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Bottom-Up Assembly of a Highly Efficient Metal-Organic Framework for Cooperative Catalysis

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Supporting Information

ABSTRACT: In this study, we demonstrate a bottom-up assembly of a monomeric copper complex and a two-dimensional (2-D) heterometallic metal-organic framework (MOF) from a carboxylate-functionalized tridentate Schiff base ligand and metal ions. The obtained 2-D MOF features a unique bimetallic copper center which is different from its monometallic precursor and acts as an efficient heterogeneous catalyst for the Friedel-Crafts reaction and Henry reaction. The MOF catalyst shows a remarkably superior activity compared to its homogeneous counterparts in a wide range of substrates. It is presumably ascribed to the dual activation of the substrates by the active bimetallic copper center confined in the MOF network, which is supported by the significant changes in catalytic activity at low catalyst/substrates ratios when using the 2-D MOF and its precursor as catalysts, respectively. Moreover, the MOF catalyst also shows an excellent stability and recyclability. Our work, therefore, provides a stepwise strategy to design a heterogeneous cooperative catalyst, by taking advantage of the modulated structure of MOF and tunable functionality of the tridentate Schiff base, with high performance in a variety of organic synthesis.



INTRODUCTION

Enzyme catalysis is a predominant process in nature due to its excellent conversion, specificity, efficiency, as well as transformation range, which usually requires cooperation between metal centers and protein residues to activate substrates.¹ Therefore, great efforts have been devoted to the synthesis of enzyme-mimicking cooperative catalysts with bi- or polynuclear metal centers in the past few decades. Numerous homogeneous cooperative catalysts, especially bimetallic catalysts, were first studied due to their facileness in design and synthesis, while they were limited in stability and recyclability.² In order to overcome shortcomings of homogeneous catalysis, one strategy to design heterogeneous cooperative catalysts was to load molecular catalysts onto inorganic or organic supports.³ For example, Li and co-workers recently developed a series of high-performance solid catalysts with multiple active sites working cooperatively in asymmetric catalysis by utilizing the inorganic microporous/mesoporous materials or porous organic frameworks as supports.⁴ Even though such heterogeneous cooperative catalysts have achieved success, the concise structure of active centers in solid catalysts is still mysterious. As we know, the configuration and spatial distance of the active sites greatly affect the efficiency of catalysts, and thus the rational design and synthesis of cooperative catalysts based on precise structure details are challenging and gaining more and more interest.

Metal-organic frameworks (MOFs) have emerged as a class of crystalline materials,⁵ which offer great potential in heterogeneous catalysis owing to their high porosity, excellent stability, composition tunability, and well-defined reaction microenvironments.⁶ In particular, structure engineering and modulated synthesis of MOFs have achieved appreciable progress in recent years, allowing for the possibility of spatial control of active centers and making MOFs an ideal platform to design high-performance cooperative catalysis.' For instance, Cui and co-workers recently reported examples of metallosalen MOF catalysts, which showed high efficiency and selectivity in asymmetric cyanosilylation of aldehydes and kinetic resolution of epoxides, respectively, by taking advantage of bimetallic cooperative catalytic effect.⁸ In another group, Lin and co-workers confined Co(III)(porphyrin) pairs in an interpenetrating MOF to realize high-efficient cooperative catalysis for hydration of terminal alkynes.⁹ Despite these impressive advances, cooperative catalysis based on MOFs is rarely reported, and the design of novel catalysts with high efficiency in organic transformations is of ongoing interest. To

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Scheme 1. Synthesis of Tridentate Schiff Base Ligand H₃L, Mononuclear Copper Complex 1 and MOF 2



obtain a MOF-based cooperative catalyst with bi- or multiple active centers, a judicious choice of ligands and metals is demanding. It is a straightforward strategy to integrate catalytic centers into ligands that can tolerate the harsh synthetic environment of the targeting MOF.

The tridentate Schiff base is a well-known ligand in numerous catalytic systems.¹⁰ In these catalytic systems, the tridentate ligands can bind strongly to metal ions via the ONO coordination pockets and form complexes with multiple metal centers to afford a synergistic catalytic center.¹¹ To integrate the Schiff base complex into a MOF, terminal carboxylic moiety is introduced to transform the complex into a MOF linker, allowing further extension to an infinite network. Since the tridentate ONO pocket and the terminal carboxylate exhibit different binding ability to metals, it is possible to organize the metal center step by step. The copper(II) ion usually shows tetra-, penta-, and hexa-connected coordination geometry through bonding to N or O donors of various ligands,¹² making it promising to form a multinuclear metal center. Our strategy is (1) obtain a discrete mononuclear Cu (II) complex based on a tridentate Schiff base ligand bearing a spare carboxylic group; (2) use the copper complex as a secondary building unit (SBU) to assemble a MOF with another metal; (3) perform catalytic reactions by using this heterogeneous MOF catalyst.

Herein, we report the bottom-up assembly of a porous twodimensional (2D) MOF (2) through a reaction between a strategically installed Schiff-base monomeric copper complex (1) and two and four connected cadmium clusters. Unlike the mononuclear precursor, the as-formed 2 has a dinuclear copper center connected by bridging oxygen atoms. Because of the suitable distance and geometry of the two metal ions in the active site of 2, the MOF exhibits efficient cooperative Friedel–Crafts alkylation of indole with nitrostyrene and Henry reaction between aromatic aldehydes and nitromethane, respectively. To the best of our knowledge, complex 2 is the first example of heterogeneous MOF catalyst based on a tridentate Schiff base with dinuclear copper center, which shows high performance cooperative catalytic properties.

EXPERIMENTAL SECTION

Materials and General Procedures. All of the chemicals used in this study were commercially available and used without further purification. The IR (KBr pellet) spectra were recorded (400-4000 cm⁻¹ region) on a Nicolet Magna 750 FT-IR spectrometer. ¹H and ¹³C NMR data were collected on an Agilent VNMRS-600 spectrometer. Electrospray ionization mass spectra (ES-MS) were recorded on a Finnigan LCQmass spectrometer using DMSO as mobile phase. Single-crystal X-ray (XRD) data of 1 were collected on an D8 VENTURE diffractometer using Cu K α radiation ($\lambda = 1.54184$ Å) at 100 K, while single-crystal XRD data of 2 were collected at 100 K at NFPS (Shanghai) synchrotron radiation on BL17B beamline using $\lambda = 0.65251$ Å. All of the data were indexed, integrated, and scaled using the APEX3 program. The structures of 1 and 2 were determined by the direct method and refined on F^2 by the full-matrix least-squares technique using the SHELX-2018 program package.¹ All the hydrogen atoms attached to the ligand were placed in calculated positions and refined using a riding model. Contributions to scattering due to these highly disordered guest molecules in 2 were removed using the SQUEEZE subroutine of the PLATON software package.¹⁴ The structure was then refined again using the resulting new HKL file. Crystals 1 and 2 can be best formulated as [Cu(HL). MeOH] \cdot [Cu(HL) \cdot (MeOH)₂] and [Cd₃(CuL)₈ \cdot (DMF)₆ \cdot (H₂O)₈ \cdot $(NMe_2)_2$], respectively, on the basis of single-crystal diffraction, IR spectra, and thermogravimetric analysis (TGA). Crystal data and details of the data collection are given in Table S1, while the selected bond distances and angles are presented in Tables S2 and S3. CCDC 1863032 (for 1) and 1863033 (for 2) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre. Powder X-ray diffraction (PXRD) experiments were carried out on a DMAX2500 diffractometer using Cu K α radiation. The simulated PXRD spectra were produced using the SHELXTL-XPOW program based on the single-crystal data. TGA data were performed in an argon atmosphere with a heating rate of 5 °C/min on a TGA-50 (SHIMADZU) thermogravimetric analyzer.

Synthesis of H_3L . As outlined in Scheme 1, the carboxylatefunctionalized tridentate Schiff base ligand (H_3L) was readily synthesized by the condensation reaction of (1S, 2R)-(-)-cis-1amino-2-indanol (0.82 g, 5.5 mmol) with 3'-tert-butyl-5'-formyl-4'hydroxybiphenyl-4-carboxylic acid (1.49 g, 5.0 mmol) in methanol (MeOH) at 60 °C. After the reaction, the ligand was washed several times with MeOH and characterized by ¹H NMR, ¹³C NMR, and



Figure 1. A view of (a) the single framework of 2 along the *a* axis and (b) 2-fold interpenetrated structure of 2 (Cd, teal; Cu, green; O, red; N, blue; C, gray; Cd1O₈ and Cd2O₇ units are shown as teal and yellow polyhedron, respectively; only the O atom of DMF molecules are shown for clarity)

mass spectroscopy, respectively (Figures S1–S3). Fourier transform infrared (FT-IR) data (KBr pellet, cm⁻¹) (Figure S5): 3480(w), 2952(s), 2910(s), 2867(m), 1700(w), 1670(w), 1630(s), 1605(s), 1533(s), 1480(m), 1460(m), 1440(m), 1386(s), 1268(m), 1251(m), 1224(w), 1169(m), 1095(w), 1052(w), 1016(w), 993(w), 952(w), 888(w), 860(m), 790(m), 775(w), 750(s), 712(w), 651(w), 634(w), 620(w), 564(w), 527(m), 500(w), 449(w).

Synthesis of $[Cu(HL)·MeOH] \cdot [Cu(HL)·(MeOH)_2]$ (1). A mixture of $Cu(OAc)_2$ ·H₂O (20.0 mg, 0.1 mmol) and H₃L (42.9 mg, 0.1 mmol) was placed in a glass vial containing N_iN' -dimethylformamide (DMF) (0.5 mL), MeOH (3.5 mL), and water (0.10 mL). The vial was sealed and heated at 60 °C for 24 h. Blue, needle-like crystals were formed and washed with MeOH and dried in air at room temperature. The yield was ~75.0% based on H₃L. FT-IR data (KBr pellet, cm⁻¹) (Figure S6): 3480(s), 2950(s), 2910(s), 2870(m), 2360(w), 1700(w), 1620(s), 1604(s), 1533(s), 1478(w), 1458(w), 1420(m), 1386(s), 1328(m), 1275(s), 1258(m), 1228(m), 1166(s), 1107(s), 1072(m), 1053(w), 1013(w), 980(w), 950(w), 895(w), 857(m), 805(w), 788(m), 774(m), 751(m), 731(w), 711(w), 680(w), 640(w), 605(w), 548(w), 521(m), 491(w), 448(w).

Synthesis of $[Cd_3(CuL)_8 \cdot (DMF)_6 \cdot (H_2O)_8 \cdot (NMe_2)_2]$ (2). A mixture of CdBr₂ (5.44 mg, 0.02 mmol) and complex 1 (21.5 mg, 0.02 mmol) was placed in a glass vial containing DMF (3.0 mL), MeOH (2.0 mL), and water (0.2 mL). The vial was sealed and heated at 80 °C for 36 h. Blue, block-like crystals were collected, washed with MeOH, and dried in air at room temperature. The yield was ~60.0% based on cadmium ion. Notably, complex 2 cannot be prepared by a one-pot reaction of Cu²⁺, Cd²⁺, and H₃L. FT-IR data (KBr pellet, cm⁻¹) (Figure S7): 3450(s), 2951(s), 2908(s), 1660(s), 1620(s), 1603(s), 1529(s), 1478(w), 1457(m), 1393(s), 1324(m), 1277(s), 1257(s), 1230(m), 1199(w), 1163(s), 1099(m), 1010(w), 892(w), 860(s), 806(w), 788(s), 776(s), 752(s), 712(m), 662(m), 607(m), 544(m), 519(w), 464(m).

RESULTS AND DISCUSSION

Crystal Structure of 1 and 2. A single-crystal X-ray diffraction analysis reveals that 1 crystallizes in $P2_1$ space group, and its asymmetric unit contains a $[Cu(HL)\cdot MeOH]$ and a $[Cu(HL)\cdot (MeOH)_2]$ unit. In the structure of 1, the ligand H₃L acts as a tridentate ONO chelator through the imine group and two hydroxyl groups. As shown in Scheme 1, the Cu1 center in the $[Cu(HL)\cdot MeOH]$ unit is four-coordinated by the ONO atoms from tridentate ligand H₃L and one MeOH molecule, while the Cu2 center in $[Cu(HL)\cdot (MeOH)_2]$ unit is five-coordinated by ONO donors from H₃L and two MeOH molecules (Figure S12). As a four-coordinated copper center, the Cu1 is loaded in a distorted square-planar

geometry with Cu-O bond lengths ranging from 1.884(3) to 1.980(3) Å and Cu–N bond length of 1.905(3) Å, whereas the five-coordinated Cu2 center is loaded in a square-pyramidal geometry with Cu-O bond lengths ranging from 1.896(3) to 2.451(3) Å and Cu-N bond length of 1.924(3) Å (Table S2). However, the coordination of the axial methanol molecule with the Cu2 center (Cu-O distance is 2.451(3) Å) is obviously weaker than that of the equatorial methanol molecule with the Cu2 center (the Cu–O distance is 1.943(3) Å). The Cu(HL) units in 1 are linked via intermolecular hydrogen bonding interactions (O-H···O distances range from 2.49 to 2.51 Å) between carboxyl groups and neighboring two hydroxyl groups from 1-amino-2-indanol and methanol molecule, respectively, to generate a one-dimensional (1D) chain (Figure S13). After that, the 1D chains are further assembled into a threedimensional (3D) supramolecular structure by edge-to-face stacking intermolecular $\pi - \pi$ interaction ($\pi - \pi$ 3.62 Å) between adjacent benzene rings of indane moieties and $CH \cdots \pi$ interaction (C-H... π 3.71 Å) between the butyl group and adjacent benzene ring from another Cu(HL) unit and CH… π interaction (C-H··· π 3.88 Å) between CH- group of indane moiety and adjacent benzene ring from another Cu(HL) unit ligand (Figure S14). It is noteworthy that the carboxyl groups in 1 are protonated, which is consistent with the protonated COOH ν C=O stretch at 1700 cm⁻¹ comparing with the free H_3L ligand.¹⁵ Thus, in this study, the Cu(HL) moiety was utilized as a molecular building block to construct an infinite network structure as follows.

Gratifyingly, a solvothermal reaction of mononuclear complex 1 and Cd^{2+} ion yields a single crystal 2. The crystal structure determined by single-crystal XRD reveals 2 exhibits a porous 2D MOF that crystallizes in the orthorhombic space group $P2_12_12$ with half of one formula unit in the asymmetric unit. As shown in Scheme 1, the molecular building blocks of CuL in 2 possess a similar square-planar coordinated mode as Cu1(HL) unit in 1, with the Cu–O bond lengths ranging from 1.884(5) to 1.960(6) Å and Cu–N bond lengths ranging from 1.910(6) to 1.924(6) Å, respectively. Different from 1, the CuL units acting as molecular building units are bridged through two indane-bound oxygens to generate two cis dimeric $(CuL)_2$ moieties with a Cu-Cu distance of 2.806 and 2.841 Å, respectively. With two crystallographically independent Cd²⁺ ions in 2, the Cd1 center is coordinated to eight oxygen atoms from four bidentate carboxylate groups, and the Cd2 center is coordinated by one DMF molecule, two water molecules, and four oxygen atoms from two bidentate carboxylate groups. Thus, the Cd1 ion is in a distorted bicapped trigonal prismatic geometry with Cd–O distances ranging from 2.389(6) to 2.447(7) Å, while Cd2 adopts a distorted pentagonal bipyramidal coordination environment with Cd-O distances ranging from 2.279(8) to 2.411(1) Å (Table S3), and all of the Cd-O bond length is in the normal range according to previously reported Cd(II)-based carboxylates.¹⁶ As shown in Figure 1, the dimeric (CuL)₂ units can serve as 2-connected building blocks and were linked by 4-connected Cd1O₈ clusters and 2-connected Cd2O7 clusters, respectively, to generate a 2D framework, which possesses two open channels of $\sim 29.2 \times 10.8 \text{ Å}^2$ and $\sim 13.7 \times 12.0 \text{ Å}^2$, respectively, along the *a* axis (Figure. 1a) and an open channel of $\sim 14.2 \times 10.5 \text{ Å}^2$ along the c axis (Figure S17). Although the overall structure of 2 adopts a 2-fold interpenetrated framework (Figure 1b) to stabilize the porous network, an open channel of $\sim 14.2 \times 10.5$ $Å^2$ along the *c* direction still remains after its mutual interpenetration (Figure S19). Furthermore, the 2D structure is further stabilized by CH $\cdots\pi$ interactions (C–H $\cdots\pi$ 3.44 and 3.58 Å) between the butyl group and adjacent benzene ring from another Cu(HL) unit and parallel-displaced stacking intermolecular $\pi - \pi$ interactions ($\pi - \pi$ 3.33 and 3.36 Å) between the benzene ring of the indane moiety and the adjacent benzene ring from another Cu(HL) unit. Calculations show that the void space in 2 is 41.8% by utilizing the PLATON software,¹⁴ which is available for accommodating guest molecules. In addition, the permanent porosity of 2 was confirmed by N₂ adsorption isotherms at 77 K and dye adsorptions in solution. 2 exhibited a Type-I sorption behavior with a BET surface area of 499.8 m^2/g (Figure S20) and could adsorb ~1.44 methylene blue (MB, ~1.25 nm \times 0.50 nm \times 0.38 nm in size) per formula unit (Figure S21). TGA reveals that the guest molecules such as methanol, water, and DMF molecules can be readily removed in the temperature range of 25–220 °C, and the framework is stable up to ~315 °C. PXRD experiments indicate that the framework and crystallinity of 2 remains intact upon complete removal of guest molecules.

Catalytic Performance. Given that Schiff-base copper complexes are promising Lewis acid catalysts in synthetic chemistry,¹⁷ we initially selected the Friedel-Crafts (F-C) alkylation of indoles with nitrostyrenes as a model reaction to evaluate the catalytic performance of 2 because indole and its derivatives are important intermediates for a number of biologically active natural and synthetic products.¹⁸ For comparison, the mononuclear copper complex 1, CdBr₂, and a previous reported 2D Cd-MOF (Figure S22) were also employed as a control group to investigate the potential of the cooperative catalyst. The F-C reaction was carried out with a 1:1.2 molar ratio of nitrostyrene and indole at room temperature by using CH₂Cl₂ as the solvent. Under the optimized conditions, it was found that a loading of 1 mol % activated 2 could smoothly catalyze the F-C reaction of indole with β -nitrostyrene, 4-Me- β -nitrostyrene, and 4-CF₃- β -nitrostyrene, respectively, which afforded corresponding products with 96%, 92%, and 95% yield (entry 1, 3, 5 in Table 1). In contrast, when using mononuclear complex 1 as the catalyst (the same loading of CuL units as 2), the reaction yields dramatically dropped to 39%, 31%, and 42%, respectively (entry 2, 4, 6 in Table 1). To assess the role of unsaturated Cd centers in 2 in the F–C reaction, the 2D Cd-MOF and CdBr₂ were used as catalysts, respectively, in the reaction of indole

Table 1. Catalyze	d Friedel-Crafts	Alkylation	of Indoles	with
Nitrostyrenes by	1 and 2 ^{<i>a</i>}			

R	NO ₂ +	R ³ R ¹	Ca CH ₂ C	atalyst Cl ₂ , rt, 12	R ³ /r	R^1 R^2 NO_2
entry	cat. ^b	R	\mathbb{R}^1	R ²	R ³	yield (%) ^c
1	2	Ph	н	Н	Н	95
2	1	Ph	Н	Н	н	39
3	2	4-Me-Ph	Н	Н	н	92
4	1	4-Me-Ph	Н	Н	н	31
5	2	4-CF ₃ -Ph	Н	Н	н	95
6	1	4-CF ₃ -Ph	Н	Н	н	42
7	2	3-OMe-ph	Н	Н	н	96
8	2	4-Cl-Ph	Н	Н	н	89
9	2	4-NO ₂ -Ph	Н	Н	н	90
10	Cd-MoF ^d	Ph	Н	Н	н	5 ^e /13
11	$\mathrm{CdBr_2}^d$	Ph	Н	Н	н	18 ^e /29
12	2	Ph	Me	Н	Н	94
13	2	Ph	Н	Me	Н	97
14	2	Ph	Н	Ph	н	90
15	2	Ph	Me	Me	н	90
16	2	Ph	Н	Me	5-Me	93
17	2	Ph	Н	Me	5-OMe	91
18	2	Ph	Н	Me	5-Cl	92
19	2	Ph	Н	Н	6-Me	89
					1	

^{*a*}For reaction details, see Supporting Information. ^{*b*}1.0 mol % loading of 2 based on the empirical formula. For monomeric complex 1, the loading of CuL units is same with 2. ^{*c*}Determined by ¹HNMR spectroscopy of the crude reaction mixture. ^{*d*}The loading of cadmium is same with 2. ^{*e*}Reaction time is 6 h.

with β -nitrostyrene. It showed somewhat reactivity (within 6 and 12 h, 5% and 13% conversions for Cd-MOF and 18% and 29% conversions for CdBr₂, respectively. entry 10 and 11 in Table 1), which implies that the activity of this F-C reaction mainly comes from the active copper sides, even though the weak Lewis acidity of the Cd1O₈ and Cd2O₇ clusters in 2 could also contribute for the activity in some extent. From the control experiments, we noted the evident difference in catalytic performance between 1 and 2, and we presumed that the difference derives from their distinct metal centers in the structures. From the X-ray crystal structural analysis, it is known that the active catalytic center in 1 exists in the form of monomeric Cu(HL)·MeOH moiety, which was also supported by electrospray ionization mass spectrometry (the molecular ion $[M + H]^+$ with an m/z value of 523.1 corresponding to $[Cu(HL) \cdot MeOH+H]^+$, Figure S4). In contrast to 1, the active catalytic species in 2 is a bimetallic (CuL)₂ moiety bridged with two indane oxygens. The channel surfaces of 2 are uniformly lined by saddle-like (CuL)₂ dimers with coordinatively unsaturated copper sites pointing to the open channels. What is more, the Cu–Cu separation within the $(CuL)_2$ dimer is around 2.8 Å; therefore, such a close distance and appropriate spatial orientation of active CuL catalyst could provide a possibility that the indoles and nitrostyrenes were activated by this bimetallic species simultaneously. This might be the reason why the MOF catalyst 2 shows a remarkably higher activity than its homogeneous monomeric complex 1.

To ascertain the presence of the synergistic dual activation of indoles and nitrostyrenes within the channels of MOF catalyst, we further examined the catalytic activity of 1 and 2

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under much lower C/S ratios (the molar ratio of catalyst to nitrostyrene). As shown in Table 2, it was obviously

Table 2. Catalytic Performance of 1 and 2 at Different Catalyst/Substrate Ratios^a

R	2 +		→ CH ₂	catalyst cCl₂, rt, 12 h	R	NO ₂
		1	2		1	2
C/S ^b	R	conv. (%) ^c	conv. (%) ^c	R	conv. (%) ^c	conv. (%) ^c
1/100	Ph	39	95	4-Me-Ph	31	92
1/1000	Ph	14	52	4-Me-Ph	8	49
1/10000	Ph	0	17	4-Me-Ph	0	12

^{*a*}For reaction conditions, see Supporting Information. ^{*b*}The molar ratio of catalyst to nitrostyrene. The same loading of CuL units for 1 and 2 at different C/S ratios. ^{*c*}Determined by ¹HNMR spectroscopy of the crude reaction mixture.

demonstrated that the catalytic activity of 1 in the F–C alkylation of indole with β -nitrostyrene sharply decreased from 39% to 14% and 0% as the C/S ratios decreased from 1:100 to 1:1000 and 1:10000, respectively. However, at a lower C/S ratio of 1:1000 and 1:10000, MOF catalyst 2 is still capable of affording a 52 and 17% conversion for β -nitrostyrene. The similar performance was also observed when the substrate was replaced by 4-Me- β -nitrostyrene under the identical reaction conditions. The low activity of homogeneous monomeric copper complex at lower C/S ratios is possibly due to the longer distance between two CuL species, which impedes the cooperation of CuL units during the catalytic process. In contrast to the low activity of 1, the activity enhancement of 2 further confirms the proposed cooperative catalytic effect of bimetallic (CuL)₂ units that confined in the MOF structure.

Substrates tolerance of the cooperative catalyst 2 was further examined by various β -nitrostyrenes and indoles. In the presence of 2, a wide range of aromatic *trans*- β -nitrostyrene derivatives bearing both electron-donating and electronwithdrawing substituents were found to react efficiently with indole and generated corresponding products in excellent yields of 89–96% (entry 1, 3, 5, 6–9 in Table 1). Additionally, indoles scope was examined by reacting *trans*- β -nitrostyrene with various indoles derivatives, which included mono- or disubstituted groups. All these indoles gave the desired products in good to excellent yields of 89–97% (entry 12– 19 in Table 1). These results suggest that 2 containing bimetallic active centers could be used as a highly efficient catalyst in a F–C reaction with a wide range of substrates.

The recyclability of catalyst **2** for the F–C reaction of indole and *trans-* β -nitrostyrene was also investigated. Upon completion of the reaction within 12 h, catalyst **2** can be easily recovered quantitatively from the reaction mixture through centrifugation and washed by clean solvents. Then, the catalyst can be used repetitively without loss of catalytic activity for the following runs (ca. 97, 95, 94, 93, and 93% yields for runs 1–5, respectively, Figure S23). PXRD characterization of **2** after the fifth was also performed, and the results showed that the catalyst still retained high crystallinity, despite a slight structural distortion (Figure S9). Moreover, it is worth noting that the reaction will cease immediately if the catalyst was removed by centrifugation. To rationalize the observed results above, we propose a mechanism that involves the cooperative activation of the two substrates in the F–C reaction, mediated by catalyst **2**. We envision that the indole and *trans-\beta*-nitrostyrene are synergistically activated by weakly coordinating to the adjacent Lewis acidic copper site in the bimetallic (CuL)₂ moieties through N atom on the indole ring and NO₂-group of nitrostyrene, respectively (Figure 2a).¹⁹ Thus, the two organic substrates



Figure 2. (a) A proposed dual activation pathway of F-C alkylation and Henry reaction, respectively, in the cooperative catalysis; view of the optimized structures to depict noncovalent interactions in intermediates of 2 (b) and 1 (c).

were put approximately and furnished the formation of the alkylated product with higher yield. Density functional theory (DFT) calculations on the F-C reaction between indole and *trans-\beta*-nitrostyrene by utilizing the DMol³ program²⁰ provide further insight into the proposed mechanism of cooperative catalysis. We only chose the active catalytic CuL unit as a structure fragment to calculate for the complexity and large size of the primitive crystal structure. As we proposed in the dual activation mechanism, optimized structures of intermediates including two substrates and bimetallic (CuL)₂ species indicate that evident interactions between two substrates and binuclear copper center in 2 could constrain movement of indole and nitrostyrene (the closest distance of noncovalent interactions between copper centers and the two substrates are 2.77 and 3.37 Å, respectively. Figure 2b), leading to a higher reaction probability. Although the interaction between *trans-\beta*nitrostyrene and monomeric CuL unit is similar that in 2, the interaction between indole and copper center is getting much weaker (the closest distance of noncovalent interactions between copper center and indole nitrogen atom is changed from 3.37 to 4.21 Å, Figure 2c), as a result, the reaction probability will drop. Meanwhile, the affinity of substrates with the catalytic copper centers in 1 and 2 was also investigated by comparing enthalpy, which indicated that such a combination process was more favored in 2 (Figure S24).

Encouraged by the excellent performance in F–C reaction of 2, we then attempted to apply this solid cooperative catalyst to Henry reaction. The reaction was performed between aldehydes and nitromethane by using 1.0 mol % catalyst. It was satisfactory that benzaldehyde and its derivatives bearing electron-poor groups reacted with nitromethane efficiently to give the β -nitro alcohols in 86–97% yield (entry 1, 3, 5–7 of Table 3). From the control experiments from entries 2 and 4 in Table 3, it was found that the mononuclear complex 1 (the same loading of CuL units as 2) only gives yields of 48 and 53%. Such a difference in catalytic activity is getting more obviously upon the C/S ratio decreasing from 1:100 to 1:10000 (as shown in Table 4). These results displayed that catalyst 2 had a higher activity in catalyzing Henry reaction. Considering that carbonyl moiety of the aldehydes and nitro group of nitromethanes can also be activated by a Lewis acid

Table 3. Results of Henry Reaction between Aldehydes and Nitromethane Catalyzed by 1 and 2^a

Ar	+ `Н	MeNO ₂ Catal	yst H Ar	
entry	cat ^b	Ar	time (h)	yield (%) ^c
1	2	Ph	12	86
2	1	Ph	12	48
3	2	4-NO ₂ -Ph	12	96
4	1	4-NO ₂ -Ph	12	53
5	2	3-NO ₂ -Ph	12	94
6	2	2-NO ₂ -Ph	12	97
7	2	4-CN-Ph	12	95

^{*a*}For reaction details, please see Supporting Information. ^{*b*}1.0 mol % loading of **2** based on the empirical formula. For monomeric complex **1**, the loading of CuL units is same with **2**. ^{*c*}Determined by ¹HNMR.

 Table 4. Catalytic Performance of 1 and 2 in Henry
 Reaction at Different Catalyst/Substrate Ratios^a

O ₂ N H	+ MeNO ₂	catalyst MeOH, 60 °C,	→ ^{12 h} O₂N	
C/S^{b}	catalyst	yield (%) ^c	catalyst	yield (%) ^c
1:100	1	53	2	96
1:1000	1	20	2	68
1:10000	1	3	2	33

^{*a*}For reaction conditions, see support information. ^{*b*}The molar ratio of catalyst to 4-NO₂-benzaldehyde. The same loading of CuL units for 1 and 2 at different C/S ratios. ^{*c*}Determined by ¹HNMR.

catalyst, the enhanced catalytic performance in Henry reaction could be attributed to a dual activation process, which means both the aldehydes and the nitromethane were synergistically activated by the bimetallic $(CuL)_2$ catalyst fixed on the wall of the channel of MOF 2. However, for the homogeneous system, especially at a low concentration of CuL catalyst, a dual catalytic activation mode is less likely happen due to the probability for the collision of activated nucleophile and electrophile is very low. Again, this finding highlights the superiority of cooperative bimetallic catalyst confined in MOF structure.

CONCLUSIONS

In summary, a porous 2-fold interpenetrated heterometallic MOF was assembled step by step from a carboxylatefunctionalized tridentate Schiff base ligand. The MOF possesses catalytically active bimetallic copper centers, allowing cooperative activation, which results in superior activity in both the F-C reaction and Henry reaction when compared to its homogeneous counterpart. Such cooperativity was further evidenced by the control experiments of the monometallic copper catalyst at lower catalyst/substrate ratios, which gave significantly decreased activity comparing with the bimetallic copper catalyst in both F-C and Henry reactions. Besides, the cooperative catalyst can be easily recovered and reused without any apparent loss of catalytic activity. Our study, therefore, provides a high-efficient heterogeneous MOF catalyst containing cooperative bimetallic centers by taking advantage of the tunable functionality of a tridentate Schiff base and stepwise synthesis of MOF, toward a variety of organic transformations. We also believe the synthetic strategy we developed for cooperative catalysis could extend to other porous materials, like covalent organic frameworks, with chemical tunability, high porosity, and ordered structural integrities.²¹

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.8b02434.

Experimental details and spectral data (PDF)

Accession Codes

CCDC 1863032–1863033 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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