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REGULAR ARTICLE

A robust Co(II)-MOF with nitrogen-rich micropores for CO_2 transformation and protective effect on acute heart failure treatment by increasing the expression of Hif-1α

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Abstract. A 3D neutral porous MOF (**1**), $[Co_2(tdc)_2(Hdatz)\cdot DMF(H_2O)_3]_n$ (H_2tdc = 2,5-thiophenedicarboxylic acid, Hdatz = 3,5-diamino-1,2,4-triazole), which has aplenty micropores along with free groups of NH_2 was assembled via combining 2,5-thiophenedicarboxylic acid ligands and nitrogen-rich 3,5-diamino-1,2,4-triazole as well as Co(II) ion. The activated MOF (**1a**) has a fine affinity for CO_2 molecules and a fine catalytic performance for the conversion of CO_2 with internal epoxides along with various terminal ones. Furthermore, the protective activity of **1a** on acute heart failure was evaluated by measuring left ventricular ejection fraction and Left ventricular fraction shortening. And the mechanism of this compound was explored by detect the *Hif-1α* expression level.

Keywords. MOF; mixed-ligand approach; porous framework; CO_2 conversion; acute heart failure.

1. Introduction

Acute heart failure is a serious syndrome, showed as significantly and rapidly reduce of cardiac output due to acute heart disease, which will then lead to hypoperfusion of tissue and organs and acute congestion.[1,2] Clinically, compared with the acute right heart failure, the acute left heart failure is more common, mainly manifested as severe cardiogenic shock and acute pulmonary edema. Acute heart failure has a wide-reaching implication on the mortality and morbidity of patients; besides, it also needs a large number of care cost for these patients.[3,4] As reported, only in the UK, there is about £980 million costed per year on managing acute heart failure.[5] So, we urgently need to develop novel candidate drugs for acute heart failure treatment and reduce the related nursing costs.

Metal-organic framework (MOF) is a kind of crystal compound contains organic linkers and metal nodes. Because of its compositional and chemical tunability, large specific surface area as well as permanent porosity, MOFs have a wide application prospect in gas catalysis along with adsorption.[6–9] Although some catalysts of MOF have been applied to decreased CO_2 consistence within the atmosphere to obtain the value-added products, a lot of them are only effective at the condition of high pressure or when they are used with uneconomical and complex cocatalysts such as organic salt along with organic base.[10–13] Therefore, it is necessary to synthesize MOF materials of porous which have high catalytic sites, which can convert CO_2 at the pressure of atmospheric without auxiliary catalyst. The groundbreaking experimental and theoretical results shown that the synergistic action of Lewis acid base group and nucleophiles assistance is very important for the cycloaddition of CO_2. CO_2 species along with epoxides are activated via Lewis base and Lewis acid respectively. Nucleophiles contribute to promote epoxides ring opening reaction.[14–17] In addition, there are accessible nitrogen rich units along with hydroxyl within the porous MOFs structure, which is helpful to deep improve the selectivity of CO_2 to catalyst.[18] In consideration of these, within the research, a 3D neutral porous mixed-ligand metal-organic framework (MOF), $[Co_2(tdc)_2(Hdatz)\cdot DMF(H_2O)_3]_n$ (H_2tdc = 2,5-thiophenedicarboxylic acid, Hdatz = 3,5-diamino-1,2,4-triazole),

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which has aplenty micropores along with free groups of NH_2 was assembled via combining 2,5-thiophenedicarboxylic acid ligands and nitrogen-rich 3,5-diamino-1,2,4-triazole as well as Co(II) ion. The activated MOF (**1a**) has a fine affinity for CO_2 molecules and a fine catalytic performance for the conversion of CO_2 with internal epoxides along with various terminal ones. In biological research, the protective activity of **1a** on acute heart failure was evaluated, and the results of the left ventricular ejection fraction (LVEF) and left ventricular fraction shortening (LVFS) indicated the promotion activity of compound on cardiac functions in acute heart failure rats. And the *Hif-1α* expression results revealed the mechanism of the new compound.

2. Experimental

2.1 *Materials and physical measurements*

Starting solvents, reagents along with materials were purchased from the sources of commerce and could be utilized with no deep purification. With Nicolet Avatar 360 FT-IR spectrophotometer we determined FT-IR spectra. Q50 TGA (TA) thermal analysis equipment was utilized for thermogravimetry analysis within the nitrogen flow and the heating rate was 5 °C min^{-1}. By using the MiniFlex (Cu Kα, λ = 1.5418 Å) we determined the bulk samples powder X-ray diffraction patterns (PXRD) at room temperature. GC analysis was carried out on an Agilent 7890B GC analyzer. The adsorption isotherms (N_2) of gas under the low pressure (reach 1 bar) were determined on the Micrometrics ASAP 2020 porosity analyzer along with surface area.

2.2 *Preparation and characterization for* $[Co_2(tdc)_2(Hdatz)\cdot DMF(H_2O)_3]_n$ (*1*)

With the solvothermal crystallization approach we prepared the complex **1**. In general, mixing 0.50 mmol $Co(NO_3)_2\cdot 6H_2O$ which is 0.3 g and 0.1 mmol, 0.2 mmol and 34.4 mg 2,5-thiophene dicarboxylic acid as well as 3,5-diamino-1,2,4-triazole of 9.9 mg and 0.1 mmol in 10 mL DMF/H_2O with the volume rate is 9:1 within the 30 mL glass bottle. The mixture was ultrasonic treated for 15 min, then sealed with polytetrafluoroethylene tape and secondary membrane, and heated for 3 days at 120 °C. After cooling to 20 °C at 5 °C/min rate, we acquired crystals of pink prisms. The crystals were then washed by using DMF and dried for 1 day at 60 °C, yield 42% based on the 2,5-thiophenedicarboxylic acid ligand. Anal. Calcd for **1** ($C_{17}H_{21}Co_2N_6O_{12}S_2$): C, 29.88; H, 3.10; N, 12.30%; Found for **1**: C, 29.76; H, 3.23; N, 12.23%.

With Oxford Xcalibur E diffractometer we acquired compound **1**'s X-ray data. Utilizing the software of CrysAlisPro for the sake of analyzing strength data and then convert them into HKL files. Compound **1**'s original structural patterns was constructed through the SHELXS program on the basis of the direct approach and corrected by utilizing SHELXL-2014 program on the basis of the least-squares approach. Mixing all the non-H atoms of complex **1** with the anisotropic parameters, and all the H atoms were geometrically fixed to their connected C atoms through applying AFIX commands. Due to the highly disordered nature of the solvent molecules, they could not be properly modeled via the crystal data refinements, so their electronic contributions have been removed from the HKL file by using the SQUEEZE manipulation embedded in the software PLATON, which obtained the solvent-free structure **1** (after SQUEEZE). The information of the lattice solvents in the framework of **1** has been determined via a combination of the elemental analysis along with the TGA data. Table 1 describes the information of numerical value as well as crystallographic parameters reorganized of compound **1**.

2.3 *Acute heart failure rats model*

30 Wistar rats (male, 6–8 weeks, 20–22 g) were obtained from Model Animal Reaserch Center of Nanjing University (Nanjing, China). The rats were kept in the standard condition of 20–25 °C temperature and 45% humidity environment. For acute heart failure model construction, we divided rats into three distinct groups, the group of control (shame operation + PBS treatment), model group (operation+ PBS treatment) and treatment group (operation+ compound treatment). All the experiments performed within the research were approved via Affiliated Hospital Ethics Committee of Nanjing University (Nanjing, China).

2.4 *Echocardiography*

After establishing the rat acute heart failure model, the rats were treated with compound at the dosage of 5 mg/kg every day for 7 days. LVFS along with LVEF were all the cardiac function important indexes. Thus, in this experiment, after the compound treatment, the

Table 1. Compound **1**'s crystallographic parameters along with refinement details.

Empirical formula	$C_{14}H_8Co_2N_5O_8S_2$
Formula weight	556.23
Temperature/K	273.15
Crystal system	Monoclinic
Space group	C2/m
a/Å	17.963(2)
b/Å	19.9923(13)
c/Å	12.6231(12)
α/°	90
β/°	127.926(3)
γ/°	90
Volume/Å^3	3575.9(6)
Z	4
ρ_{calc}g/cm^3	1.033
μ/mm^{-1}	1.075
Data/restraints/parameters	3940/92/172
Goodness-of-fit on F^2	1.193
Final R indexes [I>=2σ (I)]	R_1 = 0.0725, ωR_2 = 0.2097
Final R indexes [all data]	R_1 = 0.0894, ωR_2 = 0.2220
Largest diff. peak/hole / e Å^{-3}	1.93/-0.90
CCDC	1960638

LVEF and the LVFS were assessed by an echocardiography system (Vevo2100, Visual Sonics, Canada).

2.5 *RT-PCR of Hif-1α*

The significant function of Hif-1α within the procession of acute heart failure was evaluated by RT-PCR according to the guidance of the instructions. The cardiac tissues were harvested from the acute heart failure rats after compound treatment, and the total RNA within the samples was separated by TRIzol reagent (Invitrogen, Carlsbad, CA, USA). The total RNA consistence was qualified, and then reverse-transcribed into cDNA using a cDNA Synthesis Kit (Thermo Fisher Scientific, Boston, MA, USA). Real-time RT-PCR performance was conducted to determine Hif-1α expression level. Relative gene expression levels were expressed as mean±SD.

3. Results and Discussion

3.1 *Crystal structure of complex 1*

The targeted complex **1** could be obtained via solvothermal reaction of 3,5-diamino-1,2,4-triazole, 2,5-thiophene dicarboxylic acid and $Co(NO_3)_2{\cdot}6H_2O$ in the solution of DMF. It should be noted that an excess amount of DMF was used in the reaction to lower the concentration of the reactants in order to avoid the formation of unknown deposition. According to the results of thermogravimetry, element analysis and single crystal X-ray diffraction, **1**'s formula is defined to be $[Co_2(tdc)_2(Hdatz){\cdot}DMF(H_2O)_3]_n$. The refinement results along with structural solution on the basis of crystal data collected at room temperature reflect that complex **1** crystallizes within the system of monoclinic crystal which has the space group of C2/m and demonstrates a three-dimensional channel-type skeleton based on the binuclear Co(II)-based secondary building unit. Its asymmetric unit contains half of 3,5-diamino-1,2,4-triazole (Hdatz) bond, a 2,5-thiophene dicarboxylate (tdc^{2-}) anion as well as a diverse binuclear Co(II) units (Figure 1a). The four carboxylic oxygen atoms (O8b, O8, O5b along with O5, b = x, 2-y, z) from two tdc^2 ligands satisfy the coordination of Co1 within the secondary structure unit of $Co_2(COO)_4$ impeller, while the Co_2 coordination environment within the $[Co_1N_1O_1]_2$ binuclear unit consists of two carboxylic oxygen atoms (O6a along with O6, a = 1-x, y, -z) from tdc^2 ion and two nitrogen atoms (N3a along with N3, a = 1-x, y) from Hdatz connector. The lengths of Co–O along with Co–N bond are between 1.955–2.031 Å and 1.972–1.993 Å, respectively, which are equivalent to the lengths observed within other MOFs based on Co(II)constructed from the N-donor and O-donor co-ligands. The structure reveals the interactions of N–H···O hydrogen bonding between carboxylate oxygens of the tdc^{2-} ion and $–NH_2$ groups of the Hdatz ligand. In addition, two symmetry-related Co_2 atoms are held

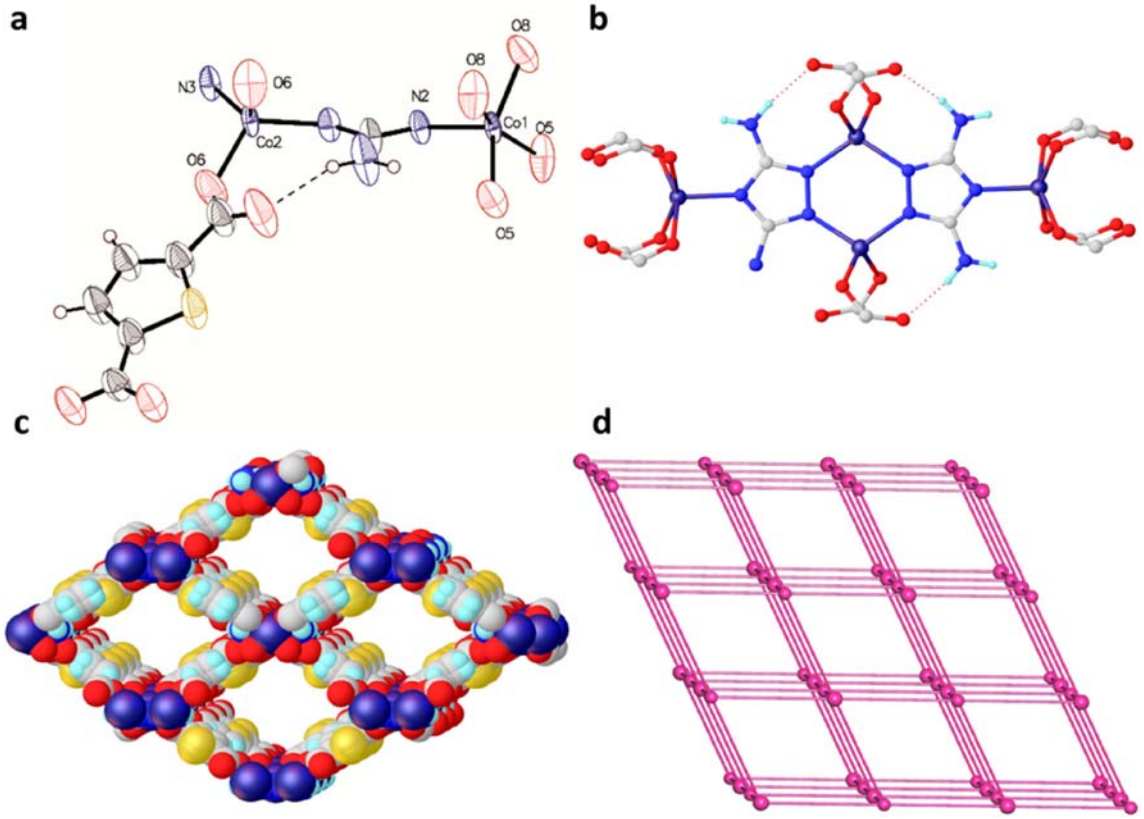


Figure 1. (a) View for the thermal ellipsoidal plot of the asymmetric unit of complex **1**. (b) View for the binuclear Co_2 cluster-based unit. (c) View for **1**'s three-dimensional structure revealing the one-dimensional channels; (d) The **pcu**-net topology for **1**.

together via a pair of Hdatz ligands to afford the binuclear Co_2 unit (Figure 1b). The Co(II) ions are connected via Hdatz connecter nitrogen atoms along with tdc^{2-} ions carboxylate groups to form the 3D microporous structure. There are two one-dimensional channels with the dimensions of 12.5 × 8.7 $Å^2$ along the crystallographic [101] direction (Figure 1c). Furthermore, Hdatz connecter $–NH_2$ groups are free and it exposed within the structure one-dimensional channels. The analysis of topology via TOPOS shows that the structure has 6-linked single-nodal **pcu** network topology which has the vertex symbol of {4^12·6^3} (Figure 1d). In addition, 57.0% (3688.7 $Å^3$) of the effective solvent can enter the vacuole after removing the guest solvent molecules.

3.2 *PXRD, TGA analysis and Gas sorption properties*

Complex **1**'s bulk phase was determined via the analyses of powder X-ray diffraction (PXRD). The new samples diffraction patterns are in fine agreement with the results of simulation, exhibiting that compound **1** is a pure phase. In addition, **1**'s activated samples shows the diffraction patterns parallel to the original sample, revealing integrity along with permanent microporosity of structure (Figure 2a). Compound's thermal stability was assessed via the thermogravimetric analysis (TGA) in atmosphere of N_2 at 25–800 °C. Synthesis **1**'s TGA curve shows the weightlessness of ∼8% (calcd 7.7wt%) from room temperature to 130 °C, which is equivalent to the three guest water molecules loss. The second weightlessness at 120–200 °C is 11.5% (calcd is 11.38wt%), which is equivalent to guest DMF molecule loss, while the third weightlessness at 220–380 °C is 47% (calcd is 47.6wt%), which is owing to Hdatz linker and tdc^{2-} combined loss (Figure 2b). In addition, **1a**'s activated sample has no weightlessness below 200 °C, exhibiting that there is no guest solvent molecule. As discussed before, the complex **1** is microporous and has one-dimensional channels along the [101] direction with the dimensions of 12.5 × 8.7 $Å^2$. In order to measure the sample's permanent porosity, the measurement of nitrogen adsorption desorption was performed. Before beginning the measurement of adsorption, synthesized sample was activated in vacuum (18 mTorr) at 373 K for 15 h to acquire the without solvent **1a**. Activated MOF pattern analysis of

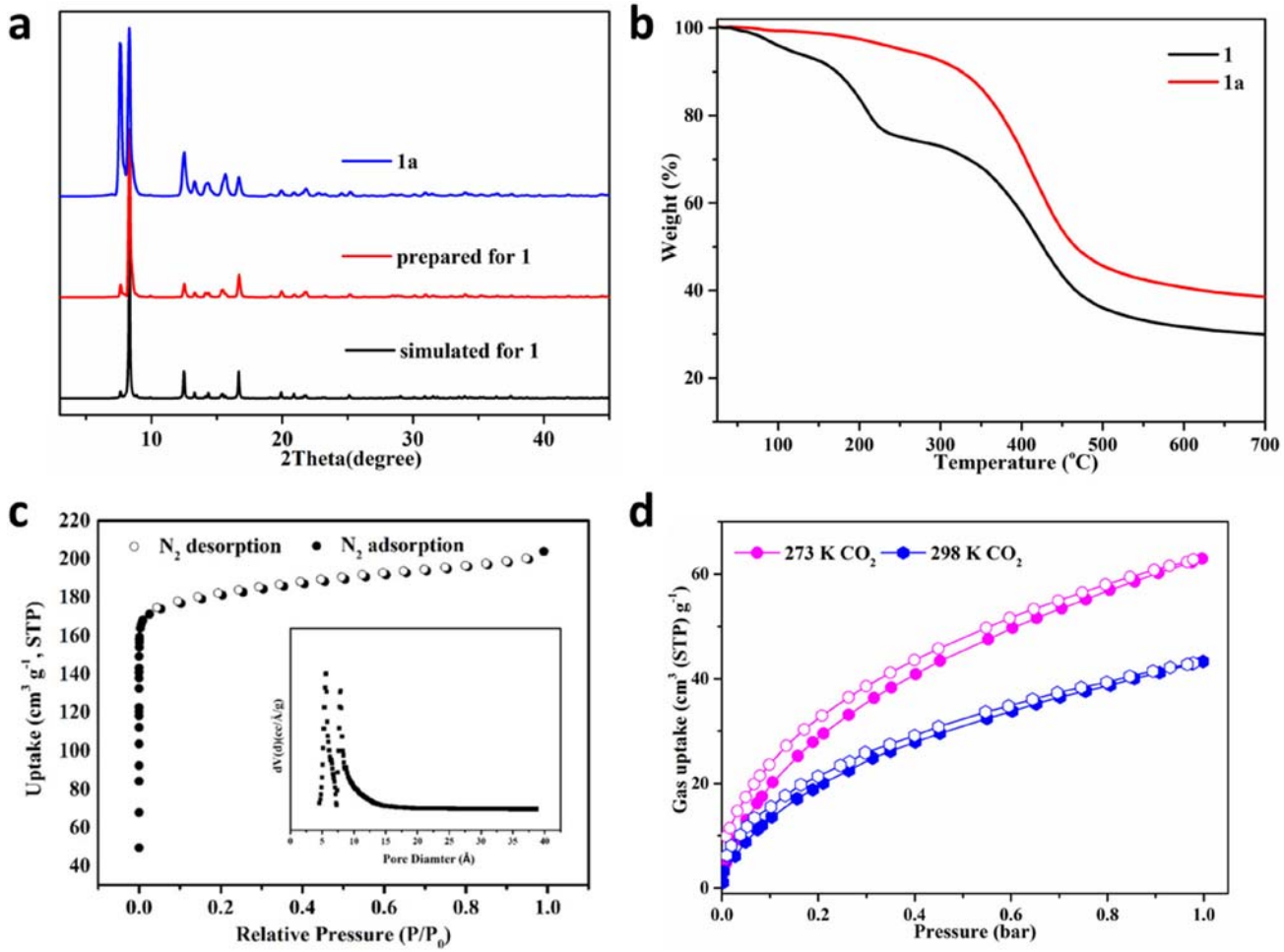


Figure 2. (a) **1a**'s and **1**'s PXRD pattern. (b) **1a**'s and **1**'s curves of TGA. (c) **1a**'s N_2 sorption data. (d) **1a**'s CO_2 sorption data at 273 K and 298 K.

powder X-ray diffraction demonstrated that the original skeleton structure of MOF was retained. In addition, **1a**'s N_2 adsorption isotherm reveals a curve of type-I. Its maximum N_2 absorption capacity is 200 cm^3/g, which supports **1a**'s microporous nature. The estimated specific surface area of Brunauer Emmett Teller (BET) is 529 $m^2\ g^{-1}$, and the distribution of pore size on the basis of density functional theory pattern is 8.6 and 5.8 Å (Figure 2c). In addition, the CO_2 sorption data for **1a** were also collected at the temperature of 273 and 298 K, and the corresponding uptake capacity is 69.2 and 43.3 cm^3/g, showing its potential use for the CO_2 sorption and chemical transformation (Figure 2d). The diffuse-reflectance UV–vis spectra of the bibp, H3nbta and nano-sized CP 1 were studied at room temperature in the solid state (Figure 3). The electronic absorption spectra (UV–vis) of the H_2datz ligand occur at 337 nm, which are attributed to the $\pi \rightarrow \pi*$ transition. Meanwhile, there are two absorption bands at 299 and 347 nm for the H_2tdc ligand, which are also assigned to the typical

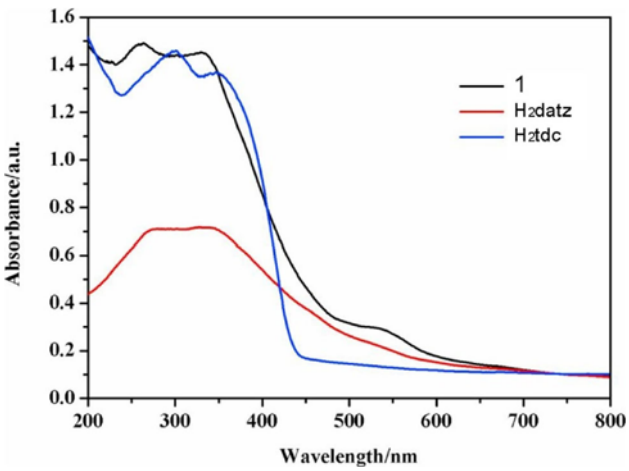
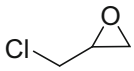
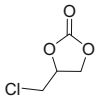
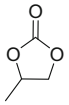
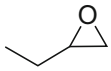
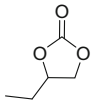
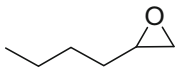
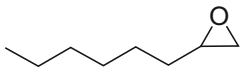
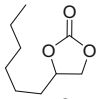
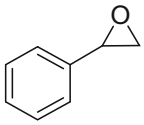
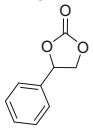


Figure 3. The electronic absorption spectra for the two ligands and complex **1**.

$\pi \rightarrow \pi*$ transition of the aromatic rings. The diffuse-reflectance UV–vis spectra also show the absorption features of complex **1**, and the main UV absorption

Table 2. 1**a** promoted the cycloaddition reaction of CO_2 and epoxides.

Entry	Substrate	Catalyst (mol%)	Co-catalyst (mol%)	Pressure (MPa)	Product	Conversion (%)[b]
1		0.1	2.5	0.1		99.2
2		0.1	2.5	0.1		91.3
3		0.1	2.5	0.1		90.2
4		0.1	2.5	0.1		72.3
5		0.1	2.5	0.1		53.1
6		0.1	2.5	0.1		80.6

[a]The conditions of reaction are temperature is 80 °C, time is 9 h, catalyst/TBAB of 0.1:2.5 mol% and epoxide of 10 mmol.
[b]Conversion: the conversions of catalytic were measured via GC.

bands at 263 nm and 330 nm can be attributed to metal-to-ligand charge transfer (MLCT).

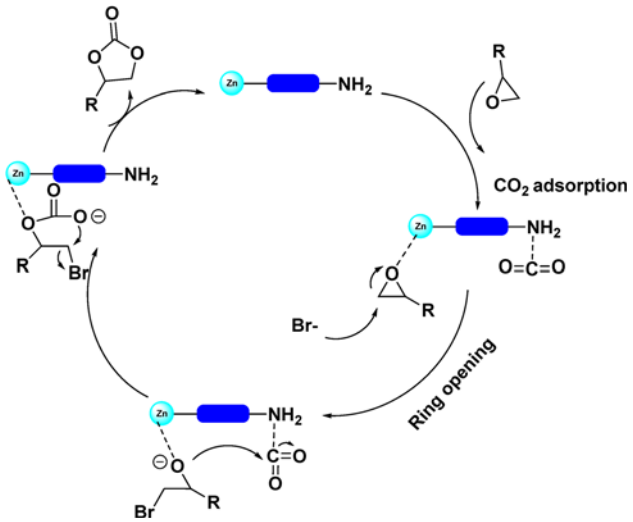
3.3 *Catalytic properties of **1a***

As discussed above, complex **1** has both Lewis acid and Lewis base sites defined by the coordinately unsaturated metal ions and the N rich Hdatz ligands, which might be helpful for the promotion of the of CO_2 cycloaddition reaction. Furthermore, the large open channels running along the [101] direction combined with the moderate high CO_2 sorption capacity are also beneficial for the CO_2 adsorption into the pore surface for the enhancement of the substrate concentration. In addition, the former researches have confirmed that for effective cyclic addition of CO_2 with epoxides the catalyst of MOF should have a high concentration of lewis/bronster acid or alkaline sites to activate epoxides/CO_2 and selectively capture CO_2, and be highly stable. With activated samples, **1a** meets these requirements, in the condition of 0.1 MPa CO_2 and 80 °C, its application in the conversion of carbon dioxide into ring carbonate with high efficiency was studied.

With epichlorohydrin as the model substrate, the reaction conditions were optimized by changing the temperature, time and pressure of CO_2. The experimental reaction of cycloaddition CO_2 was carried out with epoxychloropropane as the model substrate, **1a** as the catalyst and TBAB as the auxiliary catalyst. The results showed that the conversion rate of epoxy compound into corresponding cyclocarbonate was 84.3% within 6 h. The reaction time was extended to 9 h, and the conversion rate of epoxide was 99% (Table 2). Controlled experiments without **1a** and TBAB catalysts showed a lower rate of conversion of epoxides to ring carbonate, indicating their basic requirements. It is known that the auxiliary catalyst TBAB ACTS as a nucleophile to promote ring opening of epoxides. It should be noted that no undesirable by-products were observed in the catalytic reaction, and circular carbonates were formed with 100% selectivity. The range of this reaction is further extended to cycloaddition with other alkyl epoxides under similar reaction conditions, resulting in an increase in the length of the alkyl chain. It is interesting to note, with epoxides alkyl chain length rising from propylene oxide to 1,2-epoxydecane cyclic carbonate yield reduces gradually. This investigation can be on account of the finite diffusion of substrates with a larger size (1,2-epoxydecane) than the aperture of **1a**. In addition, to exclude the possibility of Co(II) ions leaching from **1a** into the solution from the survey

results, the catalytic reaction was stopped after 3 h, and the conversion rate of epichlorohydrin was found to be 39.3%. Then filter to remove the **1a** catalyst and stir the filtrate for 6 h, analysis of the product after 9 h revealed that the conversion rate of epichlorohydrin increased only slightly (about 3%), which may be related to the presence of TBAB catalyst.

Based on the above research results and previous reports, the possible mechanism of CO_2 cycloaddition reaction was proposed, and events sequence was revealed within Scheme 1. The Co(II) site with unsaturated coordination ACTS as lewis acid and coordinates with epoxides, That leads to the polarization of the carbon–oxygen bond. Meanwhile, the polarization of CO_2 molecules can also be found by interacting with the alkaline-HH_2 group of the Hdatz ligand. Then nitrile rubber (Br^-) and nitrile rubber (TBAB) then conduct nucleophilic attacks on carbon atoms with low steric hindrance in active epoxides, causes the epoxy ring to open. Then the oxygen anion in the ring opening reacts with CO_2 to form alkyl carbonate anion, the final ring carbonate is formed by intramolecular Br^-. Synchronous recovery of catalyst.



Scheme 1. The proposed mechanism of the catalytic cycloaddition reaction of epoxides to CO_2 catalyzed via **1a**

3.4 *Compound improve the cardiac functions of acute heart failure rats*

The LVEF and LVFS were the important marker of cardiac functions, thus, in this experiment, the values of the acute heart failure rats after compound treatment was measured when the combine treatment ended. According to the results of Figure 4, we can find the left ventricular systolic function of rats with acute heart failure was weaker than that of the control group. However, this damage could be reversed by compound treatment obviously, almost return to normal level. The result suggested that compound has excellent protective function on the cardiac functions of acute heart failure rats.

3.5 *Compound up-regulates the expression of Hif-1α*

In recent years, many reports revealed the important function of hypoxia inducible factor 1α (*Hif-1α*) within the procession of acute heart failure. Hif-1α is a transcription factor, which is only stabilized in a hypoxia environment, its up-regulation may reduce acute heart failure progression. Thus, within this experiment, *Hif-1α* relative was measured at the 3rd and 7th day of the combine treatment. According to

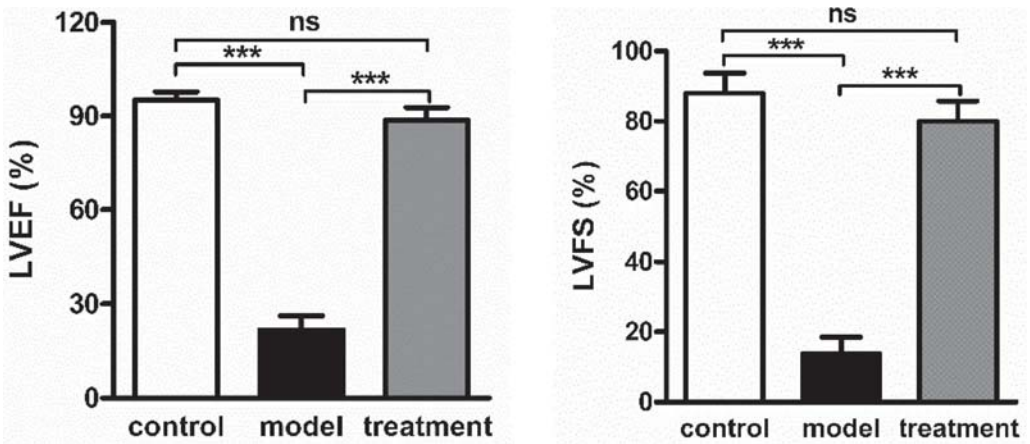


Figure 4. Improved cardiac functions of acute heart failure rats after compound treatment. Acute heart failure rats were treated with 5 mg/kg compound drug for 7 days, the cardiac effects were assessed via determining LVFS along with LVEF. $p<0.05$ was the significant difference, this study required repeating three or more times.

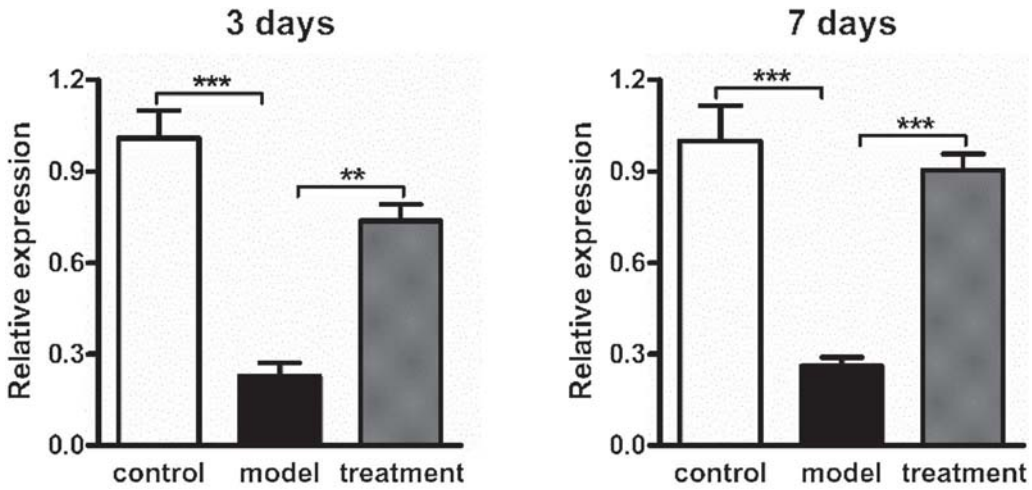


Figure 5. Increased level of the *Hif-1α* after compound treatment. The acute heart failure rats were given compound at the dosage of 5 mg/kg for 7 days treatment, the cardiomyocytes were collected for the *Hif-1α* expression detection with RT-PCR. The research was carried out three or more times.

the results of Figure 5, *Hif-1α* expression was significantly increased compared with the model group, which indicates the improved level of the hypoxia condition.

4. Conclusion

To sum up, under the conditions of solvothermal, we have triumphantly prepared a novel highly porous metal-organic framework. The measurement of X-ray of single crystal structure exhibited **1**'s three-dimensional skeleton structure with one-dimensional channels of dimensions decorated with coordinately unsaturated Co(II) ions as well as the free $–NH_2$ groups in the crystallographic a-axis. The activated MOF (**1a**) has a fine affinity for CO_2 molecules and a fine catalytic performance for the conversion of CO_2 with internal epoxides along with various terminal. In biological study, the protective activity of this compound on acute heart failure was evaluated. The LVEF and LVFS data indicated the compound could improve the cardiac functions of acute heart failure rats. And the *Hif-1α* expression results indicated the mechanism of the new compound.

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Data availability The data used to support the findings of this study are included within the article.

Conflicts of interest The author(s) declare(s) that there is no conflict of interest regarding the publication of this paper.

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