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Cluster-based MOFs with Accelerating Chemical Conversion of CO₂ through C-C Bond Formation

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Investigations on metal-organic frameworks (MOFs) as direct catalysts have been well documented, but it has never been reported that MOFs directly catalyze the chemical conversion of terminal alkynes and CO₂ as chemical feedstock into valuable chemical products. We report here two cluster-based MOFs I and II assembled by multinuclear Gd-cluster and Cu-cluster, displaying high thermal and solvent stabilities. I and II as heterogeneous catalysts possess active catalytic centers [Cu₁₂I₁₂] and [Cu₃I₂], respectively, exhibiting excellent catalytic performance in the carboxylation reactions of CO₂ and 14 kinds of terminal alkynes under 1 atm and mild conditions. This is the first time for MOFs materials to catalyze the carboxylation reaction of terminal alkynes and CO₂ without any cocatalyst/additive. This work not only reduces greenhouse gas emission but also provides high valuable materials, opening a wide space in seeking recoverable catalysts to accelerate chemical conversion of CO₂.

Metal-organic frameworks (MOFs) as catalysts have been attracting a great deal of research interest because of enormous applications in organic synthesis and catalysis¹⁻⁴. MOFs as catalysts possess unique advantages as following: 1) diversity and tunability of catalytic active sites, because both metal cations and Lewis basic species in MOFs can serve as catalytic active centers⁵⁻⁷. Furthermore, post-synthesized strategies through decorating organic linkers or metal centers can widely enrich catalytic sites⁸⁻¹⁰; 2) well-defined pores as nanoreactors can exhibit size- or shape-selective effect on substrate molecules¹¹; 3) it is very promising for MOFs with insolubility and stability in commonly solvents to act as the heterogeneous catalysts¹². Therefore, the investigations on MOFs as catalysts have been a hotspot field and made significant progress hitherto. For example, Zn- or Cu-containing MOFs display excellent catalytic activity in Friedel-Crafts alkylation¹³, cyanosilylation¹⁴, acetalization¹⁵, isomerization of *α*-pinene oxide¹⁶,

oxidation^{12,17}, aza-Michael reactions¹⁸, and Friedländer reaction¹⁹. Besides, the amino, pyridyl and amido Lewis base groups in MOFs can effectively promote Knoevenagel condensation reaction^{20, 21}. Comparably, exploring MOFs-catalyzed conversion of CO₂ is still in infant, and only cycloaddition reactions of CO₂ and epoxide were explored^{5, 7, 22, 23}, as well hydrogenation of CO₂ to formic acid²⁴. More recently, the carboxylation reactions of terminal alkyne and CO₂ can be well catalyzed by Ag nanoparticles loading into MIL-101²⁵, however it has never been reported so far for MOFs materials to directly catalyze such type of carboxylation reactions, in which new C-C bonds were generated.

The carboxylation reaction of CO₂ and terminal alkynes exhibits the some outstanding virtues.^{26, 27} for example, alkynyl carboxylic acids or esters as formed products were extensively employed in industry and pharmacy.²⁷In this aspect, development of efficacious processes using CO₂ as chemical feedstock under mild conditions particularly low CO₂ pressure (ideally at 1 bar) could be still highly desirable. On the other hand, most of catalysts used in the carboxylation reaction are homogeneous ones, and examples of using recoverable heterogeneous catalyst are scarce.^{28, 29} Therefore, it is indispensable and important for such reaction to design new materials as heterogeneous catalysts, because of their intrinsic features including easy handling, workup, purification of products, as well the robustness and reusability of the catalyst itself.

In previous work, many d-f heterometallic MOFs were systematically explored by us^{30,32}, and they possess high solvent and thermal stabilities due to variable and high coordination number of lanthanide ions, which meets the indispensable condition of heterogeneous catalysts. Recently we performed the carboxylation reactions of terminal alkynes with CO₂ by using CuI as a catalyst and ethylene carbonate as media.³²Inspired by these results, we aim to construct novel MOFs consisting of [Cu_xI_y] clusters and lanthanide ions, and can envisage the MOFs materials would have high stability and effectively promote such carboxylation reaction. To come true the target, both isonicotinic acid (HIN) as connectors in MOFs and solvothermal method were selected based on the following considerations: 1) given soft-hard acid-base theory, lanthanide and Cu ions have different affinities for N and O atoms in HIN, indicative of that HIN can bridge Cu and 4f ions into one heterometallic framework rather than homometallic one; 2) CuI salt easily forms [Cu_xI_y] clusters under the solvothermal conditions³³.

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In this contribution, two 3D MOFs [Gd₃Cu₁₂I₁₂(IN)₉(DMF)₄]_n·nDMF (I) and [Gd₄Cu₄I₃(CO₃)₂(IN)₉(HIN)_{0.5}(DMF)(H₂O)]_n·nDMF·nH₂O (II) were successfully prepared and structurally characterized with high solvent and thermal stabilities. Two robust frameworks were assembled by multinuclear Gd-cluster and Cu-cluster as active catalytic centers ([Cu₁₂I₁₂] in I and [Cu₃I₂] in II). They exhibited excellent catalytic performance in the carboxylation reactions of various terminal alkynes and CO₂ under 1 atm and mild conditions. To the best of our knowledge, this is the first time for MOFs materials to directly catalyze the carboxylation reaction of terminal alkynes and CO₂ under mild conditions without any cocatalyst/additive.

The structure determination revealed that the three dimensional framework of I is assembled by two types of building blocks: dodeca-nuclear Cu-cluster [Cu₁₂I₁₂] (Fig.1b) and tri-nuclear Gd-cluster [Gd₃(IN)₉(DMF)₄] (Fig.1c). The [Cu₁₂I₁₂] cluster comprises three crystallographically independent [Cu₄I₄] cubic units. Cu3, Cu7 and Cu10 are four-coordinate with [I₄] sets, while the remaining nine Cu atoms are also four-coordinate but with [I₃N] sets, in which N atoms come from the pyridine rings. Each of three I atoms (I4, I5 and I10) connects four Cu atoms from two [Cu₄I₄] clusters, and each of the other nine I atoms coordinates to three Cu atoms from one [Cu₄I₄] cluster. Interestingly, I4 atoms further bridge adjacent [Cu₁₂I₁₂] clusters into a complicated cluster-based 1D chain along *b* axis (Fig. S1), which is rather rare although [Cu₄I₄] clusters and Cu-I chains were well documented³³. In the [Gd₃(IN)₉(DMF)₄] cluster, three crystallography independent Gd³⁺ cations locate in the eight-coordinated distorted square antiprisms (Fig. S2). The coordination environments of Gd1 and Gd3 are similar and complete by seven carboxyl oxygen atoms from IN anions and one DMF molecule. Gd2 is coordinated with six monodentate carboxyl oxygen atoms and two DMF molecules. Both O5 and O8 as μ₂-bridges connect Gd1 and Gd2, while four carboxyl groups with the typical paddle-wheel mode bridge Gd2 and Gd3. The adjacent [Gd₃(IN)₉(DMF)₄] clusters are further connected into a 1D chain (Fig. S3) by two carboxyl groups in a μ_{1,3}-bridge mode. Each pyridine N atom in the [Gd₃(IN)₉(DMF)₄] cluster coordinates to one Cu atom from the adjacent [Cu₁₂I₁₂] cluster, constructing a mixed high-nuclear cluster-based 3D framework with 1D channels with the size of 1.2×0.5 nm along [010] direction (Fig.1a). The coordinated DMF molecules point to the channels, and the isolated ones locate in the channels. The total potential solvent accessible void is 1105 Å³ (10.4% of cell volume) calculated by PLATON program³⁴ after moving the isolated DMF molecules. To our knowledge, many impressive MOFs based on d-f heterometallic, or high-nuclear f or d clusters, have been widely investigated³⁵, however, systematic investigation on that such MOFs containing both high-nuclear f and d clusters has been less explored so far.³³

The structure of II significantly differs from that of I, and the 3D framework of II is constructed by three types of building blocks: [Gd₄(CO₃)₂(IN)₉] cluster (Fig. 2c), [Cu₃I₂] cluster (Fig. 2b) and [CuI] units ((Fig. S6)). In [Gd₄(CO₃)₂(IN)₉] cluster, four Gd³⁺ are generated by centrosymmetric operation on two crystallographically independent Gd³⁺ (Gd1 and Gd2), and further stitched by two CO₃²⁻ anions. Both Gd1 and Gd2 coordinate to eight oxygen atoms from IN ligands, CO₃²⁻ or H₂O, and the corresponding coordination configurations are slightly distorted square antiprisms. The CO₃²⁻ ions adopt the coordination mode of μ₄: η², η², η² (Fig. S4) to bridge four Gd³⁺ into a square with the side length of about 4.40 Å. The adjacent squares are further connected into a unique belt-like chain by sharing CO₃²⁻ anions along *a* axis (Fig. S5), in which many IN anions cover the periphery of the chain by coordinated to Gd

centers. In the trinuclear [Cu₃I₂] cluster, I1 as a μ₃-bridge connects three Cu^I cations to form the Cu₃I₂ cluster (Fig. S2b), and I2 links Cu1 and Cu1A with the Cu1-Cu1A distance of 2.75 Å. Four coordinated Cu1 locates in a tetrahedron comprised by two iodine anions and two nitrogen atoms, while the four coordinated environment of Cu2 is finished by one iodine, two nitrogen atoms and one DMF molecule. In [CuI] unit (Fig. S6), the four coordinated Cu3 has a tetrahedral configuration consisting of one iodine ion and three nitrogen atoms. All of the Cu-N, Cu-I and Cu-O bond lengths fall in the normal range. All pyridine N atoms in [Gd₄(CO₃)₂(IN)₉] cluster coordinate to Cu centers in adjacent [CuI] and [Cu₃I₂] building blocks, giving rise to an unprecedented 3D framework with 1D channels with the size of 0.8×0.5 nm along [100] direction. The total potential solvent accessible void is 1822.9 Å³ (18.6% of cell volume) calculated by PLATON program³⁴ upon moving the free DMF molecules.

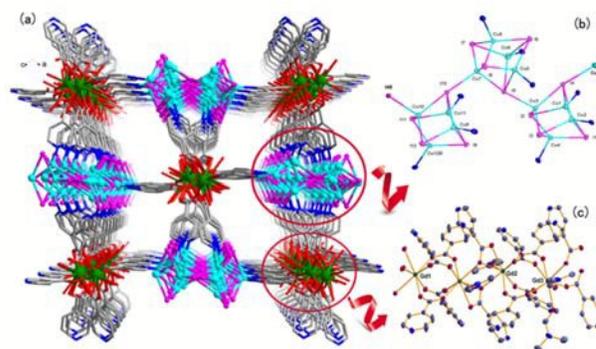


Fig. 1 (a) The three dimensional structure of I. (b) [Cu₁₂I₁₂] cluster drawn at 50% probability level. (c) tri-nuclear [Gd₃(IN)₉(DMF)₄] units drawn at 30% probability level.

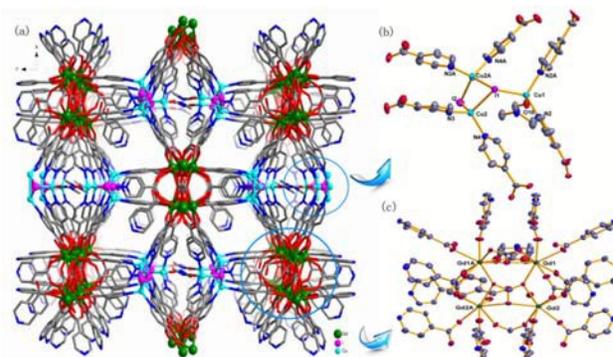
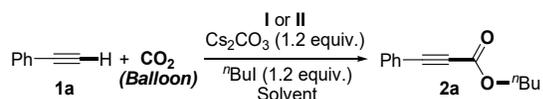


Fig. 2 (a) The three dimensional structure of II. (b) [Cu₃I₂] cluster drawn at 40% probability level. (c) Gd₄(CO₃)₂ chains in II drawn at 30% probability level.

The thermogravimetric analyses of I and II (Fig. S7 and S8) revealed 3D framework in I begins to collapse at about 430 °C, while that in II starts to decomposition at about 300 °C, implying high thermal stabilities of the two compounds. Furthermore, the PXRD patterns of I and II dipped in the ethanol, acetonitrile, DMF (100 °C), hexane and ethylene carbonate (EC) (100 °C) were investigated (Fig. S10 and 11), well consistent with the simulated one from individual single crystal data, and the results exhibit that 3D frameworks still keep intact and crystalline in solvents. X-ray photoelectron

spectroscopy (XPS) of I and II (Fig. S13 and S14) give the typical peaks of Cu(I) at 931.83 or 931.98 eV, indicative of that the oxidation state of Cu in I and II is +1.

Table 1. Optimization of the carboxylation of phenylacetylene^a



Entr y	Catalyst (mol% of Cu)	solvent	T (°C)	t (h)	Yield ^[b] (%)
1	--	DMF	80	12	9 ^c , 4 ^d
2	Cat-I (7)	DMF	80	12	47
3	Cat-I (7)	DMF	100	24	17
4	Cat-I (6)	EC	80	12	61
5	Cat-I (6)	EC	80	4	74
6	Cat-II (3)	DMF	80	12	34
7	Cat-II (3)	DMF	100	24	28
8	Cat-II (3)	EC	80	12	70
9	Cat-II (4)	EC	80	4	80

^a Reaction conditions: Phenylacetylene (51 mg, 0.5 mmol), Cs₂CO₃ (196mg, 0.6 mmol), *n*-Bul (110 mg, 0.6 mmol), DMF or ethylene carbonate (EC, 3 mL), CO₂ (99.999%, balloon), indicated amount of catalyst, 12 h.^b The yields were determined by GC with biphenyl as internal standard.^c Without catalyst. ^d Without CO₂.

Furthermore, phenylacetylene (**1a**) was chosen as the model substrate for the carboxylation with CO₂ and extensive investigations were carried out to define the optimal reaction conditions. As shown in Table 1, the carboxylative reaction was conducted under atmospheric CO₂ in DMF with the copper clusters as catalysts in the presence of Cs₂CO₃ and *n*-Bul. The product *n*-butyl 2-alkynoate (**2a**) was obtained in 47% and 34% yield, respectively, with the catalysis of **Cat-I** (7 mol%) and **Cat-II** (3 mol%) at 80 °C for 12 h (Table 1, entries 3 and 7). Control experiments established that, in the absence of catalyst or CO₂, essentially no carboxylation product was observed (entries 1 and 2). The yields of **2a** were decreased by increasing the reaction temperature to 100 °C and prolonging reaction time to 24 h (entries 3 and 7). We reasoned that the decarboxylation process might happen in the reaction mixture under relatively high temperature. On the basis of our previous report³², ethylene carbonate is thought to facilitate the carboxylation of terminal alkynes without utilizing any additional ligands or additives. To our delight, improved yields were thus attained in EC (entries 5 and 9). After further optimization, only 4 hours were required for **Cat-I** (6 mol%) and **Cat-II** (4 mol%) to afford **2a** in yield of 74% and 80%, respectively (entries 6 and 10).

After establishing optimal reaction conditions, 14 kinds of typical alkynes with various substituents were applied to this carboxylation reaction (Table 2). The carboxylation reactions of terminal alkynes (**1a-n**) and CO₂ were conducted with I (method A) or II (method B) as catalysts, providing alkyl 2-alkynoates (**2a-n**) as products. As a result, the alkynes with electron-donating substituents showed high reactivity to afford alkynoates **2a-e** in good yields. Interestingly, the alkynes with electron-withdrawing substituents, including F-, Cl-, Br-, at the *meta*- or *para*-position of the benzene ring, also gave **2f-i** with considerable yields from 56% to 74%. Additionally, the

heterocycle-containing substrates 2-ethynylthiophene (**1j**), 2-pyridylacetylene (**1k**) and 3-pyridylacetylene (**1l**) were also examined, and the products **2j-l** were obtained with good yields. Furthermore, the aliphatic alkyne **1m** underwent the reaction without any difficulties affording the desired product **2m** (entries 13). Importantly, 1,4-diethynylbenzene **1n** was also smoothly converted to the bis-carboxylative product **2n** in moderate yield, thus offering a convenient alternative route to useful poly(alkyl alkynoates) materials, accordingly.

Table 2. Carboxylation of terminal alkynes with CO₂^a

$$\text{R}^1-\text{C}\equiv\text{C}-\text{H} + \text{CO}_2 \xrightarrow[\text{EC, 80 }^\circ\text{C, 4 h}]{\text{Cat, Cs}_2\text{CO}_3 (1.2 \text{ equiv.}), n\text{-Bul (1.2 equiv.)}} \text{R}^1-\text{C}\equiv\text{C}-\text{C}(=\text{O})-\text{O}-n\text{Bu} \quad \text{2a-n}$$

(Balloon)

Entry	R ¹ C≡CH	Product	Yield (%) ^[b]	
			A	B
1	Ph-C≡C-H 1a	Ph-C≡C-C(=O)-O- ⁿ Bu 2a	80	86
2	Me-C ₆ H ₄ -C≡C-H 1b	Me-C ₆ H ₄ -C≡C-C(=O)-O- ⁿ Bu 2b	70	77
3	Et-C ₆ H ₄ -C≡C-H 1c	Et-C ₆ H ₄ -C≡C-C(=O)-O- ⁿ Bu 2c	73	85
4	ⁿ C ₆ H ₁₁ -C≡C-H 1d	ⁿ C ₆ H ₁₁ -C≡C-C(=O)-O- ⁿ Bu 2d	81	82
5	MeO-C ₆ H ₄ -C≡C-H 1e	MeO-C ₆ H ₄ -C≡C-C(=O)-O- ⁿ Bu 2e	65	74
6	Cl-C ₆ H ₄ -C≡C-H 1f	Cl-C ₆ H ₄ -C≡C-C(=O)-O- ⁿ Bu 2f	72	73
7	F-C ₆ H ₄ -C≡C-H 1g	F-C ₆ H ₄ -C≡C-C(=O)-O- ⁿ Bu 2g	67	70
8	Cl-C ₆ H ₄ -C≡C-H 1h	Cl-C ₆ H ₄ -C≡C-C(=O)-O- ⁿ Bu 2h	60	74
9	Br-C ₆ H ₄ -C≡C-H 1i	Br-C ₆ H ₄ -C≡C-C(=O)-O- ⁿ Bu 2i	56	69
10	Thiophene-C≡C-H 1j	Thiophene-C≡C-C(=O)-O- ⁿ Bu 2j	76	80
11	2-Pyridyl-C≡C-H 1k	2-Pyridyl-C≡C-C(=O)-O- ⁿ Bu 2k	66	77
12	3-Pyridyl-C≡C-H 1l	3-Pyridyl-C≡C-C(=O)-O- ⁿ Bu 2l	58	65
13	ⁿ C ₆ H ₁₃ -C≡C-H 1m	ⁿ C ₆ H ₁₃ -C≡C-C(=O)-O- ⁿ Bu 2m	71	75
14 ^c	H-C ₆ H ₄ -C≡C-H 1n	H-C ₆ H ₄ -C≡C-C(=O)-O- ⁿ Bu 2n	52	60

^a Reaction conditions: Terminal alkyne (1.0 mmol), **catalyst I** (6 mol%, method A) or **catalyst II** (4 mol%, method B), Cs₂CO₃ (0.391 g, 1.2 mmol), *n*-Bul (0.221 g, 1.2 mmol) and ethylene carbonate (3 mL), CO₂ (99.999%, balloon), 80 °C, 4 h.

^b Isolated yield.

^c **I** (12 mol%) or **II** (8 mol%), Cs₂CO₃ (2.4 mmol), *n*-Bul (2.4 mmol), EC (5 mL) were used.

When performing the carboxylation reaction of CO₂ and terminal alkynes catalyzed by I and II, the robust 3D frameworks with [Cu_xY_y] clusters play a crucial role with the following functions: 1) directly providing active catalytic centers to avoid uploading cocatalysts. Similar to the reported those³³, all Cu(I) atoms in I and II are four-coordinated, and the remaining coordinated positions allow the alkyne to interact with Cu(I) in MOFs, generating the intermediate copper acetylide. Subsequently, the insertion of CO₂ into the Cu-C bond occurs to provide the copper propynoate intermediate. Further on, the ester product can be generated through the esterification with iodoalkane, accompanying with the regeneration of the copper cluster catalyst; 2) possessing the high thermal and solvent stabilities. The case can make these MOFs materials as heterogeneous catalysts to be reused; 3) due to the intrinsic porosity feature of MOFs materials, I and II can capture CO₂ of 11.8

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and 17.3 cm³/g at 273 K and 1 atm (Fig. S17), respectively. Such adsorption possibly enhances the concentration of CO₂ around [Cu_xY_y] clusters, which maybe accounts for the divergence of catalytic active between I and II due to the higher CO₂ adsorption capacity of II than I.

In summary, two unique cluster-based d-f heterometallic 3D frameworks (I and II) were synthesized and structurally characterized. They display high solvent and thermal stabilities. Clusters [Cu₁₂I₁₂] in I and [Cu₃I₂] in II serve not only as building blocks of 3D frameworks but also as active catalytic centers. Interestingly, both of them exhibited excellent catalytic performance in the carboxylation reaction of 14 types of terminal alkynes with 1 atm of CO₂ under mild reaction conditions. Under catalyzing of I or II, the terminal alkynes with electron-withdrawing orelectron-donating substituents worked well in this protocol. Importantly, I and II as efficient heterogeneous catalysts for the carboxylation reaction of terminal alkynes and CO₂ could open a wide space in the chemical conversion field of CO₂ to valuable chemicals and materials. To the best of our knowledge, it is the first time for MOFs materials to directly catalyze the carboxylation reaction of terminal alkynes and CO₂ under mild condition without loading other catalysts.

Experimental Section

Synthesis of I. A mixture of 0.5 mmol CuI, 0.5 mmol Gd(NO₃)₃·6H₂O, 0.5 mmol isonicotinic acid and 10 mL DMF was sealed in a Teflon lined stainless steel container and heated at 125 °C for 24 h, and then cooled slowly controlled procedures to room temperature during 24 h. Finally, light green block crystals were collected with a yield of about 60% (based on CuI). Anal. Calcd. for C₆₅H_{56.5}Cu₄Gd₄I₃N_{11.5}O₂₉ (%): C: 34.02, H: 2.48, N: 7.02. Found: C:33.98, H: 2.46, N: 6.99.

Synthesis of II. A mixture of 0.5 mmol CuI, 0.5 mmol Gd₂O₃, 1 mmol isonicotinic acid, 10 mL DMF (N, N-Dimethylformamide) and 160 μL HNO₃ was sealed in a Teflon lined stainless steel container and heated at 155 °C for 96 h, and then cooled slowly controlled procedures to room temperature during 96 h. Finally, light yellow block crystals were collected with a yield of 71% (based on CuI). Anal. Calcd. for C₆₉H₇₁Cu₁₂Gd₃I₁₂N₁₄O₂₃ (%): C:19.59, H: 1.65, N: 4.60 ; Found : C: 19.63, H: 1.70, N: 4.64.

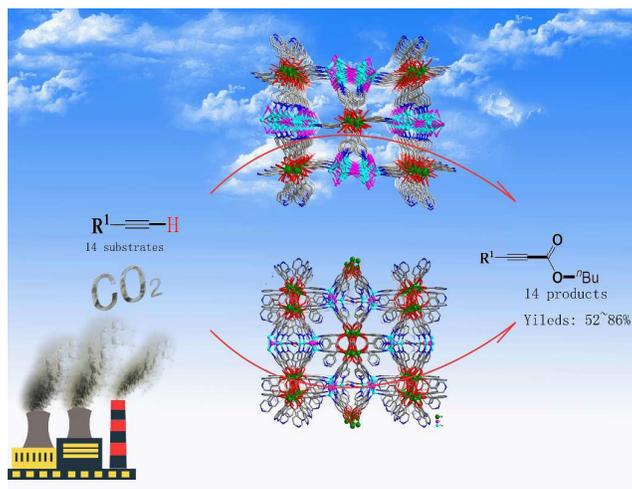
General procedure for the carboxylation of terminal alkynes with CO₂. In a 20 mL Schlenk flask, terminal alkyne (1.0 mmol), Cs₂CO₃ (0.391 g, 1.2 mmol), indicated amount of catalyst, *n*-Bul (0.221 g, 1.2 mmol) and ethylene carbonate (3 mL) were added. The flask was capped with a stopper and sealed. Then the freeze-pump-thaw method was employed for gas exchanging process. The reaction mixture was stirred at 80 °C for desired time under the atmosphere of CO₂ (99.999%, balloon). After the reaction, the mixture was cooled to room temperature, extracted with *n*-hexane. The combined organic layers were washed with saturated NaCl solution then dried with anhydrous Na₂SO₄. The residue was purified by column chromatography (silica gel, petroleum ether/EtOAc) to afford the desired product alkyl 2-alkynoates. The products were further identified by NMR and MS (see the Supporting Information), which are consistent with those reported in the literature and in good agreement with the assigned structures.

Notes and references

[1] D. Farrusseng, S. Aguado and C. Pinel. *Angew.Chem. Int. Ed.* 2009, **48**, 7502.

- [2] J. Y. Lee, O. K. Farha, J. Roberts, K. A. Scheidt, S. T. Nguyen and J. T. Hupp. *Chem. Soc. Rev.* 2009, **38**, 1450.
- [3] M. Yoon, R. Srirambalaji and K. Kim. *Chem. Rev.* 2012, **112**(2), 1196.
- [4] H. Furukawam, K. E. Cordova, M. ÓKeeffe and O. M. Yaghi. *Science*, **2013**, **341**, 974.
- [5] (a) W.-Y. Gao, Y. Chen, Y.-H. Niu, K. Williams, L. Cash, P. J. Perez, L. Wojtas, J.-F. Cai, Y.-S. Chen and S.-Q. Ma. *Angew.Chem. Int. Ed.* **2014**, **53**, 2615. (b) J. Dong, P. Cui, P.-F. Shi, P. Cheng and B. Zhao, *J. Am. Chem. Soc.*, **2015**, **137** (51), 15988. (c) H.-M. He, J.-A. Perman, G.-S. Zhu, S.-Q. Ma, *Small*, **2016**, **12**, 6309.
- [6] Z.-G. Guo, R. Cao, X. Wang, H.-F. Li, W.-B. Yuan, G.-J. Wang, H.-H. Wu and J. Li. *J. Am. Chem. Soc.* 2009, **131**, 6894.
- [7] M. H. Beyzavi, R. C. Klet, S. Tussupbayev, J. Borycz, N. A. Vermeulen, C. J. Cramer, J. F. Stoddart, J. T. Hupp and O. K. Farha. *J. Am. Chem. Soc.* 2014, **136**, 15861.
- [8] P. V. Dauand S. M. Cohen. *Chem. Commun.* 2013, **49**, 6128.
- [9] D.-Y. Hong, Y. K. Hwang, C. Serre, G. Férey and J.-S. Chang. *Adv. Funct. Mater.* 2009, **19**, 1537.
- [10] S. Bhattacharjee, D.-A. Yang and W.-S. Ahn. *Chem. Commun.* 2011, **47**, 3637.
- [11] S. Horike, M. Dincă, K. Tamaki and J. R. Long. *J. Am. Chem. Soc.* 2008, **130**, 5854.
- [12] Z.-J. Zhang, L.-P. Zhang, L. Wojtas, M. Eddaoudi and M. J. Zaworotko. *J. Am. Chem. Soc.* 2012, **134**, 928.
- [13] T.-B. Liao, Y. Ling, Z.-X. Chen, Y.-M. Zhou and L.-H. Weng. *Chem. Commun.* 2010, **46**, 1100.
- [14] D.-B. Dang, P.-Y. Wu, C. He, Z. Xie and C.-Y. Duan. *J. Am. Chem. Soc.* 2010, **132**, 14321.
- [15] F. Gándara, B. Gomez-Lor, E. Gutiérrez-Puebla, M. Iglesias, M. A. Monge, D. M. Proserpio and N. Snejko. *Chem. Mater.* 2008, **20**, 72.
- [16] L. Alaerts, E. Séguin, H. Poelman, F. Thibault-Starzyk, P. A. Jacobs and D. E. De Vos. *Chem. Eur. J.* 2006, **12**, 7353.
- [17] C. Wang, J.-L. Wang and W.-B. Lin. *J. Am. Chem. Soc.* 2012, **134**, 19895.
- [18] M. Savonnet, S. Aguado, U. Ravon, D. Bazer-Bachi, V. Lecocq, N. Bats, C. Pinel and D. Farrusseng. *Green Chem.* 2009, **11**, 1729.
- [19] E. Pérez-Mayoral and J. Čejka. *ChemCatChem* 2011, **3**, 157.
- [20] S. Hasegawa, S. Horike, R. Matsuda, S. Furukawa, K. Mochizuki, Y. Kinoshita and S. Kitagawa. *J. Am. Chem. Soc.* 2007, **129**, 2607.
- [21] Y.-K. Hwang, D.-Y. Hong, J.-S. Chang, S. H. Jung, Y. K. Seo, J. Kim, A. Vimont, M. Daturi, C. Serre and G. Férey. *Angew.Chem. Int. Ed.* 2008, **47**, 4144.
- [22] (a) J.-L. Song, Z. F. Zhang, S. Q. Hu, T.-B. Wu, T. Jiang and B.-X. Han. *Green Chem.* 2009, **11**, 1031; (b) W.-Y. Gao, H.-F. Wu, K.-Y. Leng, Y.-Y. Sun, S.-Q. Ma. *Angew.Chem. Int. Ed.*, 2016, **55**, 5472.
- [23] (a) D.-W. Feng, W.-C. Chung, Z. W. Wei, Z.-Y. Gu, H.-L. Jiang, Y.-P. Chen, D. J. Darensbourg and H.-C. Zhou. *J. Am. Chem. Soc.* 2013, **135**, 17105; (b) W.-Y. Gao, K.-Y. Leng, L. Cash, M. Chrzanowski, C.-A. Stackhouse, Y.-Y. Sun and S.-Q. Ma. *Chem. Commun.*, 2015, **51**, 4827.
- [24] J.-L. Wang, C. Wang and W.-B. Lin. *ACS Catal.* 2012, **2**, 2630.
- [25] X.-H. Liu, J.-G. Ma, Z. Niu, G.-M. Yang and P. Cheng. *Angew.Chem. Int. Ed.* 2015, **54**, 988.
- [26] D.-Y. Yu and Y.-G. Zhang. *PNAS* 2010, **107**, 20184.
- [27] F. Manjolinho, M. Arndt, K. Gooßen and L. J. Gooßen. *ACS Catal.* 2012, **2**, 2014.
- [28] D.-Y. Yu, M.-X. Tan and Y.-G. Zhang. *Adv. Synth. Catal.* 2012, **354**, 969.
- [29] W. L. Wang, G. D. Zhang, R. Lang, C. G. Xia and F.-W. Li. *Green Chem.* 2013, **15**, 635.
- [30] B. Zhao, X.-Y. Chen, P. Cheng, D.-Z. Liao, S.-P. Yan and Z.-H. Jiang. *J. Am. Chem. Soc.* 2004, **126**, 15394.
- [31] B. Zhao, P. Cheng, Y. Dai, C. Cheng, D.-Z. Liao, S.-P. Yan, Z.-H. Jiang and G.-L. Wang. *Angew.Chem. Int. Ed.* 2003, **42**, 934.
- [32] B. Yu, Z.-F. Diao, C.-X. Guo, C.-L. Zhong, L.-N. He, Y.-N. Zhao, Q.-W. Song, A.-H. Liu and J.-Q. Wang. *Green Chem.* 2013, **15**, 2401.
- [33] J.-W. Cheng, J. Zhang, S.-T. Zheng and G.-Y. Yang. *Chem. Eur. J.* 2008, **14**, 88.
- [34] S. P. Vanderand Spek A. L. *Acta Crystallogr., Sect. A* **1990**, **46**, 194.
- [35] Y.-L. Hou, G. Xiong, P.-F. Shi, R.-R. Cheng, J.-Z. Cui and B. Zhao. *Chem. Commun.* 2013, **49**, 6066.

TOC



We report here two cluster-based MOFs **I** and **II** assembled by multinuclear Gd-cluster and Cu(I)-cluster, displaying high thermal and solvent stabilities. **I** and **II** as heterogeneous catalysts possess active catalytic centers $[\text{Cu}_{12}\text{I}_{12}]$ and $[\text{Cu}_3\text{I}_2]$, respectively, exhibiting excellent catalytic performance in the carboxylation reactions of CO_2 and 14 kinds of terminal alkynes under 1 atm and mild conditions. This is the first time for MOFs materials to catalyze the carboxylation reaction of terminal alkynes and CO_2 without any cocatalyst/additive. This work not only reduces greenhouse gas emission but also provides high valuable materials, opening a wide space in seeking recoverable catalysts to accelerate chemical conversion of CO_2 .