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Communication

A stable Co(II)-based metal-organic framework with dual-functional pyrazolate-carboxylate ligand: Construction and CO₂ selective adsorption and fixation

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ABSTRACT

By taking the functional advantages of both pyrazolate and carboxylate ligands, a unique dual-functional pyrazolate-carboxylate ligand acid, 4-(3,6-di(pyrazol-4-yl)-9-carbazol-9-yl)benzoic acid (H₃PCBA) was designed and synthesized. Using it, a new Co(II)-based metal-organic framework (MOF), Co₃(PC-BA)₂(H₂O)₂ (BUT-75) has been constructed. It revealed a (3,6)-connected net based on the 6-connected linear trinuclear metal node, and showed good chemical stability in a wide pH range from 3 to 12 at room temperature, as well as in boiling water. Due to the presence of rich exposed Co(II) sites in pores, BUT-75 presented high selective CO₂ adsorption capacity over N₂ at 298åK. Simultaneously, it demonstrated fine catalytic performance for the cycloaddition of CO₂ with epoxides into cyclic carbonates under ambient conditions. This work has not only enriched the MOF community through integrating diverse functionalities into one ligand but also contributed a versatile platform for CO₂ fixation, thereby pushing MOF chemistry forward by stability enhancement and application expansion. © 2020 Chinese Chemical Society and Institute of Materia Medica, Chinese Academy of Medical Sciences.

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Metal-organic frameworks (MOFs), as an emerging family of crystalline porous materials, have attracted extensive attention for their potential applications in various fields, such as gas storage and separation [1], proton conduction [2], biomedicine [3], chemical sensing [4], heterogeneous catalysis [5] and so forth. Owing to the modular nature of MOFs, their structure and function allow precise tunability by the programmed assembly of diverse organic linkers and inorganic nodes [6â 8]. However, the issue of the unsatisfactory chemical stability of MOFs has limited their practical applications.

Based on Pearsonâ's hard/soft acid/base (HSAB) principle [9], MOFs constructed either from high-valent metals (hard acids, including Zr^{4+} , Hf^{4+} , Fe^{3+} , Al^{3+}) and carboxylate ligands (hard bases) [10,11], or from low-valent metal ions (soft acids, including Zn^{2+} , Co^{2+} , Ni^{2+}) and azolate ligands (soft bases) [12,13], inherently show good chemical stability originated from the robust coordination bonding. Despite excellent acid stability, the carboxylate-based MOFs usually have poor durability under basic conditions; by contrast, the azolate-based analogues exhibiting high base resistance are inevitably vulnerable to acidic species [14,15]. It

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can be found that the nature of coordination bond has imposed great restriction on the stability of most MOFs [16â 18]. Therefore, developing new MOFs stable in a large pH scope would advance the MOF community toward expansive applications.

The utilization of dual-functional azolate-carboxylate ligands offers a simple yet effective approach to construct stable MOFs superior to either their azolate- or carboxylate-based counterparts. In this regard, there are several dual-functional azolate-carboxylate ligands employed, showing different combinations of functional groups, size, and symmetry (Scheme 1) [19â23]. Among various azolate ligands, pyrazolates with the highest pKa value usually endow the resulting MOFs with enhanced stability by connecting low-valent metal ions. Furthermore, a multifunctional ligand containing more pyrazolate moieties tends to afford more stable MOFs. Therefore, we speculate that a dual-functional pyrazolate-carboxylate ligand bearing more pyrazolate groups would contribute to MOFs with better chemical stability. To date, dual-functional pyrazolate-carboxylate ligand-based MOFs are seldom reported mainly attributed to synthetic difficulties of these ligands and MOF crystals. In addition, the simultaneous coordination of pyrazolate and carboxylate groups with metal centers would afford novel architectures showing high robustness and diverse functionality, which attracts our interest in further exploration.

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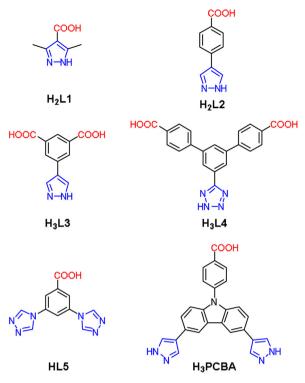
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2

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G. Si et al./Chinese Chemical Letters xxx (2019) xxx-xxx



Scheme 1. Dual-functional azolate-carboxylate ligand acids reported in the literatures and H_3PCBA used in this work.

Herein, we report a stable Co(II)-MOF, Co₃(PCBA)₂(H₂O)₂ (BUT-75, BUTâ=âBeijing University of Technology) constructed from a unique dual-functional pyrazolate-carboxylate ligand PCBA^{3â} with low symmetry (PCBA^{3a} a=a4-(3,6-di (1H-pyrazolate-4-yl)-9Hcarbazol-9-yl))benzoate). By integrating the advantages of both pyrazolate and carboxylate ligands for constructing stable MOFs, BUT-75 with linear 6-connected Co₃ clusters thus showed good chemical stability in aqueous solutions of a wide pH range (3ââ â12) and boiling water. With abundant open Co(II) sites in the framework, this MOF also presented high CO₂ affinity and thus high selective CO₂ adsorption capacity over N₂ at 298âK. In addition, BUT-75 demonstrated high catalytic activity toward the CO₂epoxide cycloaddition reaction under ambient conditions. This work offers a typical example of building stable versatile MOFs from dual-functional ligands, meanwhile contributes an effective adsorbent for selective CO₂ capture, as well as a recyclable heterogeneous catalyst for CO₂ conversion.

The solvothermal reaction between H_3PCBA and Co $(OAc)_2\hat{A}$ - $4H_2O$ in $2\hat{a}mL$ of *N*,*N*-dimethylformamide (DMF), 0.2 $\hat{a}mL$ of water and $80\hat{a}\hat{l}$ /4L of triethylamine at $120\hat{a}\hat{A}^\circ$ C for $48\hat{a}h$ afforded hexagonal dark purple crystals of BUT-75, Co₃(PCBA)₂(H₂O)₂ (Fig. S2 in Supporting information). Single-crystal X-ray diffraction

(SXRD) analysis revealed that BUT-75 crystallizes in the cubic crystal system with the I2₁3 (No.199) space group. The asymmetric unit of BUT-75 contains two kinds of crystallographically independent cobalt atoms (Co1 and Co2), one PCBA^{3â} ligand and one H_2O molecule (Fig. 1a). Co1 (1/2 site occupancy) coordinates with four N atoms of the pyrazolate moieties from four different PCBA^{3â} ligands in the tetrahedron coordination geometry. Co2 connects to two N atoms of pyrazolates from two different ligands, one O atom from the monodentate carboxylate of another ligand and one O atom of the terminal H₂O, showing a distorted tetrahedron geometry. One central Co1 and two lateral Co2 atoms are bridged together by four pyrazolates to form a linear Co₃ cluster (Fig. 1b) [24,25]. Each Co₃ cluster links six PCBA^{3â} ligands through four pyrazolates and two carboxylates, as well as two terminal H₂O molecules; each PCBA^{3â} ligand bridges three Co₃ clusters to afford the final three-dimensional (3D) structure of BUT-75. Topologically, the PCBA^{3â} ligand and Co₃ cluster node can be simplified as a 3- and 6-connected node, respectively. The 3D framework of BUT-75 can thus be seen as a (3,6)-connected net with the point symbol of $(6^3)_2(6^7.8^8)$, as calculated by Topos (Fig. S3 in Supporting information). BUT-75 has a novel framework structure, where a rhombic channel (accommodating a cylinder with a diameter of 8.4âÃ) and a triangular channel (accommodating a cylinder with a diameter of 9.7âÃ) are observed (Figs. 1c and d). The solvent-accessible volume of BUT-75 is estimated to be 56% after the removal of free solvent molecules by PLATON [26].

In the structure, the PCBA^{3â} ligand shows some configuration distortion by rotating the peripheral aromatic rings away from the central carbazole plane. The dihedral angle between the phenyl and carbazole ring is 56.79Ű, and that between pyrazolate containing the N1/N3 atom and the carbazole plane is 9.13Å °/18.29Ű, respectively, thus well matching the coordination geometry of the formed linear Co₃ cluster in BUT-75. It is worth noting that terminal H₂O molecules coordinated to the Co₃ cluster would afford open metal sites in BUT-75 after being removed.

To check the phase purity and crystallinity, the obtained BUT-75 sample was characterized by powder X-ray diffraction (PXRD). As shown in Fig. 2a and Fig. S7 (Supporting information), the diffraction pattern of the as-synthesized sample is in agreement with the simulated pattern from the crystal structural data, demonstrating high phase purity of this MOF. To investigate the coordination between ligands to metals in BUT-75, the FT-IR spectrum of the activated MOF sample was recorded in comparison with the ligand H₃PCBA. As shown in Fig. S4 (Supporting information), the characteristic peaks for stretching vibration of C=O bond in carboxyl groups and C=N bond in pyrazolyl groups at near 1720 cm^â ¹ and 1601âcm^â ¹ were found in the spectrum of H₃PCBA, however, their corresponding peaks were observed at 1599âcm^â ¹ and 1481âcm^â ¹ in BUT-75, respectively. The redshifts could be attributed to the coordination of carboxylates and pyrazolates to metal ions. The permanent porosity of BUT-75 was then examined by N₂ adsorption at 77aK. As shown in Fig. 2b, the

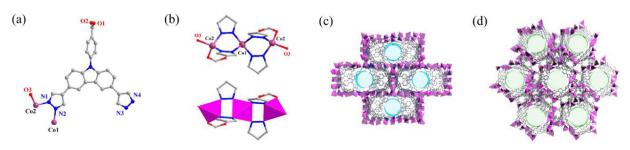


Fig. 1. (a) Asymmetric unit of BUT-75 structure. (b) Structure of the linear 6-connected Co₃ cluster in BUT-75. 3D network of BUT-75 showing 1D (c) rhombic and (d) triangular channels. H atoms are omitted for clarity.

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G. Si et al./Chinese Chemical Letters xxx (2019) xxx-xxx

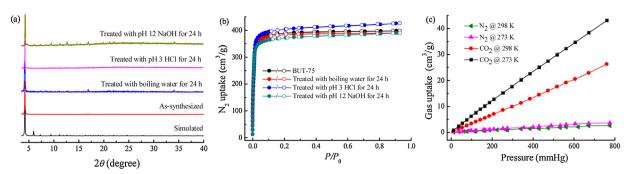


Fig. 2. (a) PXRD patterns simulated from the BUT-75 structure and of samples after different treatments. (b) N_2 adsorption/desorption isotherms of BUT-75 sample and of those after different treatments at 77 \hat{a} K. (c) CO_2 and N_2 adsorption isotherms for BUT-75 at 273 \hat{a} K and 298 \hat{a} K.

Type-I N₂ adsorption/desorption isotherms show a saturated N₂ uptake of 398 acm^3/g in the microporous BUT-75, and the evaluated Brunauer-Emmett-Teller surface area is 1498 am^2/g . Based on the N₂ adsorption data, the pore size distribution of BUT-75 is in the range from 5aA to 10aA as calculated by the density functional theory (DFT) method (Fig. S5 in Supporting information), being consistent with the result of crystallographic structure analysis. These results have further confirmed the structure of BUT-75, encouraging us to explore its properties.

The good stability of a new MOF material is necessary for its involvement in various applications. The stability of BUT-75 has thus been investigated. As can be seen from the thermogravimetric curve (Fig. S6 in Supporting information), BUT-75 can be thermally stable up to 420â°C, proving fine thermal stability. To confirm the chemical robustness of BUT-75, the samples were soaked in HCl aqueous solution (pH 3), NaOH aqueous solution (pH 12) at room temperature, and in boiling water for 24âh, respectively. As expected, the PXRD patterns of these treated samples remain almost unchanged compared with the assynthesized sample, demonstrating no phase transition or framework collapse in tests (Fig. 2a and Fig. S7 in Supporting information) [27]. It can also be seen that peak intensities of high $2\hat{I}$ Bragg angles are relatively weak, which is mainly caused by the higher peak intensity ratios of peaks located at around 4.2° compared to those of high angles. In addition, the N₂ sorption isotherms of the treated samples are nearly identical to that of the untreated sample, further indicating the high chemical stability of BUT-75 (Fig. 2b). The strong acidic/basic resistance of BUT-75 may be mainly attributed to the use of the dual-functional H₃PCBA ligand, in which the co-existence of pyrazolate and carboxylate moieties enhances the stability of the resulting MOF. Such stability lays the foundation for BUT-75 to be exploited in significant applications.

With rich open Co(II) sites and good chemical stability. BUT-75 may be an excellent sorbent candidate for gas adsorption. Therefore, the gas adsorption measurements of pure CO_2 and N_2 over BUT-75 were experimentally conducted at 298aK and 273aK, respectively, and the results are shown in Fig. 2c. The maximum uptakes of CO₂ and N₂ are 43.1 and 3.6âcm³/g at 273âK, and 26.3 and 2.6 cm³/g at 298 \hat{a} K. It can be found that the uptakes of CO₂ are significantly higher than those of N₂, showing the potential of BUT-75 in selective CO_2 adsorption over N_2 [28]. In order to evaluate the adsorption selectivities of BUT-75 for CO₂/N₂, the initial slopes of their adsorption isotherms were fitted at low-pressure ranges as reported [29]. The estimated CO₂/N₂ selectivities are 10.0:1.0 at 273âK and 8.0:1.0 at 298âK (Fig. S8 in Supporting information), suggesting that BUT-75 could selectively adsorb CO2 over N2. Based on the CO_2 adsorption data, the CO_2 sorption heat (Q_{st}) of BUT-75 is calculated to be in the range of 15.5â 17.1âkJ/mol by using the Clausius-Clapeyron equation (Fig. S9 in Supporting information) [30], which demonstrates moderate interaction between the MOF framework and guest CO₂ molecules. These findings indicate that BUT-75 would be a nice CO₂ adsorbent, favoring its application in CO_2 capture and conversion with a good affinity toward CO_2 .

Considering good chemical stability, high-density exposed Co (II) sites, and selective CO₂ sorption at room temperature, the catalytic activity of BUT-75 toward the CO₂ cycloaddition with epoxides was investigated under solvent-free conditions [31â 33]. Various reaction parameters (time, temperature, and catalyst dosage) were altered in the model reaction by using propylene oxide as the substrate, and the results are summarized in Table 1. BUT-75 catalyzed this reaction with a 30.1% conversion of propylene oxide in 24âh (Table 1, entry 1). After adding the phase transfer catalyst tetra-n-tertbutylammonium bromide (TBAB), BUT-75 gave a significantly higher propylene oxide conversion of 80.5% (Table 1, entry 2). It could be reasoned that the presence of

Table	1
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Cycloaddition of CO₂ and propylene oxide under different conditions^a.

Entry	Catalyst	Catalyst (mg)	Temperature (°C)	Time (h)	Conversion ^b (%)	TOF^{c} $(h^{\hat{a} 1})$
1	BUT-75	20	25	24	30.1	4.1
2	BUT-75/TBAB	20	25	24	80.5	11.1
3	None	â	25	24	0	0
4	TBAB	â	25	24	12.5	â
5	BUT-75/TBAB	20	25	6	12.1	6.7
6	BUT-75/TBAB	20	25	12	36.5	10.1
7	BUT-75/TBAB	20	25	48	83.2	9.2
8	BUT-75/TBAB	20	0	24	17.7	2.4
9	BUT-75/TBAB	20	50	24	93.5	12.9
10	BUT-75/TBAB	10	25	24	32.2	8.9
11	BUT-75/TBAB	30	25	24	89.3	8.3
12	BUT-75/TBAB	40	25	24	91.2	6.3

^a Reaction conditions: propylene oxide, 20âmmol; TBAB, 0.5âmmol; with a CO₂ balloon.

^b Conversion of propylene oxide was determined from the ¹H NMR spectra of the liquid mixture after reaction.

^c Turnover frequency (product (mol)/ metal (mol)/time (h)).

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G. Si et al./Chinese Chemical Letters xxx (2019) xxx-xxx

TBAB facilitates the contact of reactants and catalysts on phase interfaces (gas to liquid and liquid to solid), thereby improving the catalysis performance of BUT-75 [34â36]. Control experiments demonstrated that no conversion of propylene oxide was observed in the absence of BUT-75 and TBAB (Table 1, entry 3), and only a conversion of 12.5% was available by using the TBAB alone (Table1, entry 4). As a result, BUT-75 can catalyze the CO₂ cycloaddition with epoxides effectively with the assistance of TBAB. As shown in entries 2 and 5â7. the reaction had a slow reaction rate within the first 6âh, and the conversion reached 80.5% for 24âh, indicating an induction period required in the reaction. Further prolonging the reaction time cannot obviously increase the conversion of propylene oxide, 24âh is thus the optimum time for the reaction. The conversion of epoxide also increased with temperature (Table 1, entry 2, 8 and 9, from 17.7% at 0â°C to 93.5% at 50â° C) and catalyst dosage (Table 1, entry 2, 10â 12, from 32.2% with 10âmg to 91.2% with 40âmg). By rationally balancing the cost and catalysis performance, the reaction catalyzed by BUT-75 of 20âmg in the presence of TBAB at 25â°C for 24âh was established as the optimal conditions.

With the optimized conditions in hand, we further expanded the substrate scope of the CO₂-epoxides cycloaddition reaction catalyzed by BUT-75. Different epoxides with various substituent groups were checked. These reactions were carried out with BUT-75 under the standard conditions. As shown in Table S2 (Supporting information), the conversions of 1,2-butene oxide, epichlorohydrin, and styrene oxide to the corresponding cyclic carbonates after 24âh are 34.1%, 27.6% and 14.8%, respectively. It can be seen that the conversions of epoxides with larger substituent groups are all lower than that of the propylene oxide with a methyl substitution (80.5%) after 24âh. When the reaction time was extended to 48ah, the obtained conversions were raised to 71.5%, 63.3% and 20.4%, still being lower than that of the propylene oxide (83.2%). These lower conversions may be attributed to that the small pore aperture of BUT-75 limits the diffusion of bulky substrates in the channel, giving rise to reduced production of the resulting cyclic carbonates [37,38].

The recyclability is also significant for a heterogeneous catalyst. The cycling experiment was conducted under standard conditions. After the reaction, the BUT-75 catalyst was separated from the system, washed, and dried for the next cycle. As shown in Fig. S10 (Supporting information), the catalytic activity of BUT-75 remains almost unchanged after five cycles. Furthermore, the FT-IR spectra, PXRD patterns, and N₂ adsorption isotherms (Figs. S4 and S11 in Supporting information) of the re-collected BUT-75 samples exhibit no obvious changes compared to those of the sample used in the first cycle, indicating its structural integrity in recycling.

Overall, the above results verify the good performance of the recyclable BUT-75 MOF as an efficient heterogeneous catalyst toward the CO₂-epoxide cycloaddition. More importantly, this conversion can proceed under ambient conditions in the presence of the BUT-75 catalyst, which can reduce the energy input and meet the requirement of green chemistry. To the best of our knowledge, only a few MOFs can catalyze this reaction under ambient conditions, among which BUT-75 is superior to others with higher efficiency (Table S3 in Supporting information).

A possible reaction mechanism is then proposed on the basis of the experimental results and previous reports (Scheme S3 in Supporting information) [39,40]. The coordinately unsaturated Co (II) ions exposed in the pores of BUT-75 serve as the active Lewis acidic sites, whose interaction to the O atom of the epoxide could activate the epoxy ring [**A**]. Then the Br^â species from the TBAB attacks the less steric-hindered carbon of the epoxide, thus opening the epoxy ring to afford the intermediate [**B**]. The oxygen anion from the epoxy ring reacts with CO₂ to form an alkylcarbonate anion [**C**]. Finally, [**C**] undergoes cyclization to give the final cyclic carbonate product [**D**], with the BUT-75 catalyst recovered for the next catalysis cycle. Based on this mechanism, the practical catalytic performance of BUT-75 largely relies on the accessibility of active Co(II) sites to the substrates. Therefore, the relatively small pores of BUT-75 prevent the bulky substrates from approaching, accounting for their reduced conversions.

In summary, a stable versatile Co(II)-MOF, BUT-75, was constructed by using a newly designed dual-functional pyrazolate-carboxylate ligand H₃PCBA. This MOF possesses a (3,6)connected network structure with the 6-connected linear Co₃ cluster. Assembled by integrating Co—O and Co—N coordination bonds into one framework, BUT-75 has good acid/base stability in a wide pH range from 3 to 12. Besides, it showed selective CO₂ adsorption capacity over N₂ at 298âK. Due to high framework robustness and abundant open Co(II) sites, BUT-75 demonstrated good catalytic performance in the CO₂ cycloaddition reaction under ambient conditions, being a potential heterogeneous catalyst with good regeneration ability. This work opens a new door for building stable multifunctional MOFs through the rational ligand design, and thus expands their applications in addressing urgent environmental issues, such as the CO₂ fixation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.cclet.2020.07.023.

References

- [1] J.R. Li, J. Sculley, H.C. Zhou, Chem. Rev. 112 (2012) 869-932.
- [2] P. Ramaswamy, N.E. Wong, G.K.H. Shimizu, Chem. Soc. Rev. 43 (2014) 5913– 5932.
- [3] P. Horcajada, R. Gref, T. Baati, et al., Chem. Rev. 112 (2012) 1232–1268.
- 4] L.E. Kreno, K. Leong, O.K. Farha, et al., Chem. Rev. 112 (2012) 1105–1125.
- [5] L. Chen, Q. Xu, Matter 1 (2019) 57-89.
- 6] B. Wang, H. Yang, Y.B. Xie, et al., Chin. Chem. Lett. 27 (2016) 502–506.
- [7] T. He, Y.Z. Zhang, X.J. Kong, et al., Cryst. Growth Des. 19 (2019) 430-436.
- [8] J. Li, Y. Wang, Y. Yu, Q.L. Chin, Chem. Lett. 29 (2018) 837-841.
- [9] R.G. Pearson, J. Am. Chem. Soc. 85 (1963) 3533-3539.
- [10] F. Yang, G. Xu, Y.B. Dou, et al., Nat. Energy 2 (2017) 877-883.
- [11] X.L. Lv, S. Yuan, L.H. Xie, et al., J. Am. Chem. Soc. 141 (2019) 10283-10293.
- [12] K. Wang, X.L. Lv, D. Feng, et al., J. Am. Chem. Soc. 138 (2016) 914–919.
- [13] X.L. Lv, K. Wang, B. Wang, et al., J. Am. Chem. Soc. 139 (2017) 211-217.
- [14] Y.L. Hu, M.L. Ding, X.Q. Liu, L.B. Sun, H.L. Jiang, Chem. Commun. 52 (2016) 5734–5737.
- [15] H. He, Q.Q. Zhu, C.P. Li, M. Du, Cryst. Growth Des. 19 (2019) 694-703.
- [16] N.C. Burtch, H. Jasuja, K.S. Walton, Chem. Rev. 114 (2014) 10575-10612.
- [17] T. Devic, C. Serre, Chem. Soc. Rev. 43 (2014) 6097-6115.
- [18] X.M. Kang, H.S. Hu, Z.L. Wu, et al., Angew. Chem. Int. Ed. 58 (2019) 16610– 16616.
- [19] C. Heering, I. Boldog, V. Vasylyeva, J. Sanchiz, C. Janiak, CrystEngComm 15 (2013) 9757–9768.
- [20] N.M. Padial, E.Q. Procopio, C. Montoro, et al., Angew. Chem. Int. Ed. 52 (2013) 8290–8294.
- [21] W.Y. Gao, R. Cai, T. Pham, et al., Chem. Mater. 27 (2015) 2144-2151.
- [22] Z.J. Chen, Z. Thiam, A. Shkurenko, et al., J. Am. Chem. Soc. 141 (2019) 20480– 20489.
- [23] W.H. Jiang, J.L. Liu, L.Z. Niu, et al., Polyhedron 124 (2017) 191-199.
- [24] S. Jin, D. Wang, J. Coord. Chem. 64 (2011) 1940-1952.

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4

G Model CCLET 5748 No. of Pages 5

G. Si et al./Chinese Chemical Letters xxx (2019) xxx-xxx

- [25] H.H. Wang, L.N. Jia, L. Hou, et al., Inorg. Chem. 54 (2015) 1841–1846.
 [26] A. Spek, J. Appl. Crystallogr. 36 (2003) 7–13.
- [27] C.S. Cao, Z.J. Song, H. Xu, et al., Angew. Chem. Int. Ed. 59 (2020) 8586-8593.
- [28] O. Alduhaish, B. Li, H. Arman, et al., Chin. Chem. Lett. 28 (2017) 1653-1658.
- [29] J. An, S.J. Geib, N.L. Rosi, J. Am. Chem. Soc. 132 (2010) 38–39.
 [30] M. Dincă, J.R. Long, J. Am. Chem. Soc. 127 (2005) 9376–9377.
- [31] J. Liang, Y.B. Huang, R. Cao, Coord. Chem. Rev. 378 (2019) 32-65. [32] G. Xiong, B. Yu, J. Dong, et al., Chem. Commun. 53 (2017) 6013-6016.
- [33] L. Zhang, S. Yuan, L. Feng, et al., Angew. Chem. Int. Ed. 57 (2018) 5095-5099.
- [34] J. Song, Z. Zhang, S. Hu, et al., Green Chem. 11 (2009) 1031-1036.
- [35] Y.L. Wu, G.P. Yang, S. Cheng, et al., ACS Appl. Mater. Inter. 11 (2019) 47437-47445.
- [36] M.H. Beyzavi, R.C. Klet, S. Tussupbayev, et al., J. Am. Chem. Soc. 136 (2014) 15861-15864.
- [37] Y. Sun, X. Jia, H. Huang, et al., J. Mater. Chem. A 8 (2020) 3180-3185.
- [38] H. Hu, D.S. Zhang, H.L. Liu, et al., Chin. Chem. Lett. (2020), doi:http://dx.doi.org/ 10.1016/j.cclet.2020.02.028.
- [39] H. Xu, C.S. Cao, H.S. Hu, et al., Angew. Chem. Int. Ed. 58 (2019) 6022-6027.
- [40] S.L. Hou, J. Dong, B. Zhao, Adv. Mater. 32 (2020)1806163.

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