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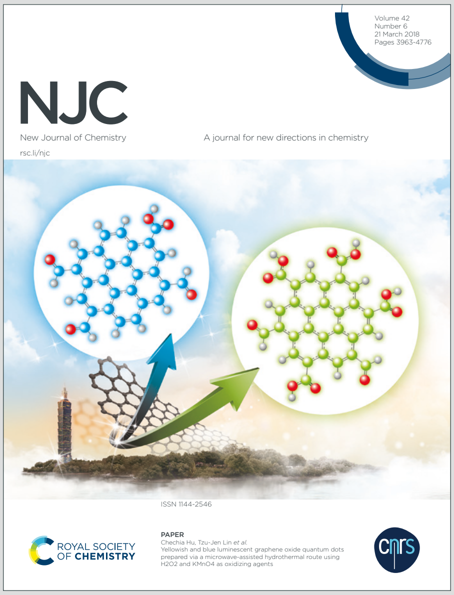

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PAPER
Chechia Hu, Tzu-Jen Lin *et al.*
Yellowish and blue luminescent graphene oxide quantum dots prepared via a microwave-assisted hydrothermal route using H2O2 and KMnO4 as oxidizing agents

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A Robust Heterogeneous Co-MOFs Catalyst in Azide-alkynes Cycloaddition and Friedel-Crafts Reactions as well as Hydrosilylation of Alkynes†

Tai-Xue Wu, [a‡] Jun-Song Jia, [a‡] Wei Luo, [a] He-Dong Bian, [ab*] Hai-Tao Tang, [a*] Ying-Ming Pan, [a] Fu-Ping Huang[a*]

Organic reactions using metal−organic frameworks (MOFs) as catalysts are promising with regard to their environmentally friendly features and potential catalyst recyclability. A robust Co(II)-MOF $\{[Co_2(L\text{-}mac)(4,4\text{-}bpt)(H_2O)]\cdot 3.5H_2O\}_n$ (**1**), and its enantiomer $\{[Co_2(D\text{-}mac)(4,4\text{-}bpt)(H_2O)]\cdot 3.5H_2O\}_n$ (**2**) (L/D-mac = basic forms of L/D-malic acid, 4,4-Hbpt = 3,5-di(pyridin-4-yl)-4H-1,2,4-triazole), have been gram-scale prepared under solvothermal conditions. Structural analysis reveals that mac manages Co(II) ions to form 1-D chains, which are further extended via 4,4-bpt connectors, into a noninterpenetrating 3D framework architecture. It was found that **1** can be as a heterogeneous catalyst for multiple organic reactions, such as azide-alkynes cycloaddition, Friedel-Crafts reactions with good isolated yields and good recycle runs (at least five times without substantial degradation). Additionally, **1** can promote hydrosilylation of alkynes reaction in harsh condition with moderate yield.

Introduction

Due to high degree of surface area, well-defined pore structure, multiple active site and adjustable pore size, metal organic frameworks (MOFs) have attracted increasing interest in recent years.[1-3] MOFs are capable of many applications for their tunable local environment and low density, which further facilitates mass-diffusion, such as gas sorption/separation, biomimetics, catalysis etc.[2b,4-6] Moreover , in order to optimize its performance to satisfy the application in multiple fields, such as catalysis ,various types of MOFs and their composites are designed, such as (2D) MOF nanosheets, the micro- and nanoscale MOF particles and metal-loaded metal–organic frameworks (metal@MOFs) and so on.[7d-e] In past decades, heterogeneous MOF-catalysts in the fields of organic reaction have aroused great interest of many researchers due to their environmentally friendly features and potential catalyst recyclability. [7-10]

For example, Zhou and co-workers reported a series of MOF-catalysts in Knoevenagel condensation reaction.[11] Besides，Jiang and Sun reported some Zn(II)-MOFs are able to catalyze the cycloaddition of CO_2.[12] What's more, Zhang and co-workers reported some Ni-MOFs are capable of efficiently catalyzing the alkene hydrosilylation.[7]

However, considering the shape and/or size limitations of the complexes, some strategies have been proposed for the development of heterogeneous MOF-catalysts. One method is to control its morphology or composition with other functional materials.[9a,13-14] For instance, Dong and co-workers reported a CuI@UiO-67-IM heterogeneous phase transfer catalyst for the azide-alkynes cycloaddition with excellent regioselectivity and yield.[13a] Another method is to expand the types of organic reactions. Eg. Dirk E. De Vos and co-workers reported a Cu/Ni-MOF, which allows to direct the selectively tandem C-C bond forming process for the desired pharmaceutical intermediate.[15] Up to now, other than the widely investigated Knoevenagel reaction[16], CO_2 cycloaddition reaction[17-18] etc., there are still a lot of classical organic reactions (eg. Azide-alkynes Cycloaddition, Friedel-Crafts) and harsh organic

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[a] State Key State Key Laboratory for Chemistry and Molecular Engineering of Medicinal Resources, School of Chemistry & Pharmacy, Guangxi Normal University, Guilin 541004, PR China. E-mail: huangfp2010@163.com (F.-P. Huang); httang@gxnu.edu.cn (H.-T. Tang).
[b] School of Chemistry and Chemical Engineering, Guangxi University for Nationalities, Key Laboratory of Chemistry and Engineering of Forest Products, Nanning, 530008, P. R. China. E-mail: gxunchem@163.com (H.-D. Bian)

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‡ These authors contributed equally.

reactions (eg. the Hydrosilylation of Alkynes), have not been widely explored in-depth when using simple but easily-prepared heterogeneous MOF-catalysts.

Herein, a novel Co(II)-MOF {[Co_2(L-mac)(4,4-bpt)(H_2O)]·3.5H_2O}$_n$ (**1**) and its enantiomer {[Co_2(D-mac)(4,4-bpt)(H_2O)]·3.5H_2O}$_n$ (**2**), have been gram-scale prepared under solvothermal conditions (L/D-mac = basic forms of L/D-malic acid, 4,4-Hbpt = 3,5-di(pyridin-4-yl)-4H-1,2,4-triazole, respectively). Structural analysis reveals that the 3D framework architecture with two types of open windows (ca. 13.445(4) × 13.445(5) Å and 6.365(45) × 6.365(45) Å). **1** can be used as a heterogeneous catalyst to promote not only the azide-alkynes cycloaddition from corresponding benzyl bromide， sodium azide and terminal alkynes as a sequential procedure, but also the Friedel-Crafts reaction of indoles with trans-*β*-nitrostyrenes resulting good isolated yields and recycle runs (at least five times without substantial degradation in crystallinity and catalytic activity). Additionally, **1** can promote hydrosilylation of alkynes reaction in harsh condition with moderate yield and selectivity.

Experimental section

Materials and Instrumentation.

The reagents and solvents employed were commercially available and used as received without further purification. THF, toluene, hexane, ethyl ether, DCM, and CH_3CN dried by molecular sieve were used. Column chromatography on silica gel (300-400 mesh) was carried out with technical grade 60-90 ℃ petroleum ether (distillated before use) and analytical grade EtOAc (without further purification). ^1H and ^{13}C spectra were recorded on a 400 MHz spectrometer and chemical shifts were reported in ppm. ^{1}HNMR spectra was referenced to $CDCl_3$, and ^{13}C-NMR spectra was referenced to $CDCl_3$ (77.0 ppm). Peak multiplicities were designated by the following abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet; brs, broad singlet and *J*, coupling constant in Hz. The C, H, and N microanalyses were carried out with a Perkin–Elmer PE 2400 II CHN elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range 4000-400 cm^{-1} on a Perkin–Elmer one FT-IR spectrophotometer. X-ray powder diffraction (XRPD) intensities were measured at 293 K on a RigakuD/max-IIIA diffractometer (Cu-Kα, λ = 1.54056 Å). The crystalline samples were prepared by crushing the single-crystals and scanned from 3-60° at a rate of 5 °/min. Calculated patterns of **1-2** were generated with Powder Cell. The solid-state circular dichroism (CD) spectra were recorded on a Jasco J-750 spectropolarimeter using KBr pellets. Micromeritics ASAP 2460 Version 3.00 was used for N_2 adsorption (**Figure S6**).

Synthesis of {[Co_2(L-mac)(4,4-bpt)(H_2O)·3.5H_2O}$_n$ (1).

1 was prepared under solvothermal conditions. A mixture of $Co(NO_3)_2·6H_2O$ (145 mg, 0.5 mmol), 4,4′-Hbpt (112 mg, 0.5 mmol), L(-)-H_3ma (67 mg, 0.5 mmol), NaOH (40 mg, 1 mmol), water (7 mL), and methanol (7 mL) was placed in a 23 mL Teflon-lined stainless steel vessel and heated at 160 °C for 48 h and then cooled to room temperature at a rate of 5 °C, and finally the red strip crystalline products of **1** were obtained by washing it with distilled water and methanol, then picking out after being dried in air. Yield: 70 % (base on Co(II)). Elemental analysis (%): Calcd: C, 34.77; H, 3.62; N, 10.87. Found: C, 34.73; H, 3.65; N, 10.90. IR (KBr, cm^{-1}): 3404m, 1609m, 1546s,1426m, 1313w, 1201w, 1087w, 841 m, 749w, 630w.

Synthesis of {[Co_2(D-mac)(4,4-bpt)(H_2O)·3.5H_2O}$_n$ (2).

2 was synthesized similarly to compound **1** except using D (-)-H_3mac (67 mg, 0.5 mmol) instead of L (-)-H_3mac (67 mg, 0.5 mmol), and red strip crystalline products were obtained in a 69% yield (base on Co (II)). Elemental analysis (%): Calcd: C, 34.77; H, 3.62; N, 10.87. Found: C, 34.79; H, 3.59; N, 10.85. IR (KBr, cm^{-1}): 3406m, 1597m, 1558s,1426m, 1315w, 1197w, 1086w, 843 m, 745w, 587w.

General procedure azide-alkynes cycloaddition reaction catalyzed by 1.

Mixed solution NaN_3 (2 mmol), $ArCH_2Br$ (1 mmol), and **1** (0.02 mmol) in H_2O (2 mL) was heated at the 60 ℃ for 2 h and stirred for another 4 h after addition of alkynes (1.5 mmol). Once the reaction finished, H_2O (3 mL) and CH_2Cl_2 (5 mL) were added and Co-MOF of **1** was recovered by filtration. The organic phase was separated and aqueous phase was extracted with CH_2Cl_2 (3 × 5 mL). The organic fractions were combined, dried ($MgSO_4$), filtered through filter paper, and concentrated *in vacuo*. The crude reaction product was purified by column chromatography (300-400 mesh silica gel, 30 mm Ø, pentane: Et_2O 10:1) to give the 1,2,3-triazoles.

General procedure for the Friedel–Crafts alkylation reaction of *trans*-*β*-Nitrostyrene and indoles catalyzed by 1.

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Under the protection of Ar, *trans-β*-nitrostyrenes (0.2 mmol), indoles (0.3 mmol) and **1** (0.01 mmol) were added to a 25 mL flask, then CH_2Cl_2 (1 mL) was added. The reaction was performed at 35 ℃ for 24 h. Co-MOF (**1**) was recovered by filter and the organic phase was concentrated *in vacuo*. The crude product was purified by column chromatography (300-400 mesh silica gel, 30 mm Ø, pentane: Et_2O 15:1) to give the indole derivatives. [19-20]

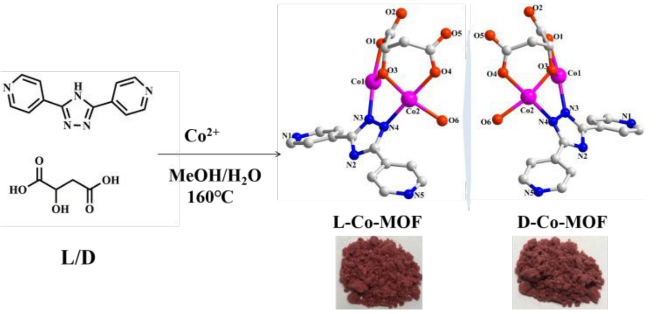
General procedure for selective hydrosilylation of alkynes catalyzed by 1.

A 25 mL flame-dried flask was cooled under dry Ar atmosphere, then Co-MOF (**1**) (0.02 mmol), THF (2.0 mL), $PhSiH_3$ (2.0 mmol) were added successively. After that, the mixture was injected with $NaBHEt_3$ (1.0 M) (60 μL, 0.06 mmol) by dropwise and then the alkyne (1.0 mmol) was injected, reaction at 50 °C for 4 h. The resulting solution was added 10 mL of ether and filtered through filter paper to recover Co-MOF (**1**). The combined filtrates were concentrated and selectivity was monitored by ^1H NMR analysis. The crude mixture was purified by column chromatography (300-400 mesh silica gel, 30 mm Ø, pentane as eluent) to get the corresponding product. [21]

Results and discussion

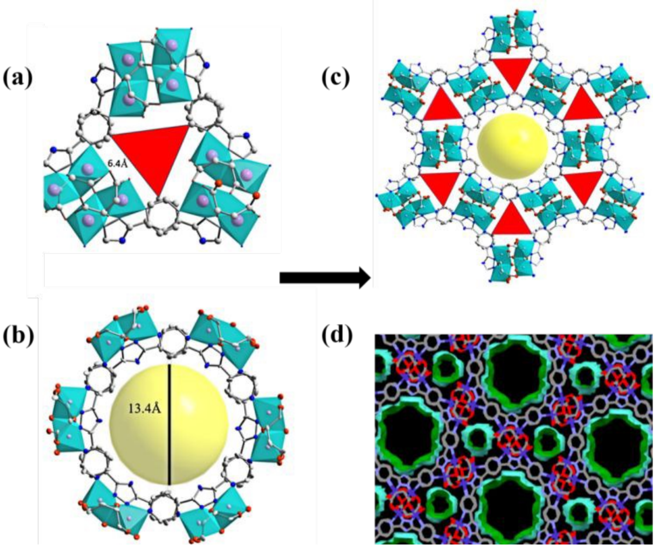
Crystal structure

As shown in Scheme 1, **1/2** was generated from a mixture of malic acid, pyridin-triazole ligand and $Co(NO_3)_2$ under solvothermal conditions. **1** and **2** are revealed enantiomorphs through the X-ray crystallographic studies, then the structure of **1** to be described in detail as a representative (**1** and **2** with removal of solvent molecules is 28.1% and 28% of the cell volume calculated by PLATON). **1** crystallized in the hexagonal system with chiral space group $P6_3$. The asymmetric unit of **1** contains two independent Co(II) cations. Co1 is six-coordinated, showing an octahedral environment, four carboxylate O atoms (O1, O2, O3 and O5) composing the equatorial plane and two pyridyl N donors (N3 and N5) occupying the apical plane led to the formation of an octahedral environment, the corresponding bond lengths are Co–N=2.112(3)-2.114(3) Å and Co–O = 2.003(3)–2.371(3) Å, respectively. Co2 is bonded by two pyridyl N atoms (N1 and N4) and four carboxylate/water O atoms (O2, O3, O4, and O6) that displays a similar coordination octahedral environment. The Co2 is linked to Co1 through one mac hydroxyl O atom and one trizole N-N bridge to form a dimeric unit with Co1•••Co2 = 3.122(3) Å and Co1-O3-Co2 = 102.0(2) º. The $\{Co_2\}$ dimeric units are linked by carboxylate groups in mac ligands to generate a helix chain running along the crystallographic c axis. (Fig. S1 in the Supporting Information)



Scheme 1. Preparation of chiral enantiomers **1**- and **2**-MOF and their coordinate environment diagrams.

These chains are further connected by 4,4′-bpt ligands to generate a noninterpenetrating 3D open framework with two types of open windows consists of several circular micropores and chiral triangular pores (the size of ca. 13.445(4) × 13.445(5) Å and 6.365(4) × 6.365(4) Å, respectively.) which as the basic active sites. (Fig. 1 and Fig. S2). Better insight into this framework can be achieved by topology analysis. Considering the coordination modes of metal atoms, mac and 4,4′-bpt, which are all viewed to be 4-connected nodes, respectively. Thus, a novel four-connected topology in **1** with the short Schläfli symbol of $(4^3.8^3)_2(4^2.8^4)$ (4.8^5) could be observed.[22] The chiral nature of the enantiomorphs **1-2** was further confirmed by solid-state CD spectra. The spectrum for a bulk sample of **1** displays two negative peaks at 482, 525 nm and a positive peak at 583 nm, while that for **2** is approximately the mirror image of **1** (Fig.S4).



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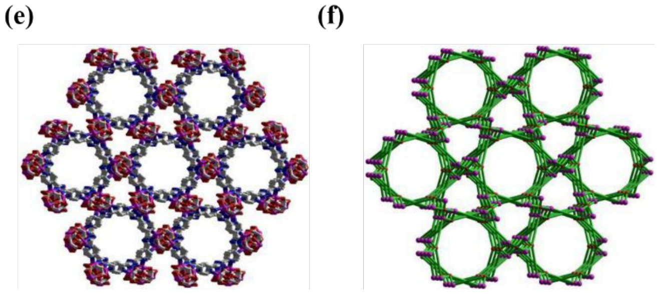

Fig 1. The triangular-like window (a), circular-like window (b) and the nonpenetrating 3D framework structure of **1** (c) and their schematic diagram of surface channel for solvent access (d), the Structure of **1** showing the view of the 3D architecture(e) and its schematic description (f).

The Stability of MOFs 1 and 2

The Co-MOFs of **1**/**2** is expected to be a promising candidate to serve as a stable heterogeneous catalyst to facilitate some organic reactions.[23] The Co-MOFs can keep stable in common solvents media, and the coordinated water molecules can be removed during activation then leaving open metal sites to participate in the catalytic reaction as lewis acid.[24] The high stability and the action of lewis acid are expected to combine to form an attractive multifunctional porous preference material. As shown in Fig. 2, Fig. S3, by the means of TG analyses, FTIR spectra and in-situ powder XRD measurements, the thermal stability of the crystalline Co-MOF material was evaluated. The TG curve of **1**-**2** suggested that the observed weight loss of *ca.* 14.9 % between 60 and 160 °C corresponds to the dehydration process. The framework started to decompose around 420 °C (Fig. S3a.). After activated samples at 160 °C for 24h, as can be seen from Fig. S3e, f, the solvent molecules of the activated samples were significantly removed with the frame of **1** remained stable. In addition, the PXRD pattern of desolvated samples is as sharp as the as-prepared **1**/**2** after heating under vacuum for 24 h, which confirms the framework is stable after losing the lattice/coordinated water molecules (Fig. 5 and Fig. 6a). The PXRD patterns of samples immersed in different solvent for about 24 h (eg. H_2O, MeOH, EtOH, DMSO, THF, CH_3CN, etc.) or different acid/base condition (pH = 2-11), are almost the same as the as- prepared **1**/**2**, which demonstrates the stability of solvent and acid/base.

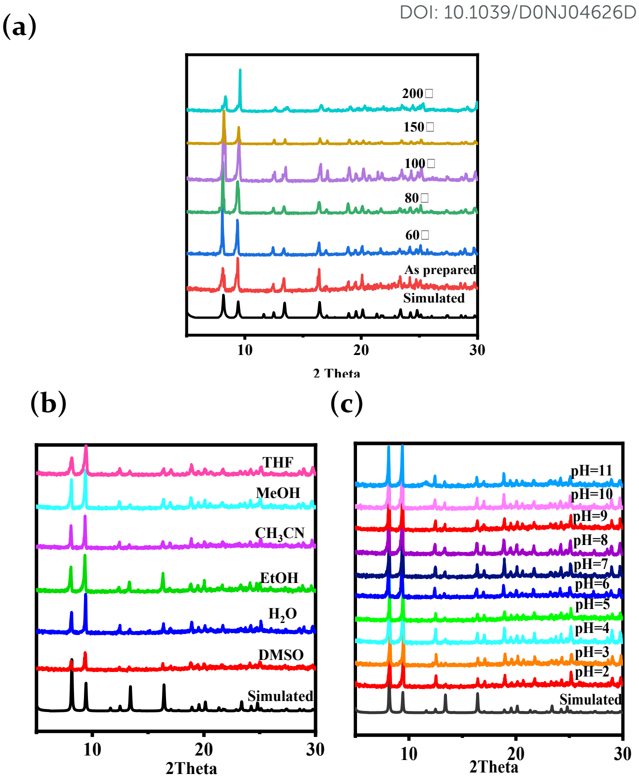

Fig 2. The XRD patterns of **1** at different temperatures (a), after immersing in different solvents (b) and different acid/base condition (c).

Azide-alkynes Cycloaddition Reactions Catalyzed by 1

The 1,2,3-triazoles have found wide used in industrial applications such as dyes, corrosion inhibition (of copper and copper alloys), photostabilizers, photographic materials, and agrochemicals.[25] Therefore, it is very necessary to develop new and more efficient catalyst to a diverse array of 1,2,3-triazole pharmacophores. The catalytic properties of **1**/**2** for the azide-alkynes cycloaddition reactions were evaluated in the follow.

To initiate our investigations, 4-*tert*-butylbenzyl bromide reacts with sodium azide to obtain intermediate **A** in 2 h. In the case of **A** without separation, the “one-pot” protocol of directly adding 4-bromophenylacetylene to obtain 1,2,3-triazole compound **5** and **5’** at the 4 h in the present of 2 mol% catalyst **1** (Scheme 2). The structure of a representative product **5** was unambiguously confirmed by X-ray crystallographic analysis (see ESI). Gratifyingly, the value of the yield **5**:**5’** is 4.4:1, which indicates the MOF-catalyst shows regioselective to the azide-alkynes cycloaddition reaction. We also investigated the reaction temperature and time (Table S1), and finally obtained **5** + **5’** with 77 % with the isolated yield

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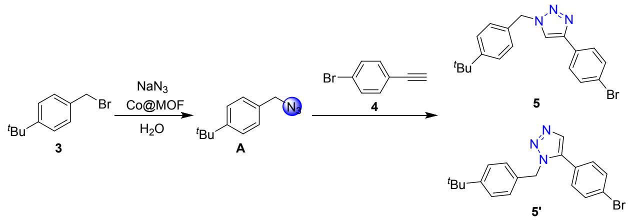
(Weighing yield after separation and purification by column chromatography) and the TON (turnover number) value is 39.



Scheme 2. The process of azide-alkynes cycloaddition reaction catalyzed by **1**.

To investigate whether the catalytic activity will be affected by an excess of heterogeneous catalyst, **1**, 4-*tert*-butylbenzyl bromide and 4-bromophenylacetylene were chosen as substrates to be a model reaction. We separated the organic matter by filtration after 30min, then the filtrate was stirred for a further 1.5 h, 3 h, 4.5 h, and 6 h. As shown in Fig. 3 (left: catalyst filtration), no obvious conversion of 1,2,3-triazoles compound is observed by GC-MS. At the same time, a control trial under the same conditions without filtration the catalyst was evaluated as shown in Fig. 3 (left: no filtration) and the catalytic conversions in the absence of **1** was tested Fig. 3 (left: no catalyst). Therefore, the conclusion that **1** is a heterogeneous catalyst can be drew. In practice, the separability and reusability are the key parameters to evaluate heterogeneous catalysts. Here, the reusability and stability of **1** were further studied with 1,4-*tert*-butylbenzyl bromide as substrate. Within 6 h (2 + 4 h), the amount of **5** remains the same, which indicates that the catalytic process had been completed to some extent. Subsequently, the regenerated **1** was collected by filtration, then washed 3 times with methanol after that dried naturally at room temperature for the next use. As illustrated in Fig. 4 (left), we studied the regenerated catalytic efficiency of **1**. After 5 runs, the conversion efficiency was reduced by about 9 % but still retained a good value. Besides, we can observe that the crystalline structure of **1** was maintained after 5 runs (Fig. 5 (left)). These indicated that **1** suggested high efficiency in the azide-alkynes cycloaddition reaction and can be regenerated easily and directly.

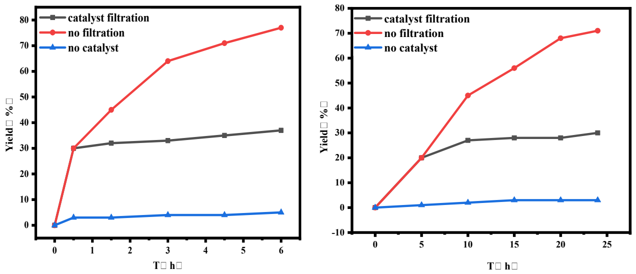


Fig 3. The leaching test of azide-alkynes cycloaddition reaction (left) and Friedel–Crafts alkylation reaction (right).

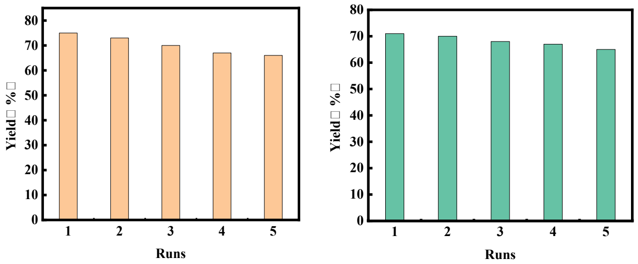


Fig 4. Recycling test of azide-alkynes cycloaddition reaction (left) and Friedel–Crafts alkylation reaction (right).

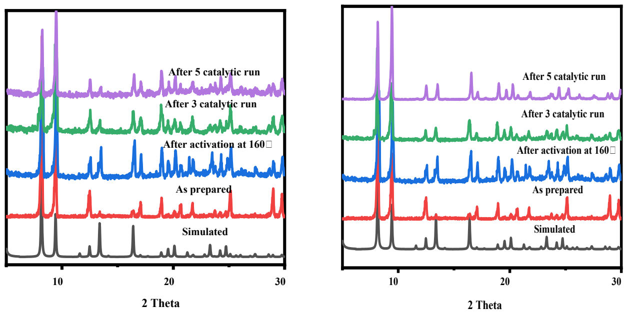


Fig 5. PXRD patterns of as-synthesized **1** and after three and five catalytic runs for the reactions of azide-alkynes cycloaddition reaction (left) and Friedel–Crafts alkylation reaction (right).

Using our optimized experimental conditions, the scope of the MOF-catalyzed formation of 1,2,3-triazoles was examined. The results are summarized in Table 1. First, we used benzyl bromide as the reaction substrate to investigate the electronic effects of alkynes. Both 4-methylphenylacetylene and 4-fluorophenylacetylene can react with benzyl bromide to obtain the target product 1,2,3-triazoles with moderate to good yield (entries 1-2, Table 1). In addition, *para-* large steric substituted arylalkyne, 4-*tert*-butylphenylacetylene, which could smoothly react with benzyl bromide and provided the corresponding product in 70% isolated yield (entry 3, Table 1). Subsequently, we explored the reaction of 4-*tert*-butylbenzyl bromide with phenylacetylene and 3-methoxyphenylacetylene, where both obtained desired products in good yield (entries 4-5, Table 1). Compared with the reported complicated catalysts of CuI@UO-67-IM by Dong's group and PEG-tris-trz-Cu^I by Astruc's groups, there are rarely reported easy-prepared pure MOFs with considerable catalytic effect, for this rection.[13 (a),26]

Table 1. Substrate Scope for the Reaction of Benzyl Azide and Alkynes.[a]

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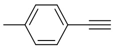
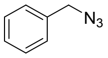
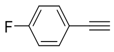
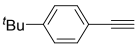
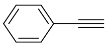
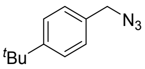
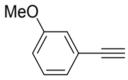
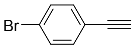
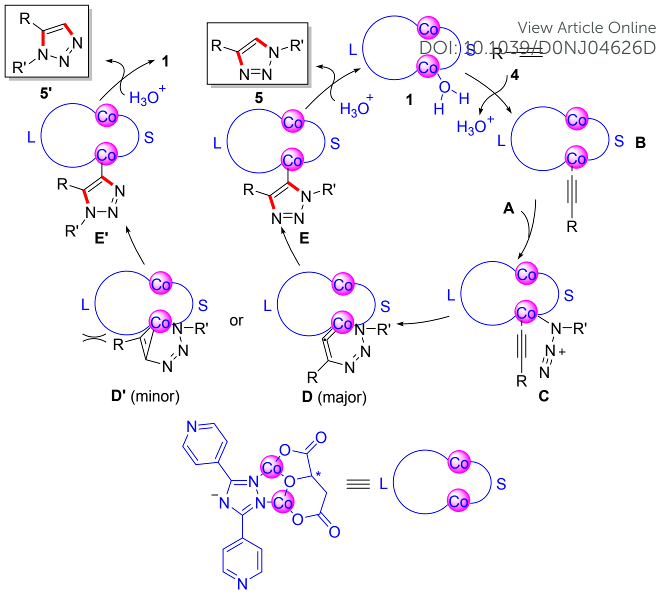
Entry	3	4	Isolated yield of 5+5'/ %
1			68
2			71
3			70
4			74
5			75
6			77

[a] Reaction conditions: benzyl halide (1 mmol), NaN_3 (1.5 mmol), H_2O (2 mL), Co-MOF (0.02 mmol), temperature (60 °C), alkynes (1.5 mmol) and reaction time (2 + 4 h).

As shown in Scheme 3, based on the experimental results and previous literature reports, we proposed a possible mechanism of the azide-alkynes cycloaddition reaction catalyst by **1**. First, catalyst **1** combined with alkynes **4** to furnished acetylide-MOF complex **B** along with release a molecule H_3O^+. Followed by smoothly interacts with azide compound **A** afford intermediate **C**.[27] The formation of intermediate **C** favors the alkyne carbon atom nucleophilically attack the nitrogen atom at the end of the azide.[28] Subsequently, alkyne and azide compounds undergo a cycloaddition reaction to obtain intermediate **D** or **D'**.[29] Compared with **D** and **D'**, the steric hindrance between R and MOF, R and R' in **D'** is greater than **D**, which leads to the predominance of intermediate **D**. Subsequent ring contraction of the generated **D/D'** would lead to intermediate **E/E'**. Finally, **E/E'** abstracts a proton from H_3O^+ that obtained the desired 1,2,3-triazole product and followed by regeneration of the **1** completes catalytic cycle.



Scheme 3. The possible mechanism of azide-alkynes cycloaddition reaction by catalyst **1**.

Friedel–Crafts Alkylation Reaction of *trans-β*-Nitrostyrenes and Indoles Catalyzed by 1

Friedel-Crafts alkylation reaction of indoles with *trans-β*-nitroalkenes is one of the most important paths for preparing tryptamine and its derivatives.[30] Different synthetic strategies and new heterogeneous catalysts have been proposed to access this type of compounds, so we further examined the activity of **1** for the reaction of Friedel–Crafts alkylation.

In order to expand the application range of catalyst **1**, we explored the catalytic performance of catalyst **1** for Friedel–Crafts alkylation reaction. Under an atmosphere of Ar, the indole derivative **8** was obtain in 56% isolated yield upon treatment of a 1: 1.5 mixture of (*E*)-(2-nitrovinyl) benzene (**6**) and 5-methoxy-2-methyl-1*H*-indole (**7**) with 10 mol% **1** in CH_2Cl_2 at 35 °C for 12 h. We explored the relationship of reaction solvent and time to determine the standard condition: *trans-β*-nitrostyrenes (0.2 mmol), indole (0.3 mmol), MOF **1** (0.01 mmol) in a solution of CH_2Cl_2 at 35 °C for 24 h. The indole derivative **8** was obtained with an isolated yield of 70% and thus the TON value is 70. Similarly, a leaching test (Fig. 3, right) and recyclability experiment (Fig. 4, right) and the catalytic conversions in the absence of **1** was tested Fig. 3 (right: no catalyst) were performed as mentioned above.

After five cycles, the conversion efficiency was slightly reduced (about 6 %) but still retained a good yield, and we tested the PXRD of MOF **1** and found the crystalline structure of **1** had no significant change as shown in Fig. 5 (right). Therefore, we can draw the

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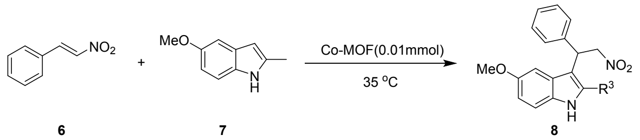
conclusion that **1** suggested high efficiency in the Friedel–Crafts alkylation reaction and can be regenerated easily and directly.

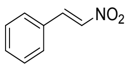
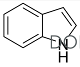
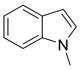
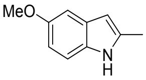
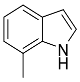
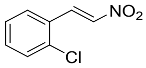
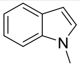
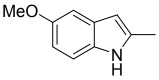
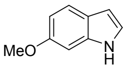
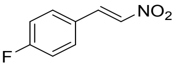
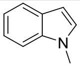
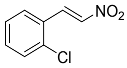
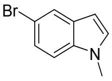
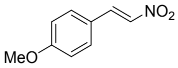
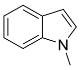


Scheme 4. The process of Friedel–Crafts alkylation reaction of *trans-β*-Nitrostyrenes and Indoles catalyzed by **1**.

Using **1** as the catalyst, we then examined the scope of this Friedel–Crafts alkylation with indoles (Table 2). For the purposes of convenience, reaction conditions always refer to standard conditions mentioned above. First, with (*E*)-(2-nitrovinyl) benzene as the *trans-β*-nitrostyrene substrate, we explored four electron-rich indoles with different substitution positions. As shown in Table 2, indole can make a certain degree improvement of isolated yield, and especially improved to 64% when the 1-position of indole was substituted by methyl (entry 2, Table 2), which shows that the electron-donating group on indole is conducive to product formation. The indole derivative 5-methoxy-2-methyl-1*H*-indole with two electron-donating groups yields the target product in a 70% isolated yield, which also shows that the more electron-rich the indole in this catalytic system, the more favorable the transformations (entry 3, Table 2).

We then changed the substrate (*E*)-(2-nitrovinyl) benzene to (*E*)-1-chloro-2-(2-nitrovinyl) benzene with an electron-withdrawing group and made reactions using three indoles with electron-donating groups to obtain the target product, which results in a good yield (entries 5-7, Table 2). We examined the reaction between (*E*)-1-fluoro-4-(2-nitrovinyl) benzene and 1-methyl-1*H*-indole, which afforded lower yields desired product (entry 8, Table 2). We found that trace yields or no reactions were obtained whether electron-deficient indole was used to react with *trans-β*-nitrostyrene or electron-donated *trans-β*-nitrostyrene was reacted with indole (entries 9-10, Table 2). Compared with the reported catalyst,[31] MOFs **1** can promote the reaction under mild conditions (shorter reaction time, lower temperature and no cocatalyst) and expanded wide scope of substrates with a good catalytic activity.

Table 2. Substrate Scope for the Reaction of *trans-β*-Nitrostyrenes and Indoles. [a]

Entry	6	7	Isolated yield of **8**/ %
1			43
2			64
3			70
4			45
5			63
6			68
7			51
8			40
9			0
10			trace

[a] Reaction conditions: *trans-β*-nitrostyrenes (0.2 mmol), indoles (0.3 mmol), CH_2Cl_2(1 mL), Co-MOF (0.01 mmol), 35 °C, 24 h.

According to the experimental result and conducting a wide literature survey, a possible mechanism Scheme 5 was proposed. *Trans-β*-nitrostyrene and coordinate water in the MOF form a H-bond, increasing the electrophilic character of the aliphatic carbon atom and thus favors the attack from the indole.[32] Indole interaction with the carbonyl oxygen in the MOF form a H-bond not only increases the nucleophilicity but also brings two substrates efficiently close for the formation of the alkylated product (Scheme 5, **F**).[31a] There is no H-bond between 1-methyl-1*H*-indole and the carbonyl oxygen in the MOF, but the electron donating effect of methyl also enhances the nucleophilic ability of indole.[33] *Trans-β*-nitrostyrene and indole undergo nucleophilic addition reaction to obtain intermediate **G**. The generated intermediate **G** underwent to the subsequent hydrogen transfer to afford the expected product **8**.

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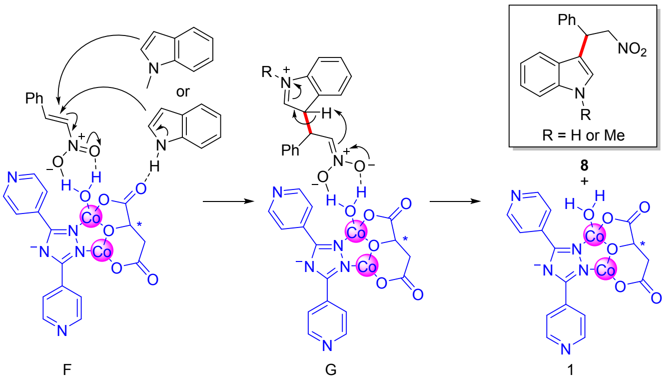
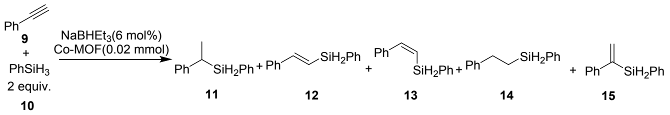


Scheme 5. The possible transformation mechanism of Friedel–Crafts alkylation reaction by **1.**

Selective Hydrosilylation of Alkynes Catalyzed by 1

Organosilanes are important synthetically valuable skeleton in various fields, such as organic synthesis, polymer chemistry, and drug discovery.[34] We here intend to explore the possibility of catalyzing the selective hydrosilylation of alkynes.[35]



Scheme 6. Selective Hydrosilylation of Alkynes Catalyzed by **1**

We started our investigations by testing the hydrosilylation of phenylacetylene with $PhSiH_3$ as a benchmark reaction. The transformation was initially achieved in the presence of 2 mol% MOF catalyst **1** and 6 mol% of $NaBHEt_3$ as an activator in tetrahydrofuran (THF) at 50 ℃。 We obtained five products with a total yield of 52% and their ratio was determined as 51:32:13:3 by ^1H NMR. Subsequently, we screened solvent and temperature of the reaction (Table S5) to get the optimal conditions: alkynes (1 mmol), $PhSiH_3$ (2 mmol), **1** (0.01 mmol) and $NaBHEt_3$ (6 mol %) in a solution of THF at 50 °C for 6 h.

Under standard conditions, we explored the reaction of 4-methylphenylacetylene with $PhSiH_3$. Similarly, the result has five kinds of products, the ratio is 54:26:12:4:4 (entry 2, Table 3). However, 4-methoxyphenylacetylene only obtained a trace amount of product (entry 3, Table 3).

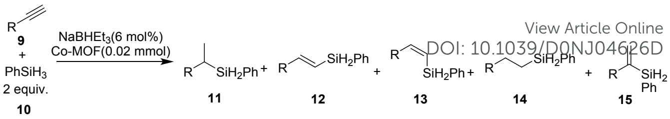
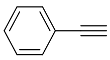
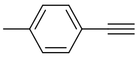
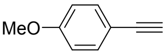
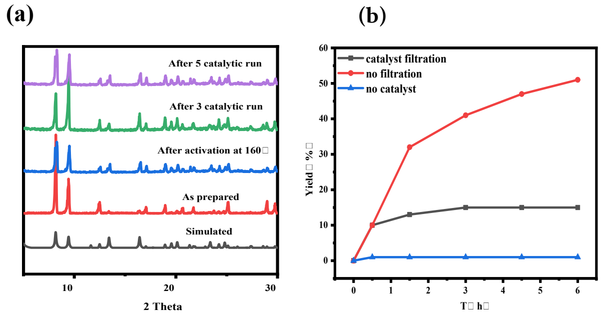


Table 3. Substrate Scope for the Reaction of Hydrosilylation of Alkynes. [a]

Entry	9	10	Isolated yield of **11-15** /%	Ratio of **11:12:13:14:15**
			52	51:32:13:3:1
2		$PhSiH_3$	16	54:26:12:4:4
3	 MeO		trace	-

[a] Reaction conditions: alkynes (1 mmol), $PhSiH_3$ (2 mmol), $NaBHEt_3$ (6 mol %), Co-MOF (0.02 mmol), temperature (50 °C), 6 h.

The leaching test, the catalytic conversions in the absence of **1** and leaching reusability was evaluated under standard conditions by selecting the hydrosilylation of phenylacetylene with $PhSiH_3$ as a model reaction. As shown in Fig 6 (b), when the reaction progressed to 30 minutes, the catalyst in the reaction system was removed. After lasted to 6 h, and the yield was 14%, the yield is much lower than with a catalyst. In our five cycles experiment, the overall yield change was within 10% (Fig 6c), which indicates that no leaching of the catalytically active sites occurs and that Co-MOF **1** features a typical heterogeneous catalyst nature. Furthermore, PXRD patterns of as-synthesized **1** show that the crystalline structure of **1** was maintained after five runs (Fig. 6a). To the best of our knowledge, there is no report of using MOF as a catalyst to directly reduce terminal alkynes to obtain alkyl silicon reagents in one step. The experiment confirms the potential feasibility of MOFs as a catalyst for this reaction. Although it is a pity that due to the space limitation of MOFs, the substrate is not expanded much, it provides a certain basis for the application of MOFs in this reaction in the future.



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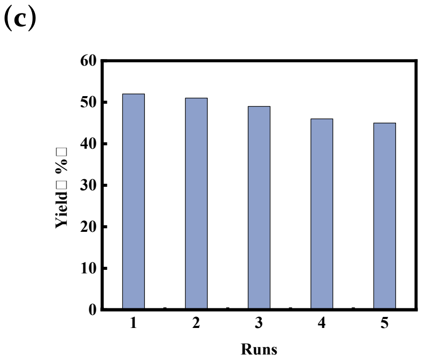

Fig. 6 PXRD patterns of as-synthesized **1** and after three and five catalytic runs (a), the leaching test (b) and recycling test (c) for the reactions of hydrosilylation of alkynes.

Conclusions

In this paper, we synthesized a pair of enantiomers Co-MOF of **1/2**. On account of the chemical stability and open metal sites in this framework, the heterogeneous catalytic performanced good recoverability and shown not only in the sequential one-pot azide-alkynes cycloaddition and Friedel-Crafts reactions of indoles with trans-β-nitrostyrenes, but also in the hydrosilylation of alkynes reactions under a relatively mild condition. Besides, the corresponding catalytic mechanism was revealed.

Conflicts of interest

The authors declare no conflict of interest.

Acknowledgements

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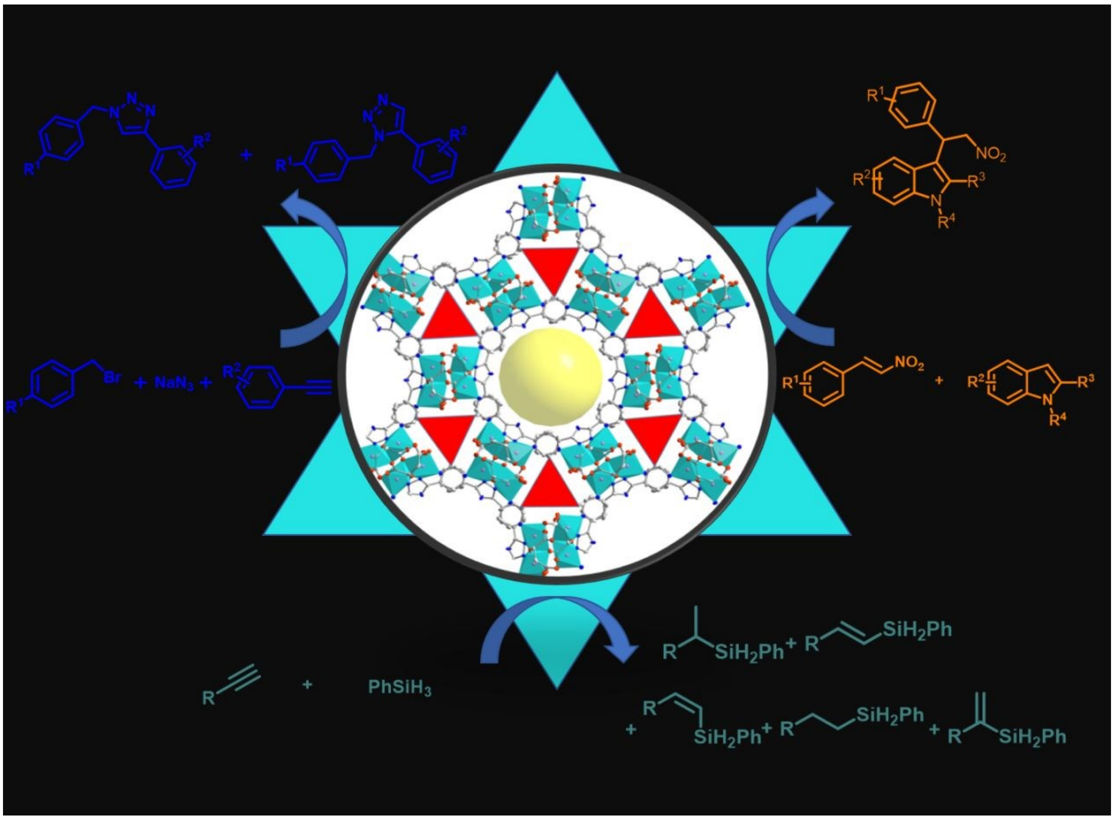
A Robust Heterogeneous Co-MOFs Catalyst in Azide-alkynes Cycloaddition and Friedel-Crafts Reactions as well as Hydrosilylation of Alkynes†

Tai-Xue Wu,[a‡] Jun-Song Jia,[a‡] Wei Luo,[a] He-Dong Bian,[ab*] Hai-Tao Tang,[a*] Ying-Ming Pan,[a] Fu-Ping Huang[a*]



A robust Co(II) MOFs with high stability in high temperature, different solvent and strong acid/base condition, were gram-scale prepared to be an effective heterogeneous catalyst to promote azide-alkynes cycloaddition reaction, Friedel-Crafts reactions of indoles and hydrosilylation of alkynes reactions.