}$TBAB (32.4 mg, 0.1 mmol) and $ZnCl_2$ (15.3 mg, 0.112 mmol).

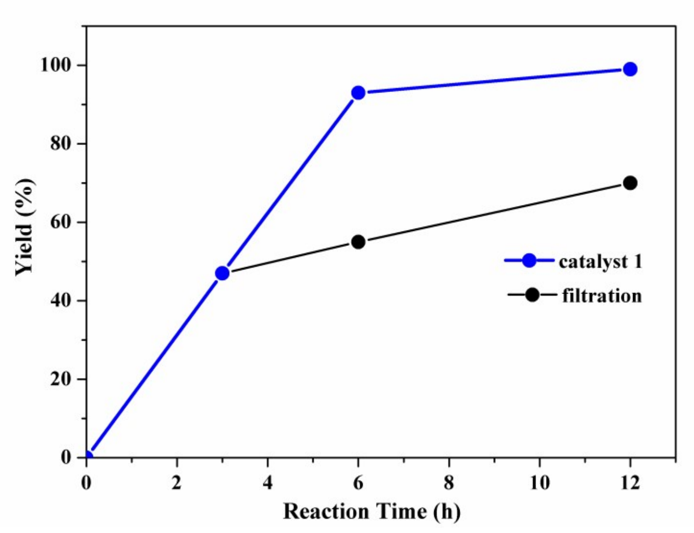


Fig. S6 Catalyst filtration test experiment for the cycloaddition of phenylethylene epoxide and CO_2.

Sample	Zn (ppm) (after the first time)	Zn (ppm) (after the tenth time)
1	7.780	10.55

Table S3 The ICP results of **1** after cyclic cycloaddition reaction of phenylethylene epoxide and CO_2.

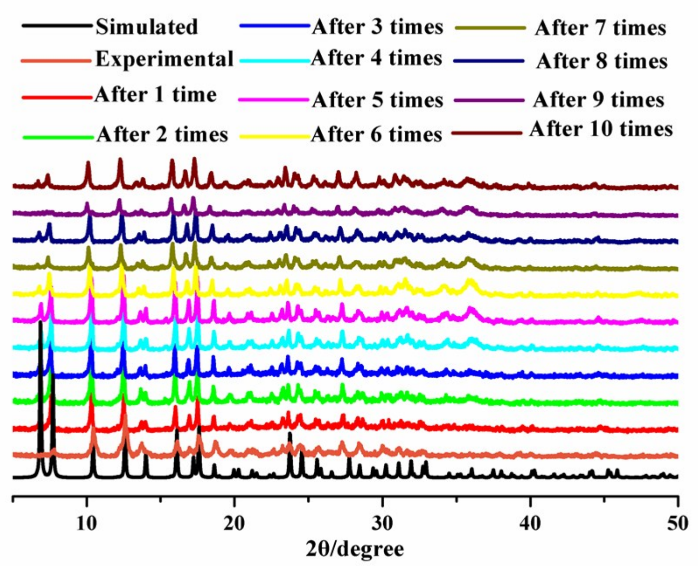
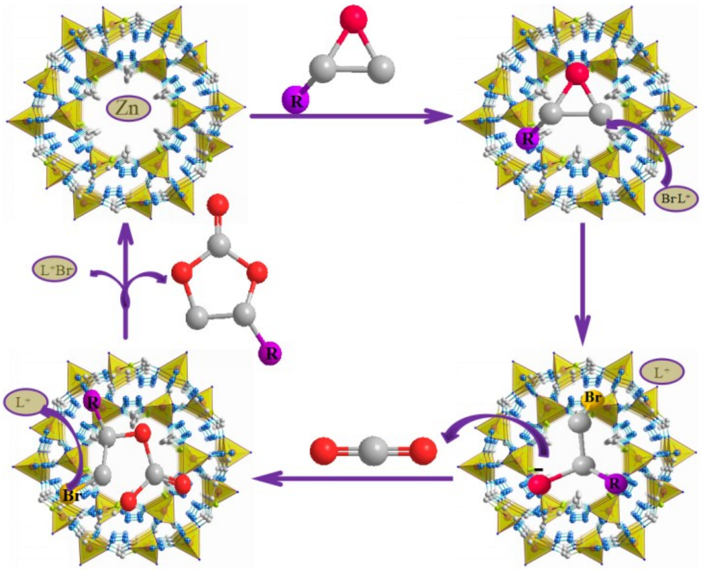


Fig. S7 The PXRD patterns of **1** after ten cyclic cycloaddition reaction of phenylethylene epoxide and CO_2.



Scheme S3. A representation of the tentatively proposed catalytic mechanism for the cycloaddition of CO_2 and expoxides into cyclic carbonates catalyzed by the catalyst **1** (L^+ = tetra-n-tertbutylammo-nium).

Luminescent Behaviors and Sensing Properties.

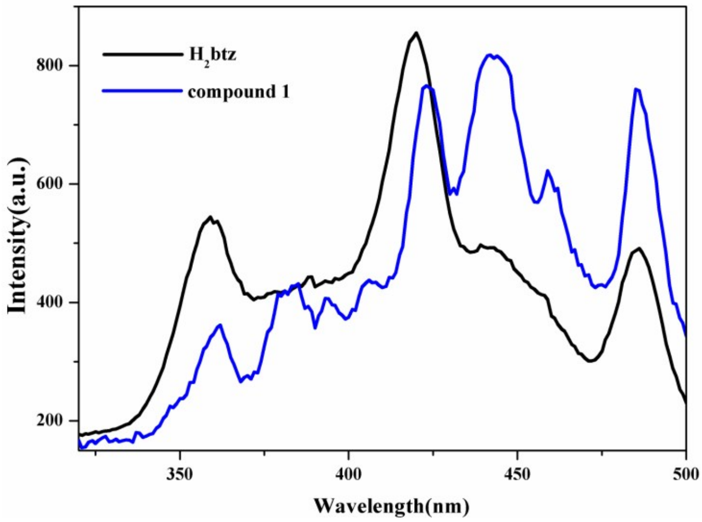


Fig. S8 Solid-state photoluminescence spectra of H_2btz and the compound **1** ($\lambda_{excited}$ = 260 nm)

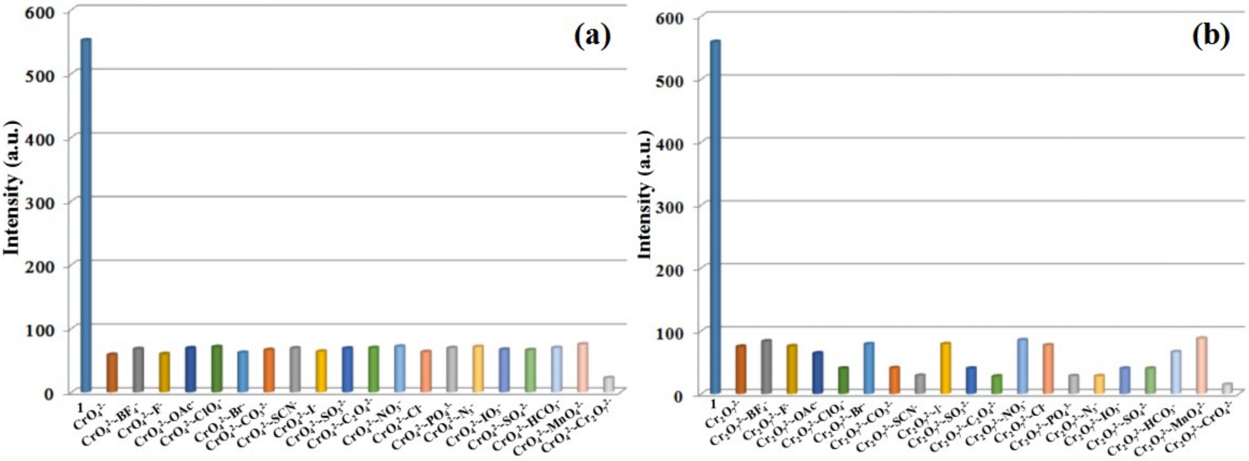


Fig. S9 Comparison of the luminescence intensity of **1**-CrO_4^{2-} (a) and **1**-$Cr_2O_7^{2-}$ (b) under mixed anions (10^{-3} mol L^{-1}).

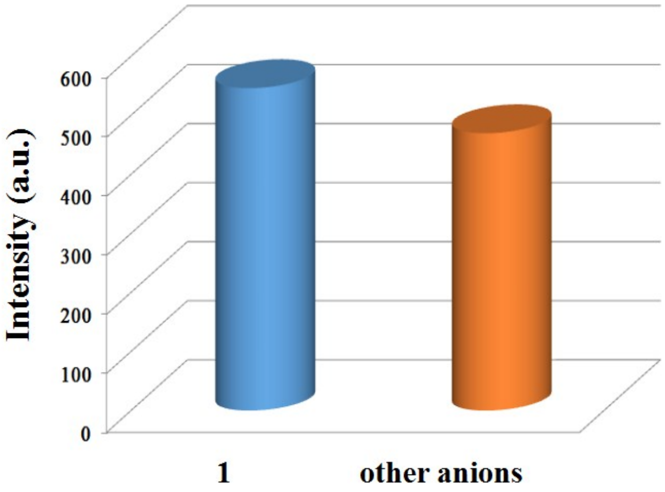


Fig. S10 The luminescence intensity of **1** before and after dropping others anions except for Cr(VI) anions.

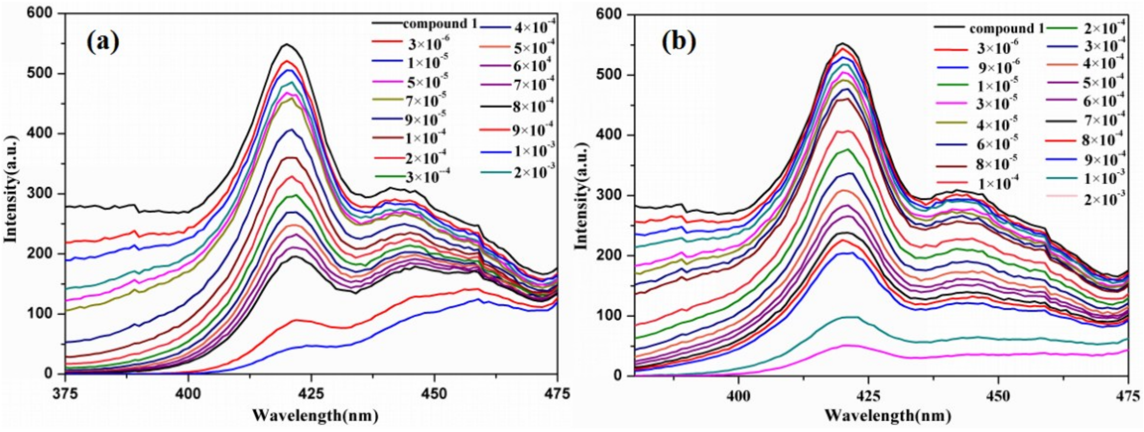


Fig. S11 The liquid luminescence spectra of **1** under different concentrations of CrO_4^{2-} (a) and $Cr_2O_7^{2-}$ (b) aqueous solutions.

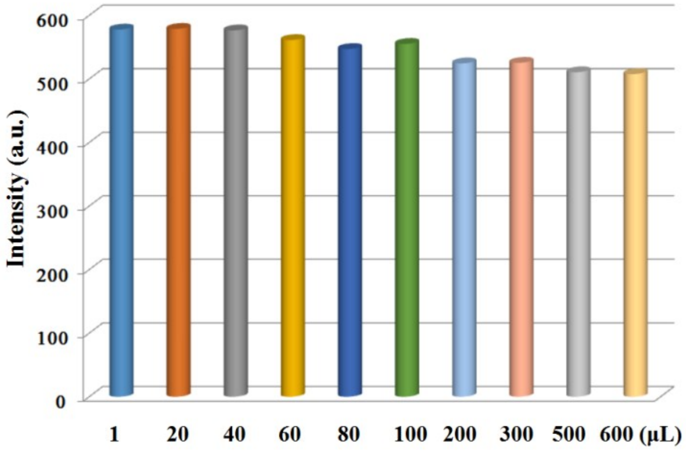


Fig. S12 The luminescence intensity of **1** before and after dropping some amount of pure water.

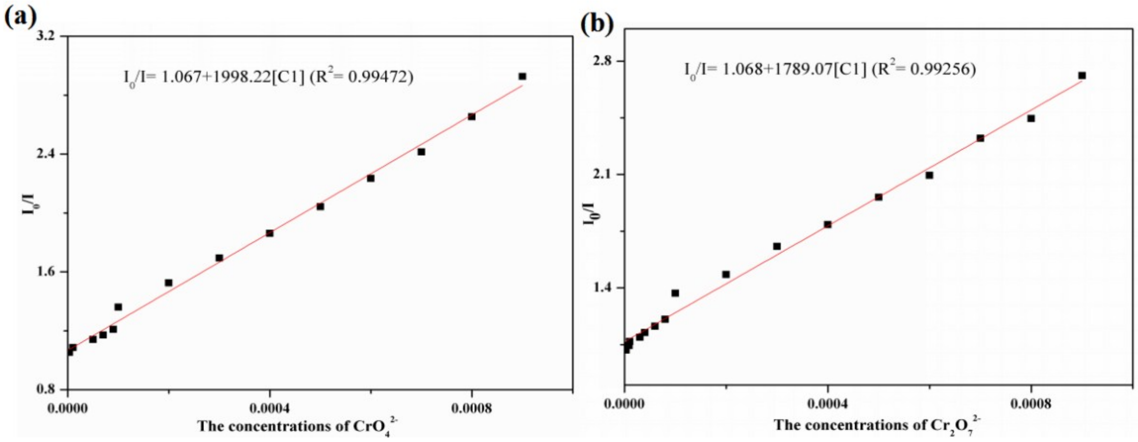


Fig. S13 The intensity plots of **1** vs [CrO_4^{2-}] (a) and **1** vs [$Cr_2O_7^{2-}$] (b).

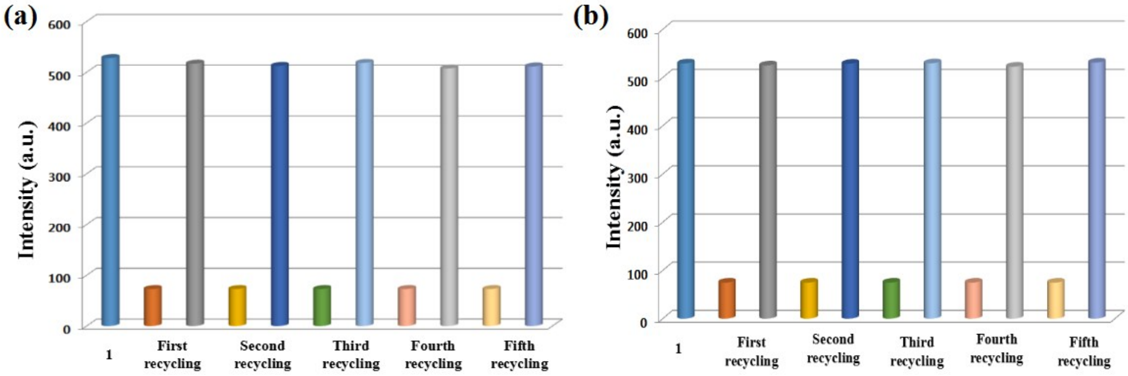


Fig. S14 The luminescence intensity of compound **1** for the recognition of CrO_4^{2-} (a) and $Cr_2O_7^{2-}$ (b) after five recycling processes. The intensity is measured at 420 nm under the excitation wavelength of 260 nm.

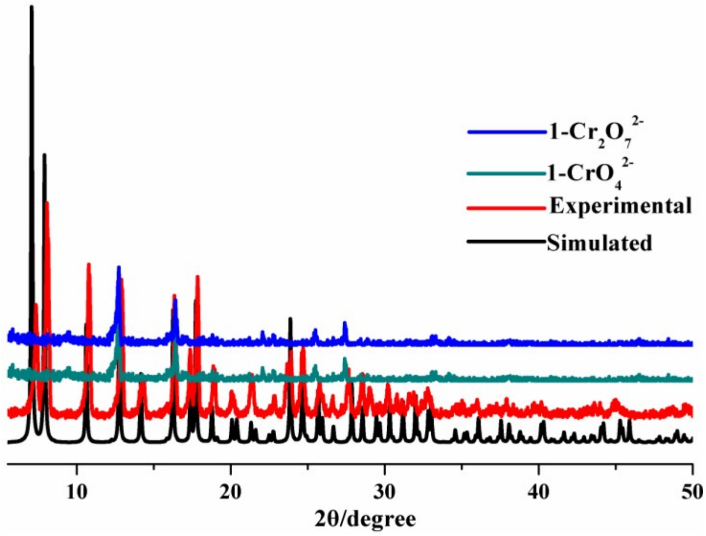


Fig. S15 The PXRD patterns of **1** after recycling.

Sample	Cr (VI) of CrO_4^{2-} (ppm)	Cr (VI) of $Cr_2O_7^{2-}$ (ppm)
1	<0.0110	<0.0110
detectable limit	0.0110	

Table S4 The ICP results of recycled **1** after luminescence detection.

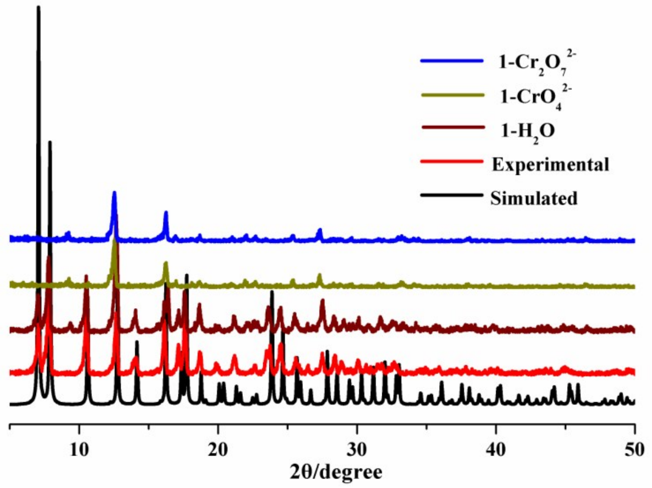


Fig. S16 The PXRD patterns of **1** being immersed in H_2O, CrO_4^{2-} and $Cr_2O_7^{2-}$ solutions.

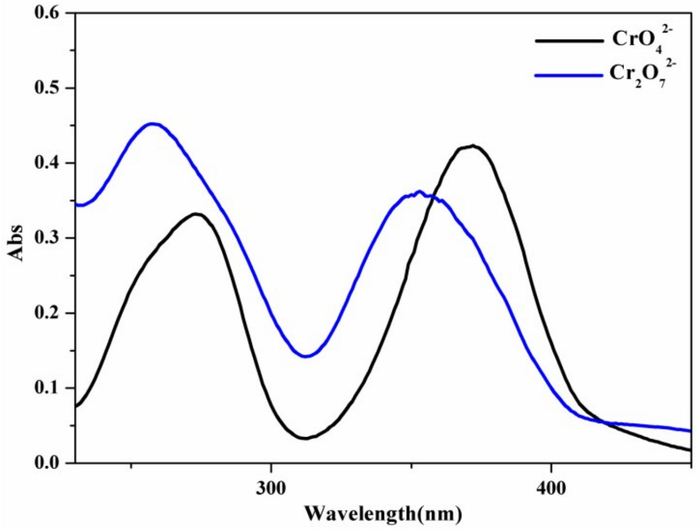


Fig. S17 UV-vis spectra of the K_2CrO_4 and $K_2Cr_2O_7$ solutions.

References

1 A. Chafin, D. J. Irvin, M. H. Mason and S. L. Mason, *Tetrahedron Lett.*, 2008, **49**, 3823.

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