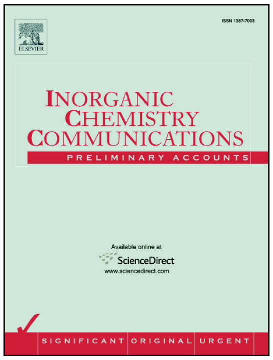


A mononuclear Cu(II)-based metal-organic framework as an efficient heterogeneous catalyst for chemical transformation of CO2 and Knoevenagel condensation reaction

Feng Guo

PII: S1387-7003(18)31120-1
DOI: https://doi.org/10.1016/j.inoche.2019.01.022
Reference: INOCHE 7238

To appear in: *Inorganic Chemistry Communications*

Received date: 19 December 2018
Revised date: 9 January 2019
Accepted date: 16 January 2019

Please cite this article as: Feng Guo , A mononuclear Cu(II)-based metal-organic framework as an efficient heterogeneous catalyst for chemical transformation of CO2 and Knoevenagel condensation reaction. Inoche (2019), https://doi.org/10.1016/j.inoche.2019.01.022

A mononuclear Cu(II)-based metal-organic framework as an efficient heterogeneous catalyst for chemical transformation of CO_2 and Knoevenagel condensation reaction

Feng Guo,[a*]

[a] *School of Chemistry and Chemical Engineering, Yangtze Normal University, Chongqing 408100, China*

Corresponding Authors: Prof. Feng Guo

E-mail address: guofeng1510@yeah.net

Abstract

A novel 2D Cu(II) metal-organic framework, $[(Cu(L)_2\cdot(H_2O)_2\cdot(NO_3)_2]_n$ (namely **1**), can be synthesized by the self-assemble of 4-(5-methyl-3-pyridine)-1,2,4-triazole (namely L) and Cu(II) ion. The as-synthesized MOF **1** has mononuclear $\{CuN_4O_2\}$ and only one coordination mode of this L. The inorganic parts and organic ligands are connected by each other to construct a 2D layer framework. The obtained MOF **1** has been characterized and analysed in detail by single crystal X-ray diffraction, powder X-ray diffraction (PXRD), elemental analysis, Fourier-transform infrared spectra (FT-IR), and thermogravimetric analysis (TGA). Furthermore, MOF **1** has open Cu metal sites and lots of N atoms as Lewis basic sites, resulting in that it can be employed as a heterogeneous catalysis for chemical transformation of CO_2 and epoxides into targeted cyclic carbonate and Knoevenagel condensation reaction. It also can be reused four times at least without significantly reduced activity for these catalytic reactions.

Keywords: metal-organic framework; catalysis; carbon dioxide; epoxide; Knoevenagel condensation reaction.

Up to now, super large amounts of metal-organic frameworks (MOFs),[1-3] as a novel class of inorganic-organic hybrid crystalline materials, have really attracted surge of interesting, not only thanks to their fascinating structures,[4-6] but also their potential practical applications in small gas adsorption,[7-12] enzyme immobilization,[13, 14] luminescence sensor,[15-27] optical device material,[28-30] and catalysis[31-35]. Among allthe related works, design and preparation of novel MOFs with interesting frameworks is still a very interesting research field. Various distinctive constructions and topologies have been successfully designed and generated by rationally using the synthetic strategy, including organic linker, metal cation, temperature, pH value, pressure, and solvent system.[36-39] Innumerous influencing factors, it is almost no doubt that the organic linkers really show a very important role to adjust and control the skeleton structures. Multifarious methods have been tried to design and prepare novel linkers to synthesize interesting topologies and attractive frameworks. The neutral ligands based on pyridine rings without any carboxylic acid groups have been widely used to construct cationic MOFs,[40-44] which can be used as host materials for exchanging or capturing pollutions. Inspired by many similar investigations on design such MOFs, it is also very interesting research area to design and synthesize an organic ligand to construct these cationic MOFs in the crystallographic point, which not only can form lots of fascinating architectures but also excellent applications. As we know, CO_2 is a common greenhouse gas to result in a series of serious problems to affect people's life and health. The most promising method to solve this problem is CO_2 capture and transformation. CO_2 as C1 source can react with epoxides to generate cyclic carbonates, which is a useful raw and processed material in numerous industrial fields.[45] In addition, the Knoevenagel condensation reaction is also a common organic reaction and widely used in many application fields. Hence, it is a significant important job to design and prepare high-efficient heterogeneous catalysts for these reactions.

In this communication, we selected a neutral organic ligand without carboxylic acid groups 4-(5-methyl-3-pyridine)-1,2,4-triazole (namely L).[46] As we expected, this ligand can be successfully assembled with $Cu(NO_3)_2$ to synthesize a novel two-dimensional (2D) cationic MOF material, $[(Cu(L)_2\cdot(H_2O)_2\cdot(NO_3)_2]_n$ (namely **1**). The blue block crystals can be generated *via* mixing this ligand and $Cu(NO_3)_2\cdot2.5H_2O$ in a 20 mL capped vessel containing water and EtOH mixed solution and evaporation at room temperature for one week.[47] Meanwhile, the resultant **1** can be considered as a high-efficient heterogeneous catalysis not only for chemical conversion of CO_2 and epoxides into cyclic carbonate without any solvent due to the open metal Cu(II) sites as Lewis acid sites, but also can catalyze the Knoevenagel condensation reaction because of their Lewis basic sites.

The single crystal X-ray diffraction data showed that the obtained 2D MOF **1** crystallizes in the trigonal crystal system and *R*–3c space group.[48] In the corresponding asymmetric unit, it contains a half Cu(II), one L organic ligand, a half NO_3^-, one third NO_3^-, and one terminal coordinated H_2O molecule (Fig. S1). As seen in Fig. 1a, the L ligand has only one coordination mode, which connects two crystallographic independence Cu(II) cations by the priding N atom and one atom in the 1,3,4-triazole group. On the other hand, each Cu(II) has only one coordinated mode and octahedral configurationas shown in Figs. 1b and 1c, which is linked with four nitrogen atoms (Cu-N = 2.0227-2.0314 Å) form three different ligands and two oxygen atoms (Cu-O = 2.4296 Å) coming from two coordinated water molecules. As illustrated in Figs. 1d and 1e, the terminal framework shows a 2D structure and packs as a hexagon structure, which also contains NO_3^- in all structures as counter ions. The results obviously demonstrate that **1** not only has lots of open metal Cu(II) sites but also contains lots of free nitrogen atoms as Lewis basic sitessimultaneously, resulting in its great potential applications, especially in the catalytic field.

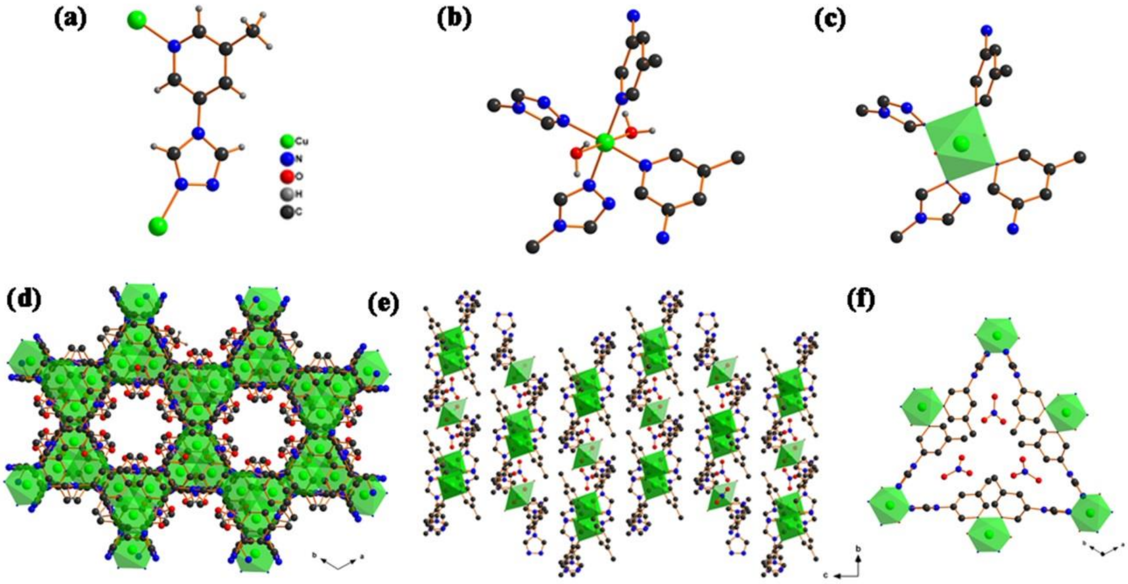


Fig. 1.(a) The coordination mode of the L ligand; (b and c) the coordination environment octahedral configurationof Cu(II); (d and e) view of a single 2D network and the 2D networks along different axises (the hydrogen atoms are omitted for clarity and C, black; N, blue; O, red; Cu, green); (f) the triangle in the 2D layer.

As obviously displayedin Fig. 2a, the TGA result of the fresh as-synthesized **1** demonstrated a slow weight loss of 28.76% before 300 °C prevailingly due to the loss of guest and coordinated molecules (calculated 28.88%). When the heating temperature further increased in air, the structure of MOF **1** began to decompose, resulting in the last remnant CuO (expt: 14.83%; calcd: 14.71%). The PXRD profile of the as-synthesized solid sample was carried outat ambient temperature. The characteristic diffraction lines of prepared **1** are similar with the simulated from the single crystal data of **1** (Fig. 2b). The PXRD profiles exhibited that the final phase purity of the obtained crystalline materials.

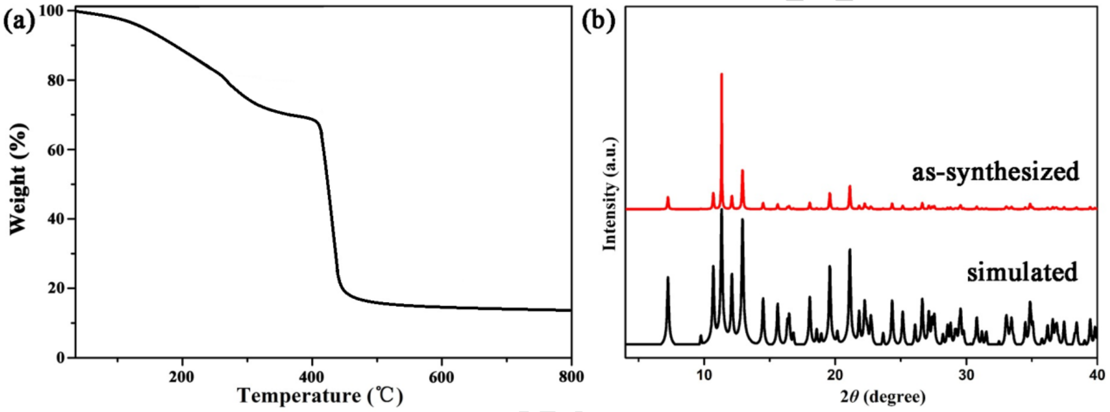
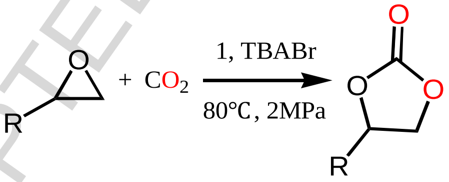
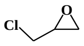
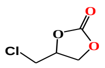
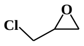
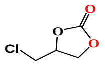
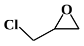
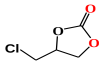


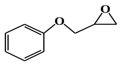
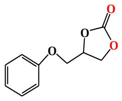
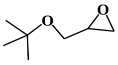
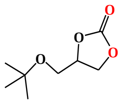
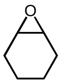
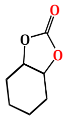
Fig. 2. (a) The TGA data of the as-synthesized **1**; (b) the PXRD patterns of the simulated (black) and the as-synthesized (red) sample.

In virtue ofopen Cu(II) metal sites in **1**, MOF **1** was applied to as a Lewis acid catalysis to investigateits catalytic performancefor the solvent-free conversion of CO_2 and epoxides into cyclic carbonate (Table 1).[49-56] The as-synthesized **1** was collected by filtering and drying in air. In a typical trial, a mixture of epoxide substrate (20mmol), catalyst (**1**, 100 mg), and tetrabutylammonium bromide (TBABr, 100mg) as a co-catalyst was performed the catalytic reaction with 2.0 MPa CO_2 at 85°C for 4 hours under the free-solvent condition. Table 1 contained the results of the CO_2 cycloaddition reaction with different epoxides, which was easily calculated by using the GC method. As seen in entry 1, the propylene carbonate yield of CO_2 and 2-(chloromethyl)oxirane reached up to 99% after 4 hours. Nevertheless, the final propylene carbonate efficiencies of only MOF **1** or TBABr were only 8% and 11% under the same reaction besides the catalytic as control experiments to illustrate the necessary of MOF **1** (entries 2 and 3). The different epoxides were further expanded to investigate the influence of different functional groups for this CO_2 reaction using MOF **1** as catalytic. The measurement results illustrated that the yields were decreased from 99% for propylene oxide to 91% for styrene oxide, 83% for *tert*-butyl glycidyl ether, and 67% of styrene oxide, respectively (entries 4-6). Based on the other similar reports, this performance can be predominantly ascribed to large-sized epoxides and different electronic effects of these groups in substrates to influence the catalytic results.[49-56] The catalytic mechanism may be attributed to the common process as the other reports. Firstly, this reaction can be initiated by the interaction between the open Cu(II) Lewis site and the oxygen atom in the epoxide ring. Then, the epoxide rings are further opened by the Br^- ion from TBABr to attack the less-hindered carbon atoms from the coordinated epoxides. Subsequently, the oxygen anions of the opened epoxy rings can rapidly interact with the surrounding CO_2 molecules to form alkycarbonate anions. Finally, the corresponding cyclic carbonates can be achieved through the cyclization process.[49-56]

Table 1. The catalytic results of cyclic carbonates from CO_2 and different epoxides.

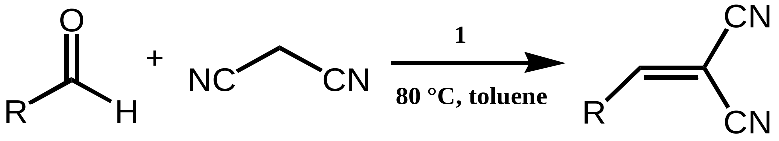


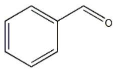
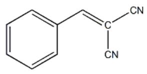
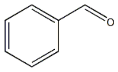
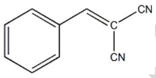
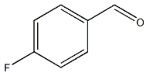
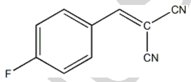
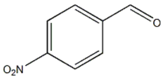
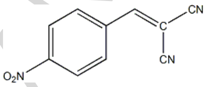
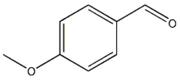
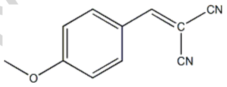
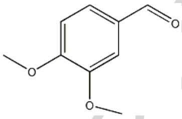
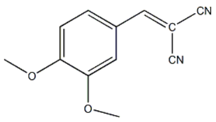
Entry	Substrate	Product	Yield (%)
1			99
2			8
3			11

4			91
5			83
6			67

Meanwhile, the basic catalytic ability of **1** for the Knoevenagel condensation reaction was further studied in detail due to the various Lewis basic sites in the whole structure like the other previous reports.[57-65] The typical experiment was performed as the following condition in Table 2: substrate (1 mmol), malononitrile (1.1 mmol), catalyst (**1**, 100 mg), and toluene (5 mL) in a 20 mL glass flask at 80 °C under continuously stirring. The corresponding yields of targeted products were successfully monitored by applying the GC approach. Table 2 summed up the results based on different aldehyde substrates and malononitrile in the presence of **1**. As found in entry 1 of Table 2, the final yield of 2-benzylidenemalononitrile was about 96% after reacting 3 hours. To prove the necessary of MOF **1** for this reaction, the catalytic reaction almost didn't happen in the absent of **1** as a control experiment (entry 2). Various different substituted aldehyde reactants have been applied to study the effects of different substituents with the catalysis **1**. The catalytic results furthermore demonstrated that the superior conversions (>99%) can be detected during existing the withdrawing groups (–F and –NO_2, entries 3 and 4), while the catalytic yields of the electron donor groups on the aldehyde for one –OMe group in entry 5 and two –OMe groups in entry 6 were reduced to 89 and 74, respectively. The catalytic performance is also similar with the previous reports.[57-65] The catalytic mechanism for this reaction may be ascribed to lots of N atoms in MOF **1**, which can served as common Lewis basic sites to activate this reaction like other similar reports.[57-63]

Table 2. The yields of Knoevenagel condensation reaction.



Entry	Substrate	Product	Yield (%)
1			96
2			5
3			>99
4			>99
5			89
6			74

Additionally, it is significantly important for heterogeneous catalyses to handily recollect and reuse after reactions. For MOF **1**, it can be recycled by centrifuging at 8000 r·min^{-1} for 3 minutes and further re-catalyse these two different reactions. The reactions of CO_2 and 2-(chloromethyl)oxirane, and benzaldehyde and malononitrileas the reaction models. As shown in Fig. 3, Figs. S2, and S3, the PXRD profiles of reused **1** after using four times and the catalytic performance both clearly indicated that the structure of **1** can retain very well for these catalytic reactions and the catalytic effects. The above mentioned results obviously illustrated that **1** can be implemented as a bifunctional heterogeneous catalysis for the solvent-free chemical transformation of CO_2 and epoxides into cyclic carbonate, and the Knoevenagel condensation reaction.

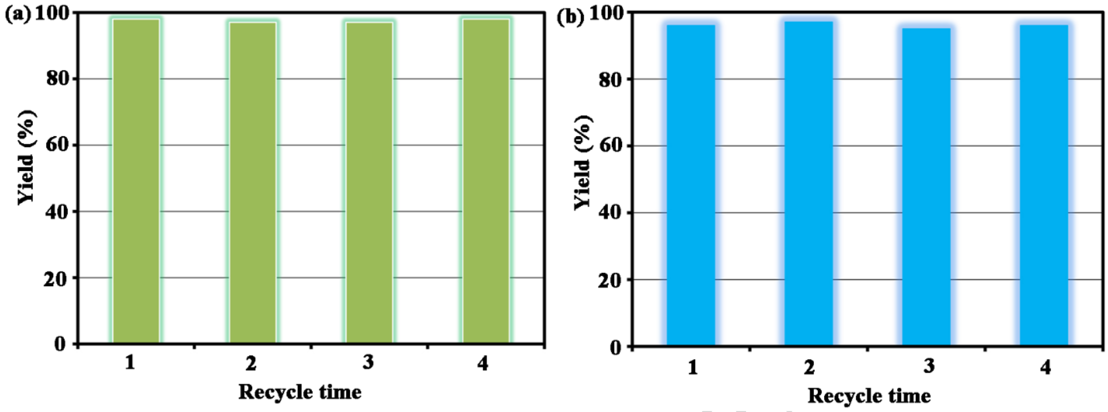


Fig. 3. The recyclability of MOF **1** for chemical transformation of CO_2 (a) and Knoevenagel condensation reaction (b).

In conclusion, a novel mononuclear Cu(II)-based metal-organic framework was successfully generated, which can be considered as an outstanding heterogeneous catalyst for the CO_2 cycloaddition reaction and Knoevenagel condensation reaction. More importantly, MOF **1** exhibited excellent recyclability for these reactions at least four times. We hope that this work can offer a useful and meaningful method to use such ligands to synthesize MOFs with targeted functions.

References

[1] L. Zhu, X.-Q. Liu, H.-L. Jiang, L.-B. Sun, Metal–organic frameworks for heterogeneous basic catalysis, Chem. Rev. 117 (2017) 8129-8176.

[2] H. He, Y.-Q. Xue, S.-Q. Wang, Q.-Q. Zhu, J. Chen, C.-P. Li, M. Du, A double-walled bimetal–organic framework for antibiotics sensing and size-selective catalysis, Inorg. Chem. 57 (2018) 15062-15068.

[3] Y.-J. Yang, F.-S. Wang, D. Liu, G.-H. Cui, A unique (4, 4, 5)-connected 3D zinc (II) metal-organic framework for highly efficient photodegradation of Rhodamine B under UV light, Inorg. Chem. Commun. 100 (2019) 60-63.

[4] H. He, F. Sun, N. Zhao, R. Yuan, G. Zhu, Three novel zinc(II) metal-organic frameworks based on three tetrazolate ligands: synthesis, structures and photoluminescence, RSC Adv. 4 (2014) 21535-21540.

[5] Z.-W. Zhai, S.-H. Yang, M. Cao, L.-K. Li, C.-X. Du, S.-Q. Zang, Rational design of three two-fold interpenetrated metal–organic frameworks: luminescent Zn/Cd-metal–organic frameworks for detection of 2, 4, 6-trinitrophenol and nitrofurazone in the aqueous phase, Cryst. Growth Des. 18 (2018) 7173-7182.

[6] H. He, J. Du, H. Su, Y. Yuan, Y. Song, F. Sun, Four new metal-organic frameworks based on bi-,tetra-, penta-, and hexa-nuclear clusters derived from 5-phenyldiazenyl)isophthalic acid: syntheses, structures and properties, CrystEngComm 17 (2015) 1201-1209.

[7] H. He, Y. Song, C. Zhang, F. Sun, R. Yuan, Z. Bian, L. Gao, G. Zhu, A highly robust metal-organic framework based on an aromatic 12-carboxyl ligand with highly selective adsorption of CO_2 over CH_4, Chem. Commun. 51 (2015) 9463-9466.

[8] Y. Zhang, L. Wang, M. Zeng, M. Kurmoo, Fabrication of a capillary column coated with the four-fold-interpenetrated MOF Cd(D-Cam)(tmdpy) for gas chromatographic separation, Inorg. Chem. Commun. 83 (2017)123-126.

[9] H. He, F. Sun, S. Ma, G. Zhu, Reticular synthesis of a series of HKUST-like MOFs with carbon dioxide capture and separation, Inorg. Chem. 55 (2016) 9071-9076.

[10] C. Lv, W. Li, Y. Zhou, J. Li, Z. Lin, A new porous Ca(II)-organic framework with acylamide decorated pores for highly efficient CO_2 capture, Inorg. Chem. Commun. 99 (2019) 40-43.

[11] H. He, F. Sun, B. Aguila, J. A. Perman, S. Ma, G. Zhu, A bifunctional metal-organic framework featuring the combination of open metal sites and Lewis basic sites for selective gas adsorption and heterogeneous cascade catalysis, J. Mater. Chem. A 4 (2016) 15240-15246.

[12] D. Liu, G. Wen, W. Zhou, Two anionic low-connectivity microporous indium-organic frameworks with selectivity adsorption of CO_2 over CH_4, Inorg.

Chem. Commun. 95 (2018) 22-26.

[13] H. He, H. Han, H. Shi, Y. Tian, F. Sun, Y. Song, Q. Li, G. Zhu, Construction of thermophiliclipase-embedded metal–organic frameworks *via* biomimetic mineralization: a biocatalyst for ester hydrolysis and kinetic resolution, ACS Appl. Mater. Interfaces 8 (2016) 24517–24524.

[14] X. Lian, Y. Huang, Y. Zhu, Y. Fang, R. Zhao, E. Joseph, J. Li, J.-P. Pellois, H.-C. Zhou, Enzyme-MOF nanoreactoractivates nontoxic paracetamol for cancer therapy, Angew. Chem., Int. Ed. 57 (2018), 5725-5730.

[15] H. He, Y. Song, F. Sun, Z. Bian, L. Gao, G. Zhu, A porous metal-organic framework formed by a V-shaped ligand and Zn(II) ion with highly selective sensing for nitroaromatic explosives, J. Mater. Chem. A 3 (2015) 16598-16603.

[16] N. Xu, Q. Zhang, B. Hou, Q. Cheng, G. Zhang, A novel magnesium metal–organic framework as a multi responsive luminescent sensor for Fe(III) ions, pesticides, and antibiotics with high selectivity and sensitivity, Inorg. Chem. 57 (2018) 13330-13340.

[17] H. He, Y. Song, F. Sun, N. Zhao, G. Zhu, Sorption properties and nitroaromatic explosives sensing based on two isostructural metal-organic frameworks, Cryst. Growth Des. 15 (2015)2033-2038.

[18] S.-Q. Lu, Y.-Y. Liu, Z.-M. Duan, Z.-X. Wang, M.-X. Li, X. He, Improving water-stability and porosity of lanthanide metal–organic frameworks by stepwise synthesis for sensing and removal of heavy metal ions, Cryst. Growth Des. 18 (2018) 4602-4610.

[19] H. He, F. Sun, J. Jia, Z. Bian, N. Zhao, X. Qiu, L. Gao, G. Zhu, Fluorescent dodecapus in 3D framework, Cryst. Growth Des. 14 (2014) 4258-4261.

[20] H. He, D.-Y. Zhang, F. Guo, F. Sun, A versatile microporous Zinc(II) metal–organic framework for selective gas adsorption, cooperative catalysis, and luminescent sensing. Inorg. Chem. 57 (2018) 7314-7320.

[21] W.-X. Li, J.-H. Gu, H.-X. Li, M. Dai, D. J. Young, H.-Y. Li, J.-P. Lang, Post-synthetic modification of a two-dimensional metal–organic framework *via* photo dimerization enables highly selective luminescent sensing of aluminium

(III), Inorg. Chem. 57 (2018) 13453-13460.

[22] P. C. Rao, S. Mandal, Europium-based metal–organic framework as a dual luminescence sensor for the selective detection of the phosphate anion and Fe^{3+} ion in aqueous media, Inorg. Chem. 57 (2018) 11855-11858.

[23] H. He, S.-H. Chen, D.-Y. Zhang, R. Hao, C. Zhang, E.-C. Yang, X.-J. Zhao, A micrometer-sized europium(III)–organic framework for selective sensing of the $Cr_2O_7^{2-}$ anion and picric acid in water systems. Dalton Trans. 46 (2017) 13502-13509.

[24] D. K. Singha, P. Majee, S. Mandal, S. K. Mondal, P. Mahata, Detection of pesticides in aqueous medium and in fruit extracts using a three-dimensional metal–organic framework: experimental and computational study, Inorg. Chem. 57 (2018) 12155-12165.

[25] H. He, S.-H. Chen, D.-Y. Zhang, E.-C. Yang, X.-J. Zhao, A luminescent metal–organic framework as an ideal chemosensor for nitroaromatic compounds. RSC Adv. 7 (2017) 38871-38876.

[26] L.-Q. Zuo, T.-F. Zhang, Z.-K. Zhang, J.-X. Hou, G.-J. Liu, J.-L. Du, L.-J. Li, A 3D binuclear salen-based multifunctional MOF: Degradation of MO dye and highly selective sensing of Fe^{3+}, Inorg. Chem. Commun. 99 (2019) 113-118.

[27] S.-Q. Wang, H. He, Construction and structural diversification of eight rare-earth M^{III}coordination complexes with 5-bromonicotinic acid *N*-oxide, Inorg. Chem. Commun. 97 (2018) 63-68.

[28] D. Zhang, Z.-Z. Xue, J. Pan, M.-M. Shang, Y. Mu, S.-D. Han, G.-M. Wang, Solvated lanthanide cationic template strategy for constructing iodoargentates with photoluminescence and white light emission, Cryst. Growth Des. 18 (2018) 7041-7047.

[29] H. He, F. Sun, T. Borjigin, N. Zhao, G. Zhu, Tunable colors and white-light emission based on a microporous luminescent Zn(II)-MOF, Dalton Trans. 43 (2014) 3716-3721..

[30] Y. Wang, S.-H. Xing, F.-Y. Bai, Y.-H. Xing, L.-X. Sun, Stable Lanthanide–organic framework materials constructed by a triazolylcarboxylate ligand: multifunction

detection and white luminescence tuning, Inorg. Chem.57 (2018) 12850-12859.

[31] Y. Fan, Y. Ren, J. Li, C. Yue, H. Jiang, Enhanced activity and enantioselectivity of henry reaction by the post synthetic reduction modification for a chiral Cu(salen)-based metal–organic framework, Inorg. Chem. 57 (2018) 11986-11994.

[32] W.-M. Liao, J.-H. Zhang, Z. Wang, Y.-L. Lu, S.-Y. Yin, H.-P. Wang, Y.-N. Fan, M. Pan, C.-Y. Su, Semiconductive amine-functionalized Co(II)-MOF for visible-light-driven hydrogen evolution and CO_2 reduction, Inorg. Chem. 57 (2018) 11436-11442.

[33] Z. Li, Y. Liu, X. Kang, Y. Cui, Chiral metal–organic framework decorated with TEMPO radicals for sequential oxidation/asymmetric cyanationcatalysis. Inorg. Chem. 57 (2018) 9786-9789.

[34] X. Deng, J. Albero, L. Xu, H. Garcia, Z. Li, Construction of a stable Ru–Re hybrid system based on multifunctional MOF-253 for efficient photocatalytic CO_2 reduction, Inorg. Chem.57 (2018) 8276-8286.

[35] X. Yan, K. Wang, X. Xu, S. Wang, Q. Ning, W. Xiao, N. Zhang, Z. Chen, C. Chen, Brønsted basicity in metal-organic framework-808 and its application in base-free catalysis, Inorg. Chem.57 (2018) 8033-8036.

[36] H.-Y. Liu, J. Liu, G.-M. Gao, H.-Y. Wang, Assembly of two metal–organic frameworks based on distinct cobalt dimeric building blocks induced by ligand modification: gas adsorption and magnetic properties, Inorg. Chem.57 (2018) 10401-10409.

[37] Y. Wang, H. Cao, B. Zheng, R. Zhou, J. Duan, Solvent- and pH-dependent formation of four zinc porous coordination polymers: framework isomerism and gas separation, Cryst. Growth Des. 18 (2018) 7674-7682.

[38] M.-X. Du, M-S. Wang, G.-C. Guo, Solvent-dependent chirality transformation: Construction of a helical homochiral silver(I) MOF using the V-shaped ligand 3-Aminobenzoate, Inorg. Chem. Commun. 92 (2018) 22-26.

[39] H. He, F. Sun, H. Su, J. Jia, Q. Li, G. Zhu, Syntheses, structures and luminescence properties of three metal–organic frameworks based on 5-(4-(2H-tetrazol-5-yl)phenoxy)isophthalic acid, CrystEngComm 16 (2014)

339-343.

[40] H.-R. Fu, Z.-X. Xu, J. Zhang, Water-stable metal-organic frameworks for fast and high dichromate trapping via single-crystal-to-single-crystal ion exchange, Chem Mater, 27 (2014) 205-210.

[41] J. Li, X. Wang, G. Zhao, C. Chen, Z. Chai, A. Alsaedi, T. Hayat, X. Wang, Metal-organic framework-based materials: superior adsorbents for the capture of toxic and radioactive metal ions, Chem. Soc. Rev. 47 (2018) 2322-2356.

[42] H. Fei, C. S. Han, J. C. Robins, S. R. Oliver, A cationic metal-organic solid solution based on Co(II) and Zn(II) for chromate trapping, Chem. Mater. 25 (2013) 647-652.

[43] H. Fei, M. R. Bresler, S. R. Oliver, A new paradigm for anion trapping in high capacity and selectivity: crystal-to-crystal transformation of cationic materials, J. Am. Chem. Soc. 133 (2011) 11110-11113.

[44] X. X. Li, H. Y. Xu, F. Z. Kong, R. H. Wang, A cationic metal-organic framework consisting of nanoscale cages: capture, separation, and luminescent probing of $Cr_2O_7^{2-}$ through a single-crystal to single-crystal process, Angew. Chem., Int. Ed. 52 (2013) 13769-13773.

[45] M. Yoshida, M. Ihara, Novel methodologies for the synthesis of cyclic carbonates, Chem. Eur. J. 10 (2004) 2886-2893.

[46] B. Ding, J. Huo, Y. Liu, X. Wang, X. Su, X. Wu, Z. Zhu, J. Xia, Triazole based Ag coordination clusters: synthesis, structural diversity and anion exchange properties, RSC Adv. 5 (2015) 83415-83426.

[47] Preparation of $[(Cu(L)_2\cdot(H_2O)_2\cdot(NO_3)_2]_n$ (namely **1**): A mixture of $Cu(NO_3)_2\cdot 2.5H_2O$ (10 mg, 0.043 mmol), L (5 mg, 0.031 mmol), ethanol (EtOH, 0.5 mL) and H_2O (1 mL) was putted into a 20 mL capped vessel and evaporated at room temperature for one week. The polyhedron blue crystals of the as-synthesized **1** were collected by filtration and dried in air (yield: 58% based on L). EA (%) Calc. for $C_{16}\ H_{20}\ N_{10}\ O_8$ Cu: C, 35.29; H, 2.94; N, 25.74; Found: C, 35.21; H, 2.98; N, 25.79. The selected FT-IR result (KBr pellet cm^{-1}, Fig. S4): 3410 (br), 3122 (s), 3054 (s), 1612 (s), 1545 (s), 1351 (s), 1205 (s), 1154 (s), 1111

(s), 1055 (s), 967 (s), 876 (s), 697 (s), 642 (s).

[48] Crystal data: $C_{48}H_{60}O_{21}N_{29}Cu_3$: F_w= 1569.87, trigonal, space group *R*-3c, *a*= 16.5216(12), *b*= 16.5216(12), *c*= 46.798(4)Å, *α*= 90, *β*= 90, *γ*=120,*V* = 11062.6(18) Å^3, *Z* = 6, *Dc*= 1.414 g cm^{-3}, *μ* = 1.745 mm^{-1}, *R*(int) = 0.021, *Nref* = 2457, R_1=0.0753, wR_2 = 0.2336 [I > 2σ(I)], R_1=0.0789, wR_2 = 0.2402 [all data], GOF= 1.080. The single crystal data of **1**wasmeasured on a Bruker SMART CCD diffractometer with Cu K_α (λ = 0.71073 Å) radiation at 293(2) K. The final crystal structure can be solved by the direct method and further refined by the full-matrixleast-squares on F^2 of the obtained crystal data by using the SHELXL-2015.[66] Allnon-hydrogen atoms were also refined through anisotropic displacement parameters. The selected bond lengths and angles of **1** are bothsummarised in Table S1.

[49] H. He, J. A. Perman, G. Zhu, S. Ma, Metal-organic frameworks for CO_2 chemical transformations, Small 12 (2016) 6309-6324.

[50] H. He, Q. Sun, W. Gao, J. A. Perman, F. Sun, G. Zhu, B. Aguila, K. Forrest, B. Space, S. Ma, A stable metal–organic framework featuring a local bufferenvironment for carbon dioxide fixation, Angew. Chem., Int. Ed. 57 (2018), 4657 -4662.

[51] R. Zou, P.-Z. Li, Y.-F. Zeng, J. Liu, R. Zhao, H. Duan, Z. Luo, J.-G. Wang, R. Zou, Y. Zhao, Bimetallic metal-organic frameworks: probing the Lewis acid site for CO_2 conversion, Small 12 (2016) 2334-2343.

[52] A. C. Kathalikkattil, R. Roshan, J. Tharun, R. Bahu, G.-S. Jeong, D.-W. Kim, S. J. Cho, D.-W. Park, A sustainable protocol for the facile synthesis of zinc-glutamate MOF: an efficient catalyst for room temperature CO_2 fixation reactions under wet conditions, Chem. Commun. 52 (2016) 280-283.

[53] J. Song, Z. Zhang, S. Hu, T. Wu, T. Jiang, B. Han, MOF-5/n-Bu_4NBr: an efficient catalyst system for the synthesis of cyclic carbonates from epoxides and CO_2 under mild conditions, Green Chem. 11 (2009) 1031-1036.

[54] D. Ma, B. Li, K. Liu, X. Zhang, W. Zou, Y. Yang, G. Li, Z. Shi, S. Feng, Bifunctional MOF heterogeneous catalysts based on the synergy of dual

functional sites for efficient conversion of CO_2 under mild and co-catalyst free conditions, J. Mater. Chem. A 3 (2015), 23136-23142.

[55] B. Ugale, S. S. Dhankhar, C. M. Nagaraja, Exceptionally stable and 20-connected Lanthanide metal-organic frameworks for selective CO_2 capture and conversion at atmospheric pressure. Cryst. Growth Des. 18 (2018) 2432–2440.

[56] J. Liang, Y.-Q. Xie, Q. Wu, X.-Y. Wang, T.-T. Liu, H.-F. Li, Y.-B. Huang, R. Cao, Zinc porphyrin/imidazolium integrated multivariate zirconium metal-organic frameworks for transformation of CO_2 into cyclic carbonates, Inorg. Chem. (57) 2018, 2584-2593.

[57] L. Hu, G.-X. Hao, H.-D. Luo, C.-X. Ke, G. Shi, J. Lin, X.-M. Lin, U. Y. Qazi, Y.-P. Cai, Bifunctional 2D Cd(II)-based metal–organic framework as efficient heterogeneous catalyst for the formation of C–C bond, *Cryst. Growth Des.*18 (2018) 2883–2889.

[58] C. Yao, S. Zhou, X. Kang, Y. Zhao, R. Yan, Y. Zhang, L. Wen, A cationic zinc–organic framework with Lewis acidic and basic bifunctional sites as an efficient solvent-free catalyst: CO_2 fixation and Knoevenagel condensation reaction, Inorg. Chem. 57 (2018) 11157-11164.

[59] Y. Zhang, Y. Wang, L. Liu, N. Wei, M.-L. Gao, D. Zhao, Z.-B. Han, Robust bifunctional lanthanide cluster based metal–organic frameworks (MOFs) for tandem deacetalization–Knoevenagel reaction, Inorg. Chem. 57 (2018) 2193-2198.

[60] W. Fan, Y. Wang, Z. Xiao, L. Zhang, Y. Gong, F. Dai, R. Wang, D. Sun, A stable amino-functionalized interpenetrated metal-organic framework exhibiting gas selectivity and pore-size-dependent catalytic performance, Inorg. Chem. 56 (2017) 13634-13637.

[61] H. He, Q.-Q. Zhu, F. Sun, G. Zhu, Two 3D metal–organic frameworks based on Co^{II} and Zn^{II} clusters for Knoevenagel condensation reaction and highly selective luminescence sensing. Cryst. Growth Des. 18 (2018) 5573-5581.

[62] S. Zhang, H. He, F. Sun, N. Zhao, J. Du, Q. Pan, G. Zhu, A novel adenine-based zinc(II) metal-organic framework featuring the Lewis basic sites for

heterogeneous catalysis, Inorg. Chem. Commun. 79 (2017)55-59.

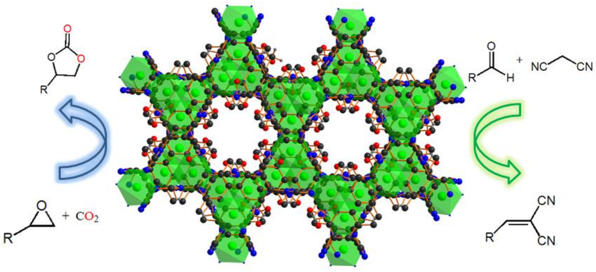
[63] F. Bigdeli, S. Abedi, H. Hosseini-Monfared, A. Morsali, An investigation of the catalyticactivity in a series of isoreticular Zn(II)-based metal-organic frameworks, Inorg. Chem. Commun. 72 (2016) 122-127.

[64] M. Joharian, S. Abedi, A. Morsali, Sonochemical synthesis and structural characterization of a new nanostructured Co(II) supramolecular coordination polymer with Lewis base sites as a new catalyst for Knoevenagel condensation, Ultrason. Sonochem. 39 (2017) 897-907.

[65] S. Beheshti, A. Morsali, Post-synthetic cation exchange in anionic metal–organic frameworks; a novel strategy for increasing the catalytic activity in solvent-free condensation reactions, RSC Adv. 4 (2014) 41825-41830.

[66] G. M. Sheldrick, Crystal Structure Refinement with SHELXL. ActaCryst. C 71 (2015), 3–8.

Graphical Abstract-Pictogram



A novel mononuclear Cu(II)-based MOF was successfully generated and used as an heterogeneous catalyst for the CO_2 cycloaddition reaction and Knoevenagel condensation reaction.

Highlights

1. A novel 2D MOF was fabricated by neutral ligand and Cu(II).
2. It can be served as a bifunctional heterogeneous catalysis.
3. It possesses excellent recyclability at least four times.