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J. Am. Chem. Soc., Just Accepted Manuscript • DOI: 10.1021/jacs.8b12372 • Publication Date (Web): 15 Jan 2019 Downloaded from http://pubs.acs.org on January 15, 2019

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Catalysis through Dynamic Spacer Installation of Multivariate Functionalities in Metal-Organic Frameworks

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Supporting Information Placeholder

ABSTRACT: We demonstrate herein a facile strategy to engineer versatile catalytically active coordination interspace in a same primitive metal-organic framework (MOF) for variable heterogeneous catalysis. Different functional ligands can be reversibly inserted into and removed from *proto*-LIFM-28 individually or successively to bring in single or binary catalytic sites for specific reactions, and switch the parent MOF to multipurpose catalysts. Alcohol-oxidation, Knoevenagel-condensation, click, acetal and Baylis-Hillman reactions are achievable through simple exchange of a single catalytic spacer, while sequential or stepwise reactions are designable via selective combination of two catalytic spacers with different functionalities, thus making *proto*-LIFM-28 as a multivariate MOF for multiuse and economic catalysis.

INTRODUCTION

Metal-organic frameworks (MOFs) have emerged as a fruitful material platform for a diversity of applications owing to their advantages in pore size adjustability, structural diversity and functional tailorability.¹⁻³ Their great prospect in heterogenous catalysis has attracted continuous interest.^{4,5} Moreover, their structural designablity and chemical variety^{6,7} may endow MOFs with synergistic effects for multivariate catalysis,^{8,9} particularly of importance in developing cooperatively sequential, stepwise, tandem, etc. reactions.^{4,8,10-12} It has been found that, by virtue of combining distinct inorganic/organic catalytic sites, for example, Lewis acid and Brønsted base centers,¹³ organocatalytic and organometallic-Ir(I) catalytic domains,14 or organic-base and acid catalytic groups,¹⁵ MOFs can act as bifunctional heterogeneous catalysts. Nevertheless, this promising field still remains in its infancy probably due to a lack of feasible strategy to engineer active interspace of coordination framework incorporating different vet cooperative catalytic centers in a single MOF for sequential reactions.¹⁶

To develop bi- or multipurpose MOF catalysis, a prerequisite is to construct bi- or multifunctional MOFs, or make the functional sites exchangeable via postsynthesis. These challenges have been successfully solved by multivariate MOFs (MTV-MOFs) strategy through one-pot synthesis with mixed linkers,¹⁷ or postsynthetic modification via linkers or metals exchange;¹⁸⁻²⁰ however, the exact location and quantity control of specific functional groups is still a challenge.²¹ Zhou developed a kinetically controlled synthetic strategy SLI (sequential linker installation) to introduce different ligands and control their positions and distributions.²² We further proposed a dynamic spacer installation (DSI) approach to construct functional Zr-MOFs by reversible installation and uninstallation of different ligands into pre-defined positions of a single *proto*- MOF LIFM-28,23 thus opening up a new way of multivariate MOFs for multifunctionality (so-called swing-role MOF approach).²⁴ This approach is adequate for design of multivariate MOF catalysts with precise location and quantity of catalytic sites, also taking advantage of resource conservation since only one parent MOF is utilized. As illustrated in Figure 1, insertion and exchange of one spacer carrying different catalytic centers can switch primitive MOF for different reactions, while insertion of two spacers carrying cooperative catalytic centers lead to multivariate MOF catalysis for sequential or stepwise reactions. Since all inserted spacers can be removed and replaced to reuse the primitive LIFM-28, such DSI approach for generation of multivariate MOF catalysts by virtue of multifunctional and synergistic coordination interspace engineering (CISE, means engineering of confined room from formation of coordination bonds where specific physical property and chemical reactivity are exhibited) strategy may provide an efficient way of environmental friendliness catalysis.25-

RESULTS AND DISCUSSION

Design of multivariate MOF catalysis. To demonstrate the CISE strategy for multivariate MOF catalysts, the robust prototype-MOF $[(Zr_6(\mu_3-O)_4(\mu_3-$ LIFM-28, $OH_4(H_2O_4(OH_4(L)_4)$ -solvents (L 2,2'bis(trifluoromethyl)-4,4'-biphenyldicarboxylate), was prepared,²⁴ and one or two types of secondary or ternary ligands with distinctive lengths were installed and uninstalled with pinpoint accuracy through the DSI approach to achieve recyclable usage of parent LIFM-28 (Figure 1, see details in Supporting Information). As listed in Table S1, installation of single spacer NH₂-BDC or BPYDC into proto-LIFM-28 leads to LIFM-28-NH₂-BDC and LIFM-28-BPYDC, respectively.

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Figure 1. Generation of multivariate MOF catalysts via DSI approach from *proto*-LIFM-28 showing their interconversion toward different catalytic purposes. The molecular structures of the inserted functional spacers are illustrated for crystal structures, in which –ArSO₃H group is simplified as orange ball and Zr₆-clusters are shown as purple polyhedrons. H and F are omitted for clarity.

While insertion of spacers BPYDC and NH₂-TPDC offers LIFM-80. The BPYDC can be further postmodified via Cu(I) metalation to turn LIFM-80 and LIFM-28-BPYDC into LIFM-80(Cu) and LIFM-28-BPYDC(Cu) with open metal sites for catalysis.^{28,29} Moreover, -NH₂ groups in LIFM-80 can be embellished with 2-sulfobenzoic anhydride (SBA) to change to LIFM-80-ArSO₃H, followed by chelation of Cu(I) to give LIFM-80(Cu)-ArSO₃H.

Interconversion among these post-functionalized MOFs via DSI approach makes it facile to switch the proto-LIFM-28 to multipurpose MOF catalysts. The open Cu(I)-chelating sites in LIFM-28-BPYDC(Cu), LIFM-80(Cu) and LIFM-80(Cu)-ArSO₃H offer a similar bpy-Cu(I)/TEMPO catalytic system which has been widely used for practical aerobic oxidation from alcohols to aldehydes in organic chemistry.³⁰⁻³² Furthermore, these Cu(I) sites can catalyze click reaction.³³ On the other hand, the -NH2 groups in LIFM-28-NH2-BDC, LIFM-80 or LIFM-80(Cu) are able to promote Knoevenagel condensation by their Brønsted basicity, which is useful in synthesis of pharmaceuticals.13,34 Postmodification on -NH2 groups can convert LIFM-80 to LIFM-80-ArSO₃H, thus turning the basic catalytic sties into the acid centers competent for acetal or Baylis-Hillman reactions. Therefore, the bifunctional LIFM-80(Cu) and LIFM-80(Cu)-ArSO₃H feature in distinct catalytic systems with synergistic effects for different purposes. As shown in Figures 1 and 2, by virtue of DSI process and metalchelation/covalent-postmodification, the Cu(I)-redox, aminebase and sulfuric-acid catalytic sites can be either individually introduced or cooperatively combined into the coordination interspace of proto-LIFM-28 to reach to or interconvert among the following purposes: (1) single-reaction catalysis of alcohol-oxidation, Knoevenagel-condensation, click, acetal, or

Baylis-Hillman reactions, (2) sequential-reaction catalysis of alcohol-oxidation \rightarrow Knoevenagel-condensation, (3) stepwise-reaction catalysis I of alcohol-oxidation \rightarrow click reaction \rightarrow Knoevenagel-condensation, (4) stepwise-reaction catalysis II of alcohol-oxidation \rightarrow acetal reaction and, (5) stepwise-reaction catalysis III of alcohol-oxidation \rightarrow Baylis-Hillman reaction.

Before testing the specific reactions, the MOF catalysts postsynthesized or postmodified with multivariate functionalities have been fully characterized, by means of ¹H NMR, single-crystal and powder X-ray diffraction (PXRD), thermogravimetric analysis (TGA), nitrogen absorption (77 K), CO₂/CH₄ adsorption (298 K), scanning electron microscope (SEM) and transmission electron microscope (TEM), for their installation and uninstallation of functionalized spacers. The results indicate that the functionalized MOFs via DSI process generally retain good thermostability with increased pore surface, keep the crystal morphology with good phase purity, and are competent for heterogeneous catalytic reactions (Supporting Information, Figures S1-15 and S31-33, Tables S1-4).

Multivariate MOF catalysts for elementary, sequential or stepwise reactions. The single reactions listed in Figure 2 have been primarily tested by MOF-catalysts postfunctionalized with Cu(I), -NH₂ and -ArSO₃H sites individually, proving that all reactions can be well performed. And then two types of bifunctional MOF-catalysts are designed and thoroughly studied. One is LIFM-80(Cu) featuring in a combination of Cu(I)redox + amine-base catalytic sites. Another is LIFM-80(Cu)-ArSO₃H characteristic of a combination of Cu(I)-redox + sulfuric-acid catalytic sites. Based on these two bifunctional MOF-catalysts, not only a series of Cu(I)-, base- and acidcatalyzed elementary reactions can be achieved, but also vari-

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able sequential or stepwise reactions can be accomplished (Tables 1-2 and Supporting Information, Figures S16-20, Tables S5-7). All products have been convincingly identified by ¹H NMR and CG-MS spectral measurements wherever necessary (Figures S21-30).



Figure 2. Multivariate MOFs catalyzed elementary, sequential or stepwise reactions.

Considering that oxidation of alcohols to aldehydes represents one of the most important processes in the chemical industry as the resulting products are valuable intermediates in fine chemistry,³⁵ we first checked LIFM-28-BPYDC(Cu) and LIFM-80(Cu) installed with Cu(I)-redox ligand, and found that they enabled efficient aerobic oxidation of primary alcohols to corresponding aldehydes using readily available substrates with ambient air as the oxidant at room temperature (RT). The catalytic performance differs in common organic solvents (Table S5), of which the mixture of DMF-MeCN (v:v = 1:1) represents the best choice in terms of the conversion from benzyl alcohol (1) to benzaldehyde (2, >99%). The catalytic nature of Cu(I) sites in LIFM-80(Cu) was verified by a hot filtration experiment (Figure S16), confirming that removing MOF-catalyst from reaction mixture will stop conversion of 1 to 2. The catalyst recycling tests suggested that the functionalized MOFs can be reused well for four times before Cu(I) being partially oxidized, verified by retention of the MOF PXRD patterns during four catalytic cycles, after which the

MOF catalyst turned into greenish and X-ray photoelectron spectroscopy (XPS) measurement indicated appearance of Cu(II) (Figures S17 and S34-35). A similar reaction condition optimization was evaluated for the catalytic activity of aminebase toward Knoevenagel-reaction. After testifying the catalytic effectiveness by use of LIFM-28-NH2-BDC, the reaction is optimized in different solvents with bifunctional LIFM-80(Cu) (Table S6). In the presence of LIFM-80(Cu) carrying amine-base sites, the condensation reaction of 2 and malononitrile (3) can finish in 8 h in a DMF-MeOH (v:v = 1:1) mixture at RT, affording product 2-benzylidenemalononitrile (4) with the highest conversion (>99%). Similarly, the catalytic nature of base-sites in LIFM-80(Cu) was verified by a hot filtration experiment, and the recycling tests of MOF-catalyst shows no detectable deactivation and PXRD change after five reaction runs (Figures S18-19). The catalytic performance of the present MOF catalysts for above two reactions are comparable with known MOF catalysts reported in literature (Tables S8-9).

Table 1 Summary of catalytic reactions with Cu(I) and base sites.

Reactions	Catalyst	Solvent	Time/h	Yield/%
Oxidation	LIFM-28-	MeCN/DMF	6	>99
reaction	BPYDC(Cu)			
	LIFM-80(Cu)	MeCN/DMF	6	>99
Click	LIFM-28-	MeOH/DMF	8	67
reaction	BPYDC(Cu)			
	LIFM-80(Cu)	MeOH/DMF	8	73
Knoevenagle	LIFM-28-	MeOH/DMF	8	>99
condensation	NH ₂ -BDC		0	
	LIFM-80(Cu)	MeOH/DMF	8	>99
G			(> 00
Sequential	LIFM-80(Cu)	MeCN/DMF	0	>99
reaction ^a		MeCN/DMF ^{<i>v</i>}	8	>99
Stamming	$I IEM 90(C_{\rm rel})$	M.CNI/DME.	(5(
Stepwise	LIFM-80(Cu)	MeCN/DMF.	0	50
reaction I ^a		MeOH/DMF:	8	60
		MeOH/DMF	8	>99

^a Results for each step. ^b With or without MeOH

The above catalytic tests turn out that the bifunctional LIFM-80(Cu) is able to promote both alcohol-oxidation and Knoevenagel-condensation individually in similar solvent systems. Therefore, a sequential reaction of alcohol-oxidation \rightarrow Knoevenagel-condensation in due succession without isolation of intermediate 2 is tried. After the first oxidation reaction of 6 h, a certain amount of 3 was added either directly or dissolved in MeOH to the reaction system, and the resulting mixture was continued to react at RT for additional 8 h, affording 4 with excellent conversion (>99%, Table 1). The comparison of the PXRD patterns before and after the consecutive reactions indicates that LIFM-80(Cu) catalyst remains unchanged (Figure S20), thereof stable enough to sustain such sequential or tandem reaction and even to be recycled for repeated usage. We further explored the catalytic performance of LIFM-80(Cu) on a wide range of substrates, carrying out the oxidationcondensation reactions on various substituted benzyl alcohols with electron-donating and electron-withdrawing groups. The results are summarized in Table S7. It was found that the alcohol-oxidation is the control step in this sequential reaction. The substituted benzyl alcohols gave relatively lower conversion rates in the first oxidation step in contrast to unsubstituted

1, probably due to a reason that the increased substrate size will retard the diffusion rate in the same coordination interspace.²² However, the following Knoevenagel reaction is a quantitative catalytic process, since the cooperative Cu(I) and $-NH_2$ catalytic centers are site-isolated but adjacent in the coordination interspace. The overall conversion also depends on the molecular nature of substrates, suggesting that the electron-donating group of substrates can benefit the sequential reaction.

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Since the Cu(I)-center in LIFM-80(Cu) is also capable of catalyzing click reaction, which is proven by use of LIFM-28-BPYDC(Cu) to promote reaction of 4-ethynylbenzaldehyde (5) and azidotrimethylsilane (6) in a DMF-MeOH (v:v = 1:1) mixture to give 7 (4-(1H-1,2,3-triazol-4-yl)benzaldehyde), we are interested to explore if a three-step reaction is possible to combine the click reaction into previous sequential reactions using the same MOF-catalyst in a stepwise way. (4-Ethynylphenyl)methanol (8) was used as an initial reactant, which was oxidized by LIFM-80(Cu) to 5 with moderate yield (Table 1). The primary product 5 and cleaned MOF-catalyst were charged in a mixture of DMF-MeOH containing 6 for click reaction, giving a main product 7 in 60% yield. After isolation and washing, the recycled LIFM-80(Cu) was still efficient to catalyze Knoevenagel-condensation from 7 to 9 in the same solvent system (Figure 2). It is worth noting that a lot of attention has been focused on homogeneous systems for stepwise catalysis, while few reports are known to use MOFs as heterogeneous catalysts for stepwise reactions.²⁸ Although the interval products have to be separated to continue the successive reactions in different solvent systems, such heterogeneous stepwise catalysis is still of significance because the MOF-catalyst is easily recycled and robust for successive reactions.

Reactions	Catalyst	Solvent	Time/h	Yield/%
Acetal reaction	LIFM-80(Cu)- ArSO ₃ H	МеОН	2	>99
Baylis-Hillman reaction	LIFM-80(Cu)- ArSO ₃ H	THF	24	53
Stenwise	LIFM-80(Cu)- ArSO ₃ H	MeCN/DMF	6	>99
reaction II ^a		MeOH	2	>99
Stepwise	LIFM-80(Cu)-	MeCN/DMF	6	>99
reaction III ^a	/100311	THF	24	47

^{*a*} Results for each step.

As an alternative bifunctional MOF-catalyst, LIFM-80(Cu)-ArSO₃H can execute acetal reaction to turn **2** completely into **10** via strong Brønsted acid -ArSO₃H groups. LIFM-80(Cu)-ArSO₃H also can carry out Baylis-Hillman reaction with 2-cyclohexene-1one (**11**) as the nucleophile, which needs DABCO (1,4diazabicyclo[2.2.2]octane) as the Lewis basic promoter,³⁶ giving a moderate conversion of **2** into **12** (Table 2). In both cases, the catalytic yields are comparable or higher than those of reported MOFs (Table S10, S11). As a consequence, two stepwise reactions can be designed based on cooperative Cu(I)-redox and ArSO₃H-acid catalytic sites. As shown in Figure 2 and Table 2, after effective oxidation of 1 into 2, quantitative formation of acetal 10 or moderate transformation into 12 can be implemented by using the single LIFM-80(Cu)-ArSO₃H as bifunctional catalyst. These results further demonstrate a successful utilization of primitive LIFM-28 for multivariate MOF catalysis toward multiple reactions in a cost-saving procedure.

CONCLUSIONS

In summary, we present a new versatile multivariate MOF synthetic strategy to construct variable heterogeneous catalysts through dynamic installation and uninstallation of functional secondary and ternary ligands into the primitive LIFM-28, in with metal-chelation combination and covalentpostmodification processes. One single or two cooperative catalytic sites can be introduced into coordination interspace with precise and quantitative control, suitable for multipurpose or consecutive reactions. For a demonstration, interconversion among multiple MOF-catalysts carrying individual Cu(I)redox, amine-base and sulfuric-acid catalytic sites, and bifunctional MOF-catalysts possessing Cu(I)-redox + amine-base or Cu(I)-redox + sulfuric-acid cooperative catalytic sites, are implemented. Both the elementary reactions, including alcohol-oxidation, Knoevenagel-condensation, click, acetal and Baylis-Hillman reactions, and the sequential or stepwise catalysis among these elementary reactions, are achieved under relatively mild conditions. These results may expand the potential of MOFs as multifunctional catalysts for organic transformations,^{37,38} and provide a promising way to push heterogeneous MOF catalysis toward more efficient and environmentally friendly catalytic chemistry.

ASSOCIATED CONTENT

Supporting Information

Materials and Instrumentation. Details of syntheses, characterization, crystallography (CIF), spectra and catalysis. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

This work was supported by the NSFC (21821003, 21720102007, 21573291, 21890380), LIRT Project of GPRTP (2017BT01C161) and the FRF for the Central Universities for funding.

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