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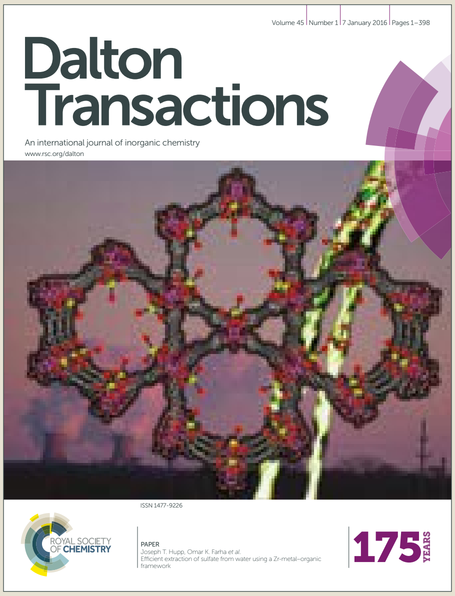
Volume 45 Number 1 7 January 2016 Pages 1–398

Dalton Transactions

An international journal of inorganic chemistry
www.rsc.org/dalton

ISSN 1477-9226

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Dalton Transactions

ARTICLE

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

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Chun-Shuai Cao,[a] Ying Shi,[a] Hang Xu,[a] and Bin Zhao*[a]

A multifunctional metal-organic framework (**1**) containing 24-nuclear zinc nanocages displays high solvent- and pH-stability. Compound **1** can be employed as catalyst for the conversion of CO_2 with aziridines or epoxides, which can be reused at least ten times just by a simple and rapid method. The PXRD of compound **1** after ten recyclings keeps well consistent with the original one. Inductively coupled plasma measurement of reaction filtrate revealed that only trace amount leakage of Zn^{2+} was observed, indicating that the framework did not collapse after recyclings. Compound **1** can effectively catalyze cycloaddition reaction of CO_2 and five aziridines or five epoxides with different substituent groups. To our knowledge, this is the first multifunctional MOFs-based catalyst serving as the conversion of CO_2 with aziridines or eopoxides. Furthermore, luminescent investigations reveal that compound **1** can also act as a luminescent probe for chromium(VI) anion species, which is seriously harmful to human and environments. After five cycle tests, the PXRD of compound **1** are still in accordance with the original one, manifesting compound **1** can be served as a circulatory luminescent probe for Cr(VI) anions.

Introduction

Environment problems and environment protection has becoming more and more important with the acceleration of industrialization. Widespread air and water pollution, as major environmental hazards, have being posing great danger to both human and animal's health. For example, Carbon dioxide (CO_2), as the major greenhouse gas from industrial and human activities, has caused global warming and acid rain in the past few decades.[1] Thus, it is a pressing need to develop novel porous materials to absorb and degrade pollutants in the atmosphere and water. Metal-organic frameworks (MOFs) with well-defined pores, high surface area and functional groups, have been extensively exploited to meet this challenge and solve the energy and environmental problems. Recently, various MOFs have shown not only structural versatility but also promising applications in gas storage/ separation,[2] optical properties,[3] magnetism,[4] catalysis,[5] fluorescence sensing,[6-7] and etc.[8] Among these applications, the catalytic reaction for CO_2 conversion becomes one of the most urgent tasks in CO_2 research field. Carbon dioxide capture and sequestration (CCS) technologies have been dedicated to meet this challenge,[9] which not only reduces greenhouse gas in the atmosphere but also generates various high value-added chemicals, such as cyclic carbonates,[10] alkynyl carboxylic acid products,[11] formic acid,[12] oxazolidinones,[13] dimethyl carbonate[14] and so on.[15] Of these, oxazolidinones, searving as one of important intermediates in organic synthesis, chiral auxiliaries and antibacterial pharmaceuticals, has received people's attention.[16] Despite significant progress has been made in previous works,[17] the recycle performance and rigorous reaction condition of CO_2 with aziridines is still restricted for its actually applications. In addition, cyclic carbonates with wide applications in textile, dyeing, batteries and drug intermediates has attracted people's great research interest in the scientific community and industry.[18] Though many kinds of homogeneous catalysts (sionic liquids, alkali metal salts, Schiff bases and metal-centered salen or porphyrin complexes)[19] have been applied in the synthesis of cyclic carbonate during actual industrial process, while the reaction requires high temperatures and pressures. Thus, it is important to develop mild reaction conditions to accelerate the conversion of CO_2 with aziridines or epoxides. At this point, high porosity and active sites make MOFs be ideal heterogeneous catalysts. Several existing MOFs with high catalytic activity in CO_2 conversion with aziridines, terminal alkynes, and epoxides have already been reported.[20] However, to the best of our knowledge, multifunctional MOFs-based catalysts used for the conversion of CO_2 with aziridines or epoxides have been not reported so far.

On the other hand, MOFs employed as chemical sensors have been of intense interest, such as the detection of cations,[21] anions,[22] small organic molecules,[23] pH,[24] etc.[25] But comparably, the luminescent probes of detecting chromium(VI) anions have been less reported.[26] Actually, chromium(VI) anion species (CrO_4^{2-} and $Cr_2O_7^{2-}$), widely used in various industrial processes,[27] can cause serious damage to human health and environment, and the two toxic and carcinogenic anions have been listed as priority pollutants by Environmental Protection Agency (EPA) in USA.[28] Therefore, extensive efforts should be devoted to develop more novel and porous materials with high chemical stability and good regeneration to detect chromate and dichromate species to prevent chromium(VI) anions from endangering human health and environment.

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Electronic Supplementary Information (ESI) available: [Synthesis, Preparation, PXRD, photoluminescence spectra, UV-vis spectra and ICP results]. See DOI: 10.1039/x0xx00000x

DOI: 10.1039/C8DT00254A

In this contribution, a multifunctional nanocage-based metal-organic framework (**1**) with high solvent- and pH-stability was prepared (**Fig. 1**), and it can act as efficient catalyst for the conversion of CO_2 with aziridines or epoxides. Importantly, compound **1** can be reused at least ten times just by simple and rapid method without any obvious loss in catalytic activity. And **1** can serve as a recyclable luminescent probe for chromium(VI) anion species among twenty anions.

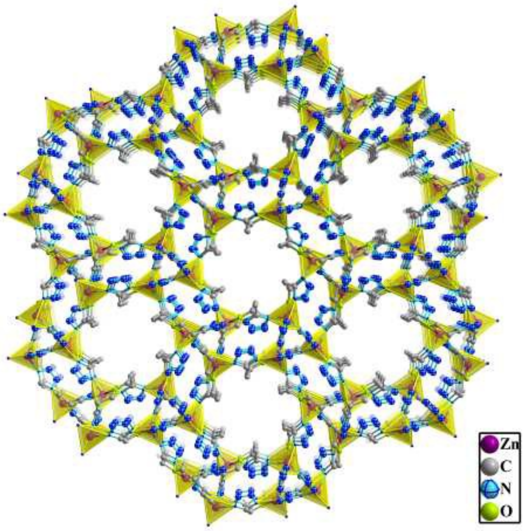


Fig. 1 The view of compound **1**.

Experimental section

Materials and methods

All reagents and reactants were purchased directly by commercial approach and were used without any purification. Powder X-ray diffraction and thermodiffractogram measurements were carried out on an Ultima IV X-ray diffractometer using Cu-Kα radiation. The fluorescent spectra were recorded by an F-4500 FL Spectrophotometer at room temperature. The metal content was measured by ICP atomic emission spectrometric analysis (IRIS Advantage). NMR spectra were recorded on a Varian Inc Mercury Vx-300 type (^1H NMR, 300 MHz) spectrometer. UV-Vis spectroscopic studies were collected on shimadzu UV-3600 spectrophotometer.

Preparation of compound 1. Compound **1** was prepared according to our previous work.[29] The preparation process was represented in **Scheme S1**.

Catalytic experiment of CO_2 with aziridines. In typical experiment, activated catalyst **1** (20 mg, 0.056 mmol) was grinded and added into 10 mL autoclave equipped with a magnetic stir bar, then $\mathbf{a_1}$ (294.4 mg, 2 mmol) and co-catalyst tetrabutylammonium bromide (TBAB) (32.4 mg, 0.1 mmol, 5 mol% relative to $\mathbf{a_1}$) were also put into the reaction tube. Then the autoclave was capped under 2 MPa CO_2 and stirred at certain temperature for 12 h. After reaction, resulting mixture was dissolved in CH_2Cl_2, and the corresponding oxazolidinones of 3-ethyl-5-phenyloxazolidin-2-one ($\mathbf{a_2}$) and 3-ethyl-4-phenyloxazolidin-2-one ($\mathbf{a_3}$) yield was determined by ^1H NMR analysis using 1,3,5-trimethoxybenzene (42.1 mg, 0.25 mmol) as an internal standard.

Catalytic experiment of CO_2 with epoxides. Similarly, **A** (240.0 mg, 2 mmol) and TBAB (32.4 mg, 0.1 mmol, 5 mol% relative to **A**) were also put into the reaction tube equipped with CO_2 balloon. After reaction, resulting mixture was dissolved in CH_2Cl_2, and the corresponding cyclic carbonates of $\mathbf{X_1}$ yield was determined by ^1H NMR analysis using 1,3,5-trimethoxybenzene (42.1 mg, 0.25 mmol) as an internal standard.

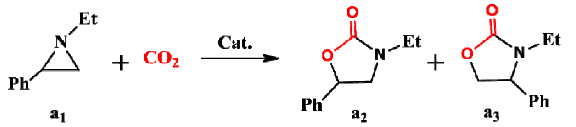
Results and discussion

Structure and stability study of 1.[29] The zeolite-like microporous tetrazole-based framework of **1** containing 24 nuclear zinc cages exhibits high CO_2 adsorption capacity with 35.6 wt % (8.09 mmol/g) at 273 K/ 1 bar. The Brunauer-Emmett- Teller (BET) and Langmuir surface areas of activated **1** are estimated to be 1151 and 1222 m^2/g, respectively. The pore size is about 5.5 Å in diameter by nonlocal DFT analysis, and total pore volume is 0.65 cm^3/g via calculating from Ar adsorption isotherm. The high CO_2 adsorption capacity at 273 K, which is mainly originated from the multipoint interaction among CO_2 and the inner wall motif of cages based on computational simulations.[29] The powder XRD diffractions of compound **1** and activated sample were measured, as shown in **Fig. S1**, and the results show the sample is in pure phase and activated sample keeps stable. In order to explore the chemical stability of compound **1**, samples of **1** were immersed in several common solvents for 24 hours, and then the PXRD patterns were tested. The corresponding PXRD patterns still remain consistent with the simulated one (**Fig. S2**), uncovering that compound **1** possesses high solvent stability. Similarly, the acid/base stability of compound **1** was also investigated. The samples of **1** were immersed in the solutions with pH values from 1.0 to 14.0 for four hours, and the PXRD patterns suggest that the frameworks in **1** remain unchanged spanning pH range of 1-14 (**Fig. S3**).

Catalyze cycloaddition of CO_2 with aziridines. Considering significant adsorbing ability of CO_2 and abundant lewis acid active sites of Zn in **1**, herein we further explored the reactions of CO_2 with aziridines. 1-ethyl-2-phenylaziridine ($\mathbf{a_1}$) was selected as a model substrate to investigate optimized reaction condition, as listed in **Table 1**. The influence of temperature on the reaction was investigated (**Table 1**, entries 1-4), and quantitative yield and excellent selectivity for $\mathbf{a_2}$ were achieved at 70 °C. Thus, 70 °C was chosen as the optimal temperature. Afterwards, the decrease of CO_2 pressure or co-catalyst reduced the yield of the reaction, indicative of that 2 MPa CO_2 and 5 % TBAB is a suitable pressure or co-catalyst amount, respectively (**Table 1**, entries 5-6). In terms of catalyst amount (**Table 1**, entries 7-8), both 40 mg and 20 mg of **1** can achieve quantitative yields and excellent selectivity for $\mathbf{a_2}$. As a result, the optimized reaction conditions should be 70 °C under 2 MPa CO_2 with 20 mg catalyst **1**.

In order to further explore and prove catalytic potential of compound **1**, several typical aziridines were prepared and employed as cycloaddition reaction, and the corresponding synthesis was shown in **Scheme S2**. Under optimized reaction conditions, all of corresponding oxazolidinones were obtained and summarized in **Table 2** (entries 1-5). For entries 1-3, three aziridines bearing different substituent groups at the nitrogen atom was tested in the reaction. The aziridine with ethyl group achieved the best yield and selectivity, which is possibly attributed to the lower stern hindrance of ethyl group than propyl group or butyl group. Additionally, different substituent groups (-CH_3 and -Cl) on phenyl ring were also investigated on the reaction. The yields of 1-ethyl-2-(4-chlorophenyl)-aziridine and 1-ethyl-2-(4-methyl)-aziridine were high (**Table 2**, entries 4 and 5). However, 1-ethyl-2-(4-chlorophenyl)-aziridine showed low activity, which can be explained as the electron-withdrawing effect of chloride group on the phenyl ring.[13] As a result, compound **1** can effectively catalyze cycloaddition reaction with extensive aziridines.

Table 1. Cycloaddition reaction of CO_2 with 1-ethyl-2-phenylaziridine under various conditions.(a)



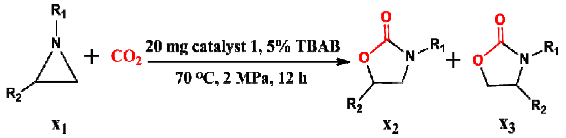
Entry	Catalyst 1(mg)	T(°C)	Yield(b) %	Regio-sel(c)
1	80	30	20	98:2
2	80	50	>99	94:6
3	80	70	>99	99:1
4	80	100	>99	98:2
5[d]	80	100	80	88:12
6[e]	80	70	86	95:5
7	40	70	>99	98:2
8	20	70	>99	98:2
9	0	70	74	98:2
10[f]	0	70	77	89:11
11[g]	0	70	62	98:2
12[h]	0	70	66	91:9
13[i]	0	70	62	98:2

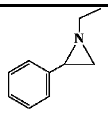
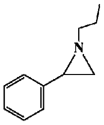
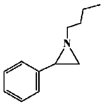
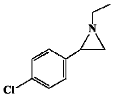
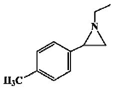
(a)Reaction conditions: 1-ethyl-2-phenylaziridine (**a_1**) (294.4 mg, 2.0 mmol), solvent-free, TBAB (32.4 mg, 0.1 mmol), CO_2 (2.0 MPa), 12 h, catalyst **1**; (b)Total yield of **a_2** and **a_3** determined by ^1H NMR using 1,3,5-trimethoxybenzene as an internal standard; (c)Molar ratio of **a_2** to **a_3**; (d)CO_2 (1.0 MPa); (e)TBAB (16.2 mg, 0.05 mmol), 2 MPa; (f)TBAB (32.4 mg, 0.1 mmol) and $Zn(OAc)_2$ (12.3 mg, 0.056 mmol); (g)TBAB (32.4 mg, 0.1 mmol) and $Zn(NO_3)_2$ (16.6 mg, 0.056 mmol); (h)TBAB (32.4 mg, 0.1 mmol) and $ZnSO_4$ (16.1 mg, 0.056 mmol);(i)TBAB (32.4 mg, 0.1 mmol) and $ZnCl_2$ (7.7 mg, 0.056 mmol).

In fact, recyclable performance of catalysts is an necessary parameter for heterogeneous catalytic reaction. Hence, the recycle tests of **1** for cycloaddition reaction of CO_2 with 1-ethyl-2-phenylaziridine were researched (**Fig. 2**). **1** can be recycled at least ten times with no obvious loss in catalytic activity. The powder X-ray diffraction (PXRD) patterns of **1** after ten recycling processes can be still well consistent with the original one (**Fig. S4**). To make clear the nature of the reaction, catalytic experiment continued to react after removing compound **1** at 3 hours (**Fig. S5**). Experimental results show that the transformation rate of aziridines decreases after removal of catalyst, so catalyst **1** has significant impact on the transformation rate of substrates. Inductively coupled plasma (ICP) measurement of reaction filtrate revealed that only trace amount leakage of Zn^{2+} was observed (**Table S1**), indicating that the framework did not collapse after recyclings. Therefore, compound **1** can be employed as the recyclable catalyst of cycloaddition reaction for CO_2 and 1-ethyl-2-phenylaziridine just by fast and simple method.

Next step, to prove the effect of **1**, the influence of different zinc sources [$Zn(OAc)_2$, $Zn(NO_3)_2$, $ZnSO_4$ and $ZnCl_2$] were employed to replace **1** to conduct the reaction (**Table 1**, entries 10-13) and the yield was less than 77 %, which mainly attributes to interaction between free Zn^{2+} and Br^- to hinder the nucleophilicity of Br^- ions.[30] Finally, the reaction mechanism for cycloaddition reaction of CO_2 with aziridines is proposed based on other reports.[13,20a] At first, the substrate aziridines and CO_2 are enriched around catalyst **1**. Then the N atoms of the aziridines coordinate with zinc sites of **1**, substrates are activated because of Zn^{2+} owning Lewis acid site. Secondly, the nucleophilic Br^- attacks the N atoms of aziridines to lead to ring opening through two different pathways I and II, as showed in **Scheme 1**. Then CO_2 interacts with the N anion of the ring-opened intermediate to form carbamate salt. At last, O^- attacks at the C-Br carbon to perform intramolecular ring-closure, and the oxazolidinones can be obtained along with regeneration of **1** and TBAB. In terms of selectivity, pathway I is the main process and obtain main product **x_2**. It is attributed to ring-opening of the aziridine at the most substituted carbon, which produced more stable carbamate salt.

Table 2. Synthesis of various oxazolidinones from CO_2 and aziridines with catalyst **1**.(a)



Entry	Substrates	Conv.(b) %	Yield(b) %	Regio-sel(c)
1		>99	>99	98:2
2		>99	91	91:9
3		>99	93	93:7
4		74	92	92:8
5		>99	99	99:1

(a)Reaction conditions: aziridines (2.0 mmol **x_1**), solvent-free, 20 mg catalyst **1** loading (based on metal center, about 2.8 mol%), TBAB (32.4 mg, 0.1 mmol), CO_2 (2.0 MPa), 70 °C, 12h; (b)Determined by ^1H NMR using 1,3,5-trimethoxybenzene as an internal standard; (c)Molar ratio of **x_2** to **x_3**.

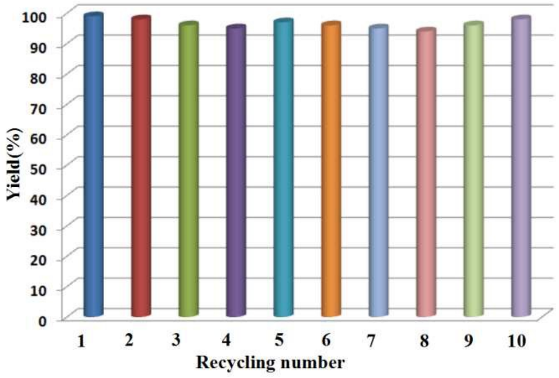


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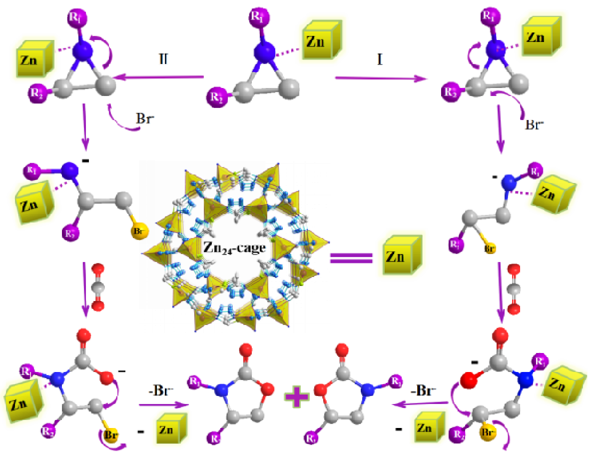
Fig. 2 Recycle tests of the compound **1** for the cycloaddition reaction of CO_2 with 1-ethyl-2-phenylaziridine.



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

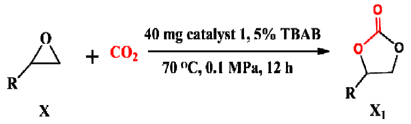
Catalyze cycloaddition of CO_2 with epoxides. We continued to evaluate its performance in the cycloaddition of CO_2 with epoxides to form cyclic carbonates at mild reaction conditions. In order to optimize the reaction condition, the reactions of CO_2 with epoxides under various conditions were investigated (**Table S2**). In the preliminary study, phenylethylene oxide (**A**) was selected as a model substrate to investigate the influence of temperature on the reaction (**Table S2**, entries 1-8). The yield increases with the rise of temperature, so higher temperature can facilitate the reaction process. Nevertheless, the yield at 90 °C and 100 °C decreased to some extent, which might be ascribed to the partial decomposition of TBAB in high temperature.[20a] As a result, 70 °C is chosen as the optimal temperature for this reaction. Next, the amount of cocatalyst TBAB and catalyst **1** were investigated (**Table S2**, entries 5, 11-14). In conclusion, the optimized reaction conditions should be 70 °C under 0.1 MPa CO_2 with 40 mg **1** and 32.4 mg co-catalyst.

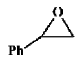
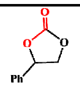
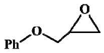
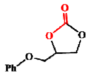
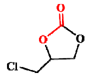
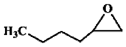
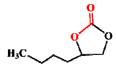
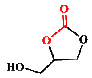
To further explore and testify the catalytic generality of compound **1**, several typical epoxides were examined for the cycloaddition reaction (**Table 3**) under optimized reaction conditions. All of corresponding cyclic carbonates were obtained in comparatively excellent yields (73-99 %, **Table 3**). The results clearly show that **1** can catalyze cycloaddition reaction with relatively extensive epoxides.

Actually, cyclicity is an essential feature of any catalyst considered for heterogeneous catalyst in industrial applications. As shown in **Fig. 3**, **1** can be reused at least ten times without any obvious loss in catalytic activity. Similarly, catalytic experiment continued to react after removal of catalyst **1** at 3 hours, as shown in **Fig. S6**. Experimental results uncover that the transformation rate of epoxides get lower after removal of catalyst, implying that catalyst **1** serves as an important role in the catalytic reactions. ICP measurement of reaction filtrate after the first and the tenth recycling process revealed that only trace amount leakage of Zn^{2+} was observed (**Table S3**). The PXRD patterns of **1** after ten recycling processes can be still well consistent with original one (**Fig. S7**), indicating that **1** may be reused just by a simple and rapid method.

Next step, to explain reaction mechanism, the influence of zinc sources on catalytic reaction were measured as control experiments. First, [$Zn(OAc)_2$, $Zn(NO_3)_2$, $ZnSO_4$, and $ZnCl_2$] were employed as catalysts to replace **1** to conduct the reaction (**Table S2**, entries 15-18), and the yield was less than 82 %, which mainly attributes to interaction between free Zn^{2+} and Br^- to hinder the nucleophilicity of Br^- ions.[30] Comparably, the yield of reaction employing **1** as catalysts is over 99 %. The results indicate that **1** has better and higher catalysis effect on cycloaddition reaction of epoxides and CO_2. The significant catalytic performance maybe result from the following factors: a) nano-sized [Zn_{24}] cages of **1** can enrich largely substrates and CO_2, and the increased concentration of reactants can increase the yield; b) the steric hindrance around Zn^{2+} and the ligand in the stable Zn_{24}-cage unit effectively prevent the coordination between Zn^{2+} and Br^-, resulting in more nucleophilic attack of Br^- on epoxides. Namely, cage-like motif in [Zn_{24}] nanocages plays a vital role in the cycloaddition reaction.

Table 3. Synthesis of various cyclic carbonates from CO_2 and epoxides with catalyst **1**.[(a)]



Entry	Substrates	Products	Yield[(b)] [%]
1			>99.00
2			96
3			94
4			99
5			73

[(a)]Reaction conditions: epoxides (2.0 mmol), solvent-free, 40 mg catalyst **1** loading (based on metal center, about 5.6 mol%), TBAB (32.4 mg, 0.1 mmol), CO_2 (0.1 MPa), 12 h; [(b)]Determined by ^1H NMR using 1,3,5-trimethoxybenzene as an internal standard.

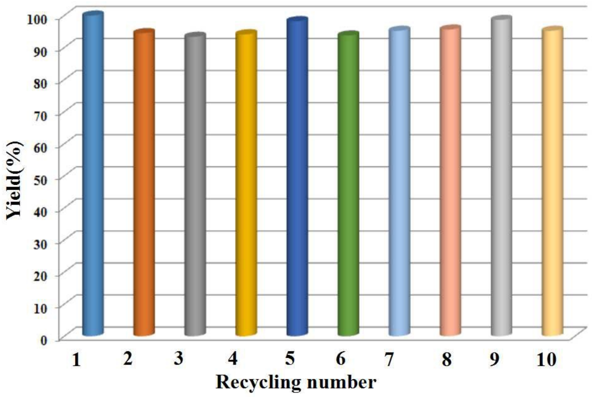


Fig. 3 Recycle tests with the compound **1** for the cycloaddition reaction of CO_2 with phenylethylene oxide.

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DOI: 10.1039/C8DT00254A

In combination with previous reports,[20] a plausible mechanism was proposed for cycloaddition reaction of epoxides with CO_2 to form cyclic carbonates with the synergistic catalytic effect of Zn^{2+} and Br^-. As shown in **Scheme S3**: initially, the oxygen atom of epoxide coordinates with Lewis acidic zinc sites of **1**, which activates the epoxy ring. Concomitantly, the Br^- generated from n-Bu_4NBr attacks the less-hindered carbon atom in the activated epoxide, thereby resulting in opening epoxide ring. Following this, CO_2 interacts with oxygen anion of the ring-opened intermediate to form alkylcarbonate anion. In the subsequent step, O^- attacks at the C-Br carbon to perform intramolecular ring-closure, cyclic carbonate together with regeneration of TBAB and the original structure could be formed. In this process, nucleophilic species is essential for the ring opening of the epoxide to form a bromo-alkoxide. Thus, we conclude that high density of zinc Lewis acid sites in **1** could promote the synergistic catalytic effect of n-Bu_4NBr, thus facilitate the cycloaddition reaction of epoxides with CO_2 under ambient conditions.

Luminescent Behavior and Sensing Property. The solid photoluminescence spectra of **1** and 1,5-bis(5-tetrazolo)-3-oxapentane ligand (H_2btz) were recorded at room (**Fig. S8**). Under excitation at 260 nm, **1** exhibits characteristic emission peaks at 360 and 420 nm, which can be attributed to $\pi^* \rightarrow \pi$ and $\pi^* \rightarrow n$ transitions of H_2btz, respectively.

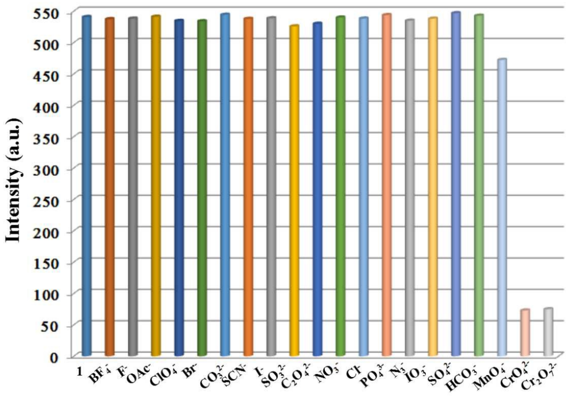

Fig. 4 The luminescence intensity of **1**-X at 420 nm in 10^{-3} mol L^{-1} different anions.

In order to explore the influence behaviors of various anions on luminescence of **1**, 10 mg of **1** was ground and dispersed in 1.96 mL of aqueous solution to form a suspension by ultrasound, and 40 μL of NaX solution (1×10^{-1} mol L^{-1}) (X = BF_4^-, F^-, OAc^-, ClO_4^-, Br^-, CO_3^{2-}, SCN^-, I^-, SO_3^{2-}, $C_2O_4^{2-}$, NO_3^-, Cl^-, PO_4^{3-}, N_3^-, IO_3^-, SO_4^{2-}, HCO_3^-, MnO_4^-, CrO_4^{2-} or $Cr_2O_7^{2-}$) was slowly dropped into the above solutions to form a 1-X suspension (2×10^{-3} mol L^{-1}). The addition of CrO_4^{2-} or $Cr_2O_7^{2-}$ solution lead to luminescence quenching, and MnO_4^- makes the luminescent intensity slightly decrease, while other anions have no obvious effect on the luminescent intensity (**Fig. 4**). Considering mixed anions in waste water, luminescence quenching of mixed solutions containing $Cr_2O_7^{2-}$ and another anions was investigated. 40 μL of $Cr_2O_7^{2-}$ solution (0.1 mol L^{-1}) and 40 μL of another anion solution (0.1 mol L^{-1}) were slowly dropped into a 1.92 mL suspension (2×10^{-3} mol L^{-1}) of **1**. Similarly, luminescent intensity of the solutions containing CrO_4^{2-} and another anion was also measured at once. As show in **Fig. S9**, quenching effect of Cr(VI) on **1** was hardly influenced by other anions. To verify whether other anions in the absence of Cr(VI) anions affects the detection, 40 μL other mixed anions (0.1 moL/L) except for CrO_4^{2-}/$Cr_2O_7^{2-}$ were added into the 1.96 mL suspension of **1**, the luminescent measurement of solutions was tested (**Fig. S10**) Other anions did not show obvious quenching effect, uncovering **1** can selectively detect Cr(VI) anions among the above anions.

Moreover, the detection limit of **1** as an efficient fluorescent probe was explored. The different concentrations of 20 μL CrO_4^{2-}/$Cr_2O_7^{2-}$ (1×10^{-4} to 1×10^{-1} mol L^{-1}) solutions were dropped into 1.98 mL suspension of **1**, forming a series of **1**-CrO_4^{2-}/$Cr_2O_7^{2-}$ (1×10^{-6} to 1×10^{-3} mol L^{-1}) suspensions. The luminescence intensity of **1**-CrO_4^{2-}/$Cr_2O_7^{2-}$ gradually decreases with the addition of CrO_4^{2-}/$Cr_2O_7^{2-}$ (**Fig. S11**). The detection limit of **1** for detecting CrO_4^{2-} and $Cr_2O_7^{2-}$ can reach 3×10^{-6} mol L^{-1}. In order to evaluate whether dilution of adding water affect luminescent intensity, some amount of pure water was dropped into suspension of compound **1**. As shown in **Fig. S12**, the luminescent intensity did not decrease significantly with the addition of water, which implies the dilution did not cause luminescence quenching.

In order to further explore the relationship between the concentration of the quenching effect and CrO_4^{2-}, the luminescence intensity vs. CrO_4^{2-} concentration plot was made (**Fig. S13**). And it can be linearly fitted into $I_0/I = 1.067 + K_{sv}[CrO_4^{2-}]$ (I_0 and I represent the luminescence intensity of **1** before and after adding CrO_4^{2-}, $[CrO_4^{2-}]$ represents the concentration of CrO_4^{2-}, and K_{sv} represents the quenching rate constant), which is close to the Stern-Volmer equation: $I_0/I = 1 + K_{sv}[CrO_4^{2-}]$.[31] Anaylysis results reveal that luminescent intensity follows the equation of $I_0/I = 1.067 + 1998.22\ [CrO_4^{2-}]$ in the range of $3.0\times10^{-6} \sim 9\times10^{-4}$ mol L^{-1} of CrO_4^{2-}; luminescent intensity follows the equation of $I_0/I = 1.068 + 1789.07\ [Cr_2O_7^{2-}]$ in the range of $3.0\times10^{-6} \sim 9\times10^{-4}$ mol L^{-1} of $Cr_2O_7^{2-}$.

In fact, recycling performance is necessary for luminescent probe to be applied in practice. **1** is immersed in an aqueous solution of 0.1 M CrO_4^{2-}/$Cr_2O_7^{2-}$ for 20 s to form **1**-CrO_4^{2-}/$Cr_2O_7^{2-}$, then **1**-CrO_4^{2-}/$Cr_2O_7^{2-}$ were washed with water and ethanol for five times. The samples of **1**-CrO_4^{2-}/$Cr_2O_7^{2-}$ were ground and then 12 mg of samples of **1**-CrO_4^{2-}/$Cr_2O_7^{2-}$ were dispersed in 2 mL of aqueous solution to form a suspension by an ultrasound method. Then the emission of **1**-CrO_4^{2-}/$Cr_2O_7^{2-}$ were tested, and luminescence intensity was nearly identical to the original one (**Fig. S14**). The PXRD patterns of **1** after recycling are still well consistent with the original ones (**Fig. S15**), revealing that **1** can be served as a circulatory luminescent probe for Cr(VI). Inductively coupled plasma (ICP) measurement (**Table S4**) reveals that recycled **1** does not contain Cr(VI). CrO_4^{2-}/$Cr_2O_7^{2-}$ have almost been removed by a simple and rapid method.

Then, possible mechanism that the introduction of CrO_4^{2-}/$Cr_2O_7^{2-}$ decreased luminescence intensity is discussed. Based on previous literatures,[6e,32] the luminescence quenching of MOFs caused by anions may result from the several aspects: (a) the collapse of the MOFs; (b) energy losing caused by the collision between frameworks and anions during energy transfering process. The PXRD patterns of **1** after being immersed in H_2O, CrO_4^{2-} or $Cr_2O_7^{2-}$ are still well consistent with the original one (**Fig. S16**), supporting high stability of compound **1** in detecting Cr(VI) in aqueous system. Thus, luminescence quenching did not result from the collapse of the frameworks in **1**. The UV-vis spectra of CrO_4^{2-} and $Cr_2O_7^{2-}$ solutions show absorption at about 270 and 370 nm for CrO_4^{2-}, 260 and 350 nm for $Cr_2O_7^{2-}$ (**Fig. S17**). While the strong excitation wavelength of **1** is 260 nm, thus CrO_4^{2-} and $Cr_2O_7^{2-}$ in the solution can significantly absorb the energy of the excited light, resulting in luminescence decrease. In conclusion, the collision between the CrO_4^{2-}/ $Cr_2O_7^{2-}$ anions and the frameworks, as well as the

DOI: 10.1039/C8DT00254A

adsorption of CrO_4^{2-}/ $Cr_2O_7^{2-}$ in the UV-vis region, reduce energy of transmission process, and finally lead to luminescence quenching.

Conclusions

In summary, a multifunctional metal-organic framework **1** with high solvent-stability and pH-stability was prepared. Compound **1** can serve as an efficient, recyclable and environmentally friendly catalyst for the conversion of CO_2 with five aziridines or epoxides containing different substituent groups. Importantly, catalyst **1** can be reused at least ten times without any obvious loss in catalytic activity, and PXRD of compound **1** after recyclings keep well consistent with the original one. To the best of our knowledge, this is the first multifunctional MOFs-based catalyst serving as the conversion of CO_2 with aziridines or eopoxides. Furthermore, the material can also act as a recyclable luminescent probe for chromium(VI) anion species among twenty anions.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by NSFC (21625103, 21571107, and 21421001), SFC of Tianjin (15JCZDJC37700) and 111 Project (B12015).

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View Article Online
DOI: 10.1039/C8DT00254A

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A multifunctional metal-organic framework (**1**) with high solvent-stability and pH-stability was prepared. Compound **1** can serve as an efficient, recyclable and environmentally friendly catalysts for the conversion of CO_2 with five aziridines or epoxides containing different substituent groups. To the best of our knowledge, this is the first multifunctional MOFs-based catalyst serving as the conversion of CO_2 with aziridines or eopoxides. Furthermore, the material can also act as a recyclable luminescent probe for chromium(VI) anion species among twenty anions.