Construction of Stable Metal-Organic Framework Platforms Embedding *N*-Heterocyclic Carbene Metal Complexes for Selective Catalysis

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ABSTRACT: We report a bottom-up approach to immobilize catalysts into MOFs, including copper halides and gold chloride in a predictable manner. Interestingly, the structures of MOFs bearing NHC metal complexes maintained a similar 4-fold interpenetrated cube. They exhibited exceptionally high porosity despite the interpenetrated structure and showed good stability in various solvents. Moreover, these MOFs possess high size activity depending on the size of the substrates in various reactions, compared to homogeneous catalysis. Also, the high catalytic activity of MOFs can be preserved 4 times without significant loss of crystallinity. Incorporation of the various metal complexes into MOFs allows for the preparation of functional MOFs for practical applications.

INTRODUCTION

Metal-organic frameworks (MOFs) are a class of porous hybrid materials constructed from organic linkers and metal nodes. By engineering inner pores, MOFs have been widely utilized in various fields including gas storage,[1] drug delivery,[2] separation,[3] sensors,[4] etc. Particularly, MOFs have been extensively studied as heterogeneous catalysts due to their recyclability and stability, compared to homogeneous counterparts.[5]

Among the various candidates for organic linkers, we chose the imidazolium ligand for the preparation of stable and enhanced catalysis of MOF. We previously reported the MOF embedding *N*-Heterocyclic carbene (NHC) precursor.[6] This imidazolium-based MOF exhibited unprecedentedly high surface area despite the interpenetrated structure. By taking advantage of its unique features, we functionalized this MOF with various transition metal catalysts.

Post-modification and *in-situ* method were mostly applied for easy implementation of catalyst inside MOF (scheme 1).[7] The post-synthetic metalation approach is a method in which MOFs are treated with metal salts after the construction of frameworks.[7a-7d,7f] The *in-situ* method is the synthesis of functionalized MOFs by the reaction of organic linkers and metal complexes in one pot.[7g-h] However, these methods resulted in irregular distributions incomplete immobilization of catalytic species.[7e,7h] On the other hand, a bottom-up method is expected to give fully functionalized building blocks in MOFs. As the bounded catalyst can interfere with framework construction during
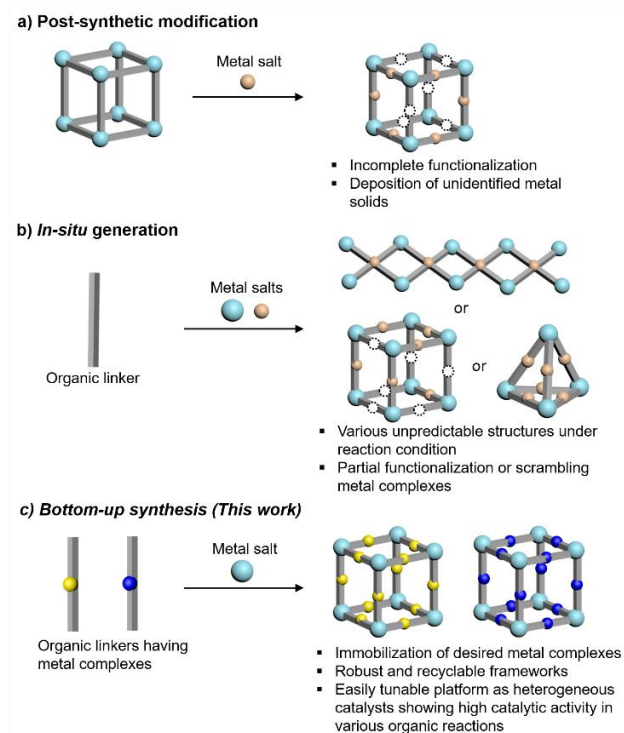
Scheme 1. Synthetic methods for the preparation of MOFs having active metal sites. (a) post-treatment of MOF with metal salts, (b) *in-situ* generation of active metal sites during MOF synthesis (c) assembly of the organic linker with active metal sites.
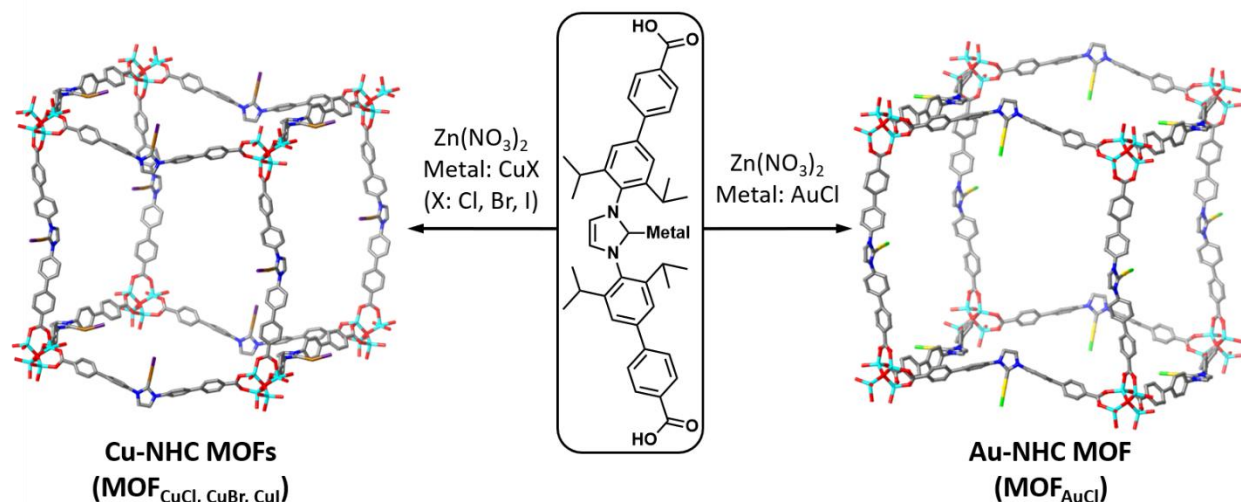
Figure 1. Schematic representation of the preparation of Cu-NHC MOFs and Au-NHC MOF (C: gray, N: blue, O: red, Zn: cyan, Cu: brown, I: blue violet, Au: yellow, Cl: light green. Hydrogen atoms and isopropyl substituents are omitted for clarity).

MOF synthesis, there are few examples of successful bottom-up construction.[7i-k] Even though those had well-defined structures, further applications are not reported[7i] or there are no size selectivities among various substrates.[7j,k] Moreover, the low surface area blocked by metal species diminishes in the inner-pore catalysis.

With the structural stability of the previous framework and the strong interaction of transition metal-NHC, we anticipate that our Zn-MOF platform led to the generation of MOFs with various catalysts. Herein, we report the synthesis of MOFs containing immobilized copper and gold NHC complexes (Cu-NHC MOFs and Au-NHC MOF) by utilizing the bottom-up approach. As shown in Figure 1, The structures of MOFs were maintained, in spite of various types of catalytic species. Because the MOFs constructed from copper and gold NHC ligands exhibited high porosity despite the interpenetrated structure and unique tolerance towards various solvents, such as NMP, DMF, THF, and dioxane, these MOFs readily catalyze various reactions such as Cu-catalyzed azide-alkyne cycloaddition reaction, Cu-catalyzed multicomponent reaction, and Au-catalyzed hydroamination. Moreover, due to NHC's high coordinating ability towards transition metal complexes,[8] the MOFs bearing NHC metal complexes exhibited low leaching of catalytic active metal sites into the reaction mixture during the organic reactions catalyzed by these MOFs and can be used as efficient heterogeneous catalysts.

RESULTS AND DISCUSSIONS

Synthesis and characterization of MOFs bearing NHC metal complexes.

To synthesize NHC ligands having metal complexes, such as copper halides, gold chloride, silver chloride, palladium allyl chloride, Ir(COD)Cl, and Rh(COD)Cl, imidazolium chloride having carboxylate functional groups was reacted with metal complexes such as CuCl, CuBr, CuI,

Me$_2$SAuCl, Ag$_2$O, [Pd(allyl)Cl]$_2$, [Ir(COD)Cl]$_2$ and [Rh(COD)Cl]$_2$ in the presence of KO^{t}Bu (see Supporting Information). At first glance, this approach is quite challenging because carboxylate parts of NHC ligand may compete the coordination to the metal ions to generate complex mixtures.[7i] The NHC ligands having copper halides and gold chloride were further reacted with zinc nitrate in a mixture of N-methyl pyrrolidone (NMP) and xylene at 80 °C to generate cubic shaped crystals of MOFs containing NHC metal complexes. However, in the case of metal complexes having organic ligands such as [Pd(allyl)Cl]$_2$, [Ir(COD)Cl]$_2$, [Rh(COD)Cl]$_2$ and labile silver chloride coordinated NHC ligands, non-crystalline and oligomeric solids were obtained under the same solvothermal reaction condition. This phenomenon may be related to the relatively lower stability of the NHC ligands having AgCl, Pd(allyl)Cl, Ir(COD)Cl, Rh(COD)Cl, compared to the NHC ligands bearing copper halides and gold chloride under the reaction conditions for MOF synthesis.
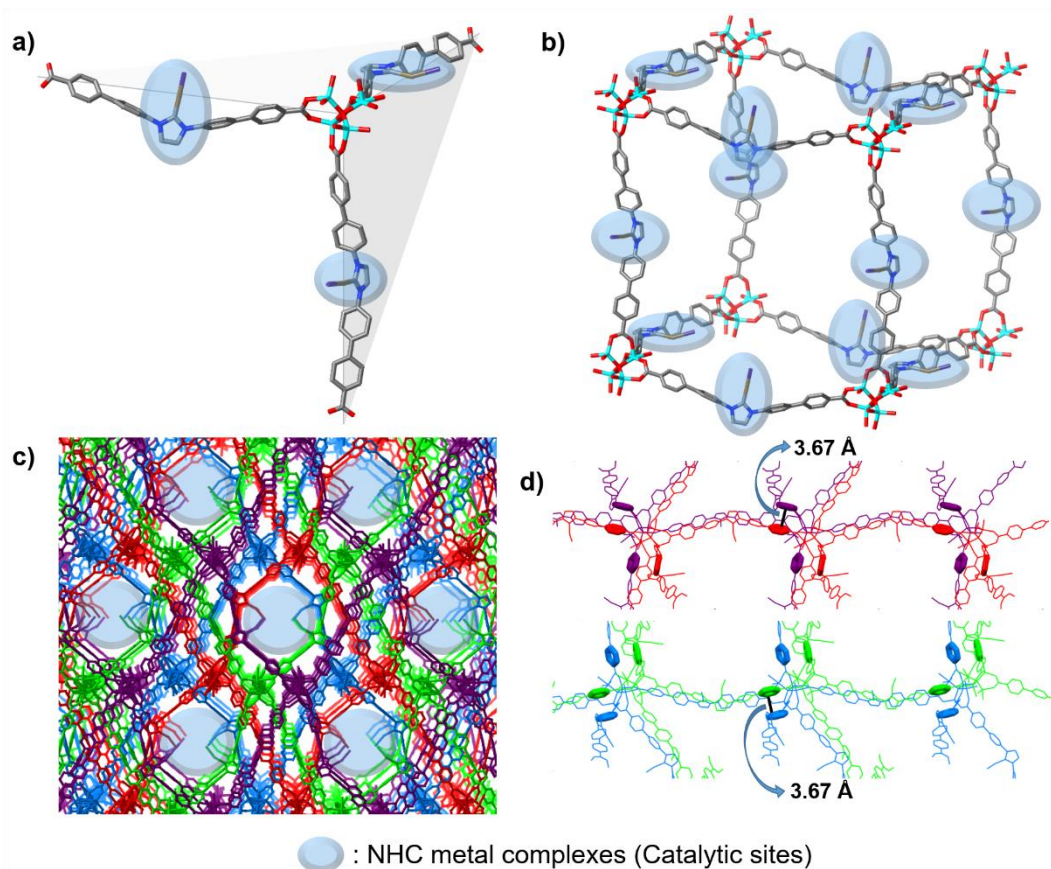
Figure 2. Single crystal X-ray structures of Zn MOF having copper(I) iodide (MOF$_{CuI}$). (a) Coordination environment, (b) single set of cubic network, (c) perspective view of 4-fold interpenetrated network, (d) π-π Interaction between each set of two different networks (C: gray, N: blue, O: red, Zn: cyan, Cu: brown, I: blue violet. Hydrogen atoms and isopropyl substituents are omitted for clarity).

By utilizing this bottom-up approach, we can obtain the crystals containing copper gold NHC ligands in the resulting MOFs. Due to the highly ordered and fully functionalized ligands, crystal structures of these MOFs can be obtained by single-crystal X-ray diffraction (SCXRD). MOFs having copper halides (Cu-NHC MOFs) such as CuCl (MOF$_{CuCl}$), CuBr (MOF$_{CuBr}$), (Figure S1), and CuI (MOF$_{CuI}$) (Figure 2) present the monoclinic space group (C2/c) and four-fold interpenetrated structure. As shown in Figure 2, the repeating unit of MOF$_{CuI}$ contained three copper NHC ligands that were placed on each axis and connected by zinc metal clusters (Figure 2a). Because the NHC metal complex having CuI has bent shape and C2 symmetry, the carboxylate functional groups in NHC ligands were bound to zinc metal clusters and led to the formation of a 3D framework with a cube structure (2.5 nm × 2.5 nm) (Figure 2b). Even though biphenyl moieties were slightly distorted due to the presence of isopropyl substituents (36.1° dihedral angle), each set of cubic networks in MOF$_{CuI}$ was packed by π-π interactions between phenyl groups (Figure 2d). Because of the repeated π-π interactions as well as large void, the resulting cubic networks were further interpenetrated with each other, giving a 4-fold interpenetrated 3D network structure (Figure 2c).

Gold NHC complex was reacted with zinc nitrate under the same solvothermal reaction condition to produce MOF having AuCl NHC complex (MOF$_{AuCl}$). Similar to Cu-NHC MOFs, cube-shaped crystals were obtained and grown to the size of 200-300 μm. SCXRD study indicated that the resulting MOF$_{AuCl}$ also presents a monoclinic space group (C2/c) and 4-fold interpenetrated three-dimensional framework which is similar to the Cu-NHC MOFs.

Powder x-ray diffraction (PXRD) patterns of resulting MOFs containing NHC metal complexes indicated that the resulting crystals were phase pure (Figure 3) and were highly stable in various solvents, including NMP, DMF, THF, and without the significant loss of crystallinity. In addition, all of the MOFs bearing NHC metal complexes we presented exhibited typical type I reversible isotherms in nitrogen sorption isotherm (Figure S2). Brunauer-Emmett-Teller (BET) surface areas of MOF$_{CuCl}$, MOF$_{CuBr}$, MOF$_{CuI}$, and MOF$_{AuCl}$ were 1070 m²/g, 1002 m²/g, 958 m²/g, and 984 m²/g, respectively. Because of their high porosity, stability, and the presence of catalytic active metal complexes inside
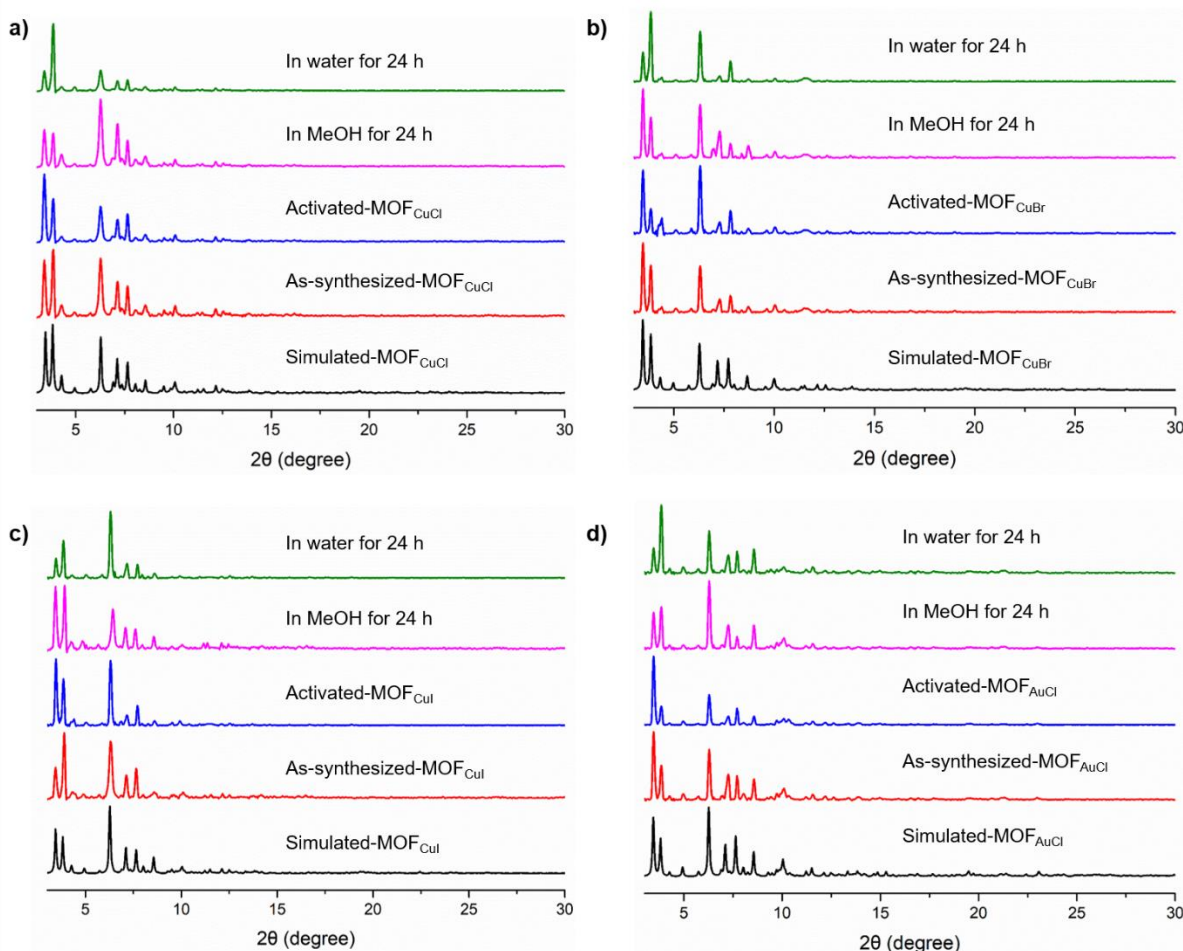
Figure 3. Powder X-ray diffraction (PXRD) profiles of (a) MOF$_{CuCl}$, (b) MOF$_{CuBr}$, (c) MOF$_{CuI}$, (d) MOF$_{AuCl}$ after soaking in methanol and water for 24 h.

the pores, these MOFs exhibited high catalytic activity in organic reactions, such as Cu-catalyzed azide-alkyne cycloaddition reaction, Cu-catalyzed multicomponent reaction, and Au-catalyzed hydroamination.

Catalytic studies of MOF$_{CuI}$ in Cu-catalyzed azide-alkyne cycloaddition reaction.

Cu-catalyzed azide-alkyne cycloaddition (CuAAC) of organic azide and alkynes is a highly versatile and regioselective reaction.[9] Because of its properties, CuAAC has been widely utilized in medicinal chemistry, organic synthesis, and polymer chemistry.[10]

Due to the properties of CuAAC and the presence of large pores and the catalytic active sites in MOFs bearing copper halides, we explored the catalytic activity of Cu-NHC MOFs in CuAAC. The reaction of phenylacetylene and benzyl azide was conducted in the presence of MOFs having copper halides (Cu-NHC MOFs) as a heterogeneous catalyst and NHC copper complexes as a homogeneous catalyst. As shown in Table 1, yield for this reaction is varied depending on the types of halides (Cl, Br, I) in copper NHC complexes.[11] As a general trend in the CuAAC reaction, iodine-containing NHC (IPrCuI, entry 3) was slightly more active than its brominated analog (IPrCuBr, entry 2),
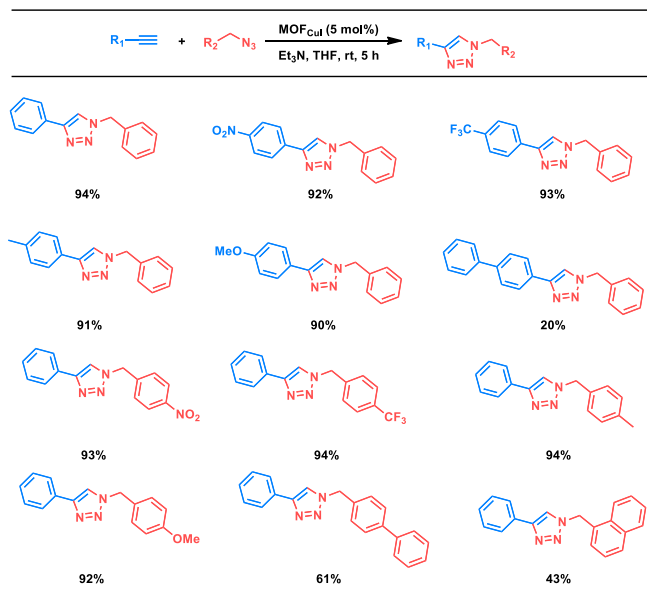
while chloride bearing NHC (IPrCuCl, entry 1) was significantly the least active. This result might be related to an easier displacement of an iodo ligand from the copper center to initiate the catalytic cycle with the generation of a copper acetylide.[11] MOFs possessing NHC copper halides (Cu-NHC MOFs) also exhibit similar behaviour in CuAAC.

Table 1. Catalyst screening for Cu-catalyzed azide-alkyne cycloaddition by homogeneous catalysts (entries 1-3) and heterogeneous catalysts (entries 4-6).[a]

Entry	Catalyst	Time (h)	Isolated yield (%)
1	IPrCuCl	4 h	45%
2	IPrCuBr	4 h	91%
3	IPrCuI	4 h	99%
4	MOF$_{CuCl}$	5 h	60%
5	MOF$_{CuBr}$	5 h	92%
6	MOF$_{CuI}$	5 h	99%

[a] The reaction was conducted at room temperature for 5 h in THF. Conditions: Phenyl acetylene (1 eq), azide (1.2 eq), trimethylamine (1.2 eq), Cu catalyst (5 mol%) at room temperature.

Table 2. Cu-catalyzed azide-alkyne cycloaddition reactions for the synthesis of [1,2,3]-triazoles of azides and alkynes in the presence of MOF$_{CuI}$ as a heterogeneous catalyst.[a]

$$R_1 \text{---} + R_2 \text{-} N_3 \xrightarrow[\text{Et}_3\text{N, THF, rt, 5 h}]{\text{MOF}_{CuI} \text{ (5 mol\%)}} R_1 \text{-triazole-} R_2$$

94%	92%	93%
91%	90%	20%
93%	94%	94%
92%	61%	43%

[a] The reaction was conducted at room temperature for 5 h in THF. Isolated yields. Conditions: Phenyl acetylene (1 eq), azide (1.2 eq), trimethylamine (1.2 eq), MOF$_{CuI}$ (5 mol%) at room temperature.

To explore the reactivity trend, CuAAC of alkyne and azide derivatives were conducted in the presence of MOF$_{CuI}$ as a heterogeneous catalyst. As shown in Table 2, similar to the studies on the CuAAC catalyzed by homogeneous NHC copper complex,[9a,9b] the electron-donating and withdrawing substituents at a para position in alkyne and azide derivatives exhibited a negligible effect on the efficiency of this reaction. Bulky substituents such as biphenyl and naphthyl groups diaplayed a tendency of decreasing reaction progress, giving the lower yields in CuAAC (Table 3). Compared to the substrate prepared from 4-ethynylbiphenyl and benzyl azide (entry 2), the substrate synthesized from phenylacetylene and 4-azidomethyl biphenyl (entry 3) represented higher yield due to the lower hin-

Table 3. Cycloaddition reactions of bulky substrates in the presence of MOF$_{CuI}$ as a heterogeneous catalyst and NHC ligand having CuI (IPrCuI) as a homogeneous catalyst.[a]

$$R_1 \text{---} + R_2 \text{-} N_3 \xrightarrow[\text{Et}_3\text{N, THF, rt, 5 h}]{\text{Cu catalyst (5 mol\%)}} R_1 \text{-triazole-} R_2$$

Entry	Alkyne	Azide	Isolated yield (%, MOF$_{CuI}$)	Isolated yield (%, IPrCuI)
1			94%	99%
2			20%	73%
3			61%	85%
4			43%	76%

[a] The reaction was conducted at room temperature for 5 h in THF in the presence of catalytic amount of MOF$_{CuI}$ and IPrCuI (Iodo[1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene]copper(I)).

drance from the rigid conjugated parts of biphenyl and triazole (3+1 vs 2+2). Interestingly, when NHC ligand having CuI (IPrCuI) was utilized as a homogeneous catalyst, the CuAAC occurred smoothly even in the presence of bigger substituents in the alkyne and azide derivatives (Table 3). Besides, we used inductively coupled plasma-optical emission spectrometry (ICP-OES) to examine the amounts of metal species leaching from MOF$_{CuI}$ during the CuAAC. The leaching of Cu and Zn into the supernatant during the CuAAC between phenylacetylene and benzyl azide was determined to be 0.08% and 0.06%, respectively. The dependence of yield on the substrate size and the low leaching of Cu (0.08%) and Zn (0.06%) indicate that the catalytic reaction was proceeded inside of pores rather than metal ions leached from MOF$_{CuI}$, which exhibited a size-selective behaviour in the CuAAC.

Catalytic studies of MOF$_{CuI}$ in Cu-catalyzed multicomponent reaction

Cu-catalyzed multicomponent reaction is a useful tool for the preparation of complex and diverse molecules in a single step.[12a,12b] In particular, multicomponent reaction (MCR) has been utilized in the field of combinatorial chemistry, drug discovery, and polymer chemistry.[12] To determine the possibility of utilization of MOFs with NHC copper halide as a catalyst for MCR, we attempted to run the reaction between alkyne, sulfonyl azide, and amine with MOFs having copper halides (Cu-NHC MOFs) as heterogeneous catalyst.

MCR was conducted in the presence of NHC ligands having copper halide complexes. As shown in Table 4, in the case of homogeneous catalysts, the yield for the MCR is highest when NHC ligands having copper iodide (IPrCuI) was utilized as a catalyst (entry 3). Similarly, among the MOFs having NHC copper halide complexes (Cu-NHC MOFs), MOF$_{CuI}$ also exhibited high activity in MCR (entry 6).
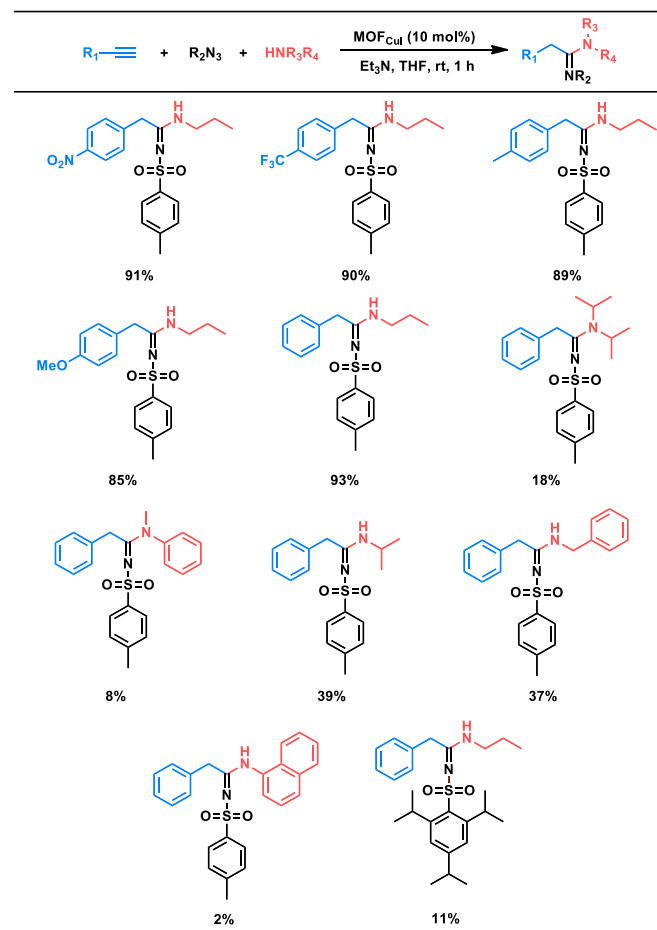
To explore the effect of the substrate, MCR was conducted by using alkyne, sulfonyl azide, and amine derivatives in the presence of the catalytic amount of MOF$_{CuI}$ as a heterogeneous catalyst. As shown in Table 5, similar to the previous examples regarding MCR in the presence of

Table 4. Catalyst screening for Cu-catalyzed multicomponent reaction by homogeneous catalysts (entries 1-3) and heterogeneous catalysts (entries 4-6).[a]

$$\text{Ph} \text{---} + \text{TsN}_3 + \text{R-NH}_2 \xrightarrow[\text{Et}_3\text{N, THF, rt}]{\text{Cu catalyst (10 mol\%)}} \text{Ph-amidine-NTs}$$

Entry	Catalyst	Time (h)	Isolated yield (%)
1	IPrCuCl	0.5 h	74%
2	IPrCuBr	0.5 h	87%
3	IPrCuI	0.5 h	99%
4	MOF$_{CuCl}$	1 h	61%
5	MOF$_{CuBr}$	1 h	73%
6	MOF$_{CuI}$	1 h	99%

[a] The reaction was conducted at room temperature for 1 h in THF. Conditions; Phenyl acetylene (1 eq), sulfonyl azide (1.2 eq), amine (1.2 eq), triethylamine (1.2 eq), Cu catalyst (10 mol%) at room temperature.

Table 5. Cu-catalyzed multicomponent reactions of alkynes, sulfonyl azides, and amines in the presence of MOF$_{CuI}$ as a heterogeneous catalyst.[a]

R$_1$—≡ + R$_2$N$_3$ + HNR$_3$R$_4$ →[MOF$_{CuI}$ (10 mol%) / Et$_3$N, THF, rt, 1 h] product

91%   90%   89%

85%   93%   18%

8%   39%   37%

2%   11%

[a] The reaction was conducted at room temperature for 1 h in THF in the presence of catalytic amount of MOF$_{CuI}$. Isolated yields. Conditions: Phenyl acetylene (1 eq), azide (1.2 eq), trimethylamine (1.2 eq), MOF$_{CuI}$ (5 mol%) at room temperature.

homogeneous CuI catalyst,[12a] electronic variation on alkyne derivatives causes no significant effect on this reaction. Moreover, Bulky groups such as diisopropyl amines, benzyl amines, *N*-methylaniline, isopropyl groups, and naphthyl groups tend to affect the decline in the reaction process, offering low yields (Table 6). Substrates bearing benzyl amine (entry 5) showed relatively better yield than the substrate bearing N-methylaniline (entry 4). This phenomenon is related to the different nucleophilicity of benzylamine and *N*-methylaniline and the rigidity of products depending on the presence of the benzyl group of amine in MCR. Also, the presence of bulky substituents such as isopropyl substituents in the sulfonyl azide (entry 7) also exhibited a lower yield. In the case of the amines and sulfonyl azide with large substituents, the yield in the MCR catalyzed by NHC ligand having CuI (IPrCuI) as a homogeneous counterpart was not significantly reduced (Table 6). Due to the presence of the catalytic active site in the confined space in MOF$_{CuI}$, unlike the NHC ligand having a copper halide (IPrCuI), bulky substrates tend to greatly reduce yield in MCR. Besides, the leaching of Cu and Zn into the supernatant in MCR between phenylacetylene, tosyl azide,

Table 6. Multicomponent reactions of bulky substrates in the presence of MOF$_{CuI}$ as a heterogeneous catalyst and NHC ligand having CuI (IPrCuI) as a homogeneous catalyst.[a]

R$_1$—≡ + R$_2$N$_3$ + HNR$_3$R$_4$ →[Cu catalyst (10 mol%) / Et$_3$N, THF, rt, 1 h] product

Entry	Alkyne	Azide	Amine	Isolated yield (%, MOF$_{CuI}$)	Isolated yield (%, IPrCuI)
1	Ph≡	—SO$_2$N$_3$	NH$_2$	93%	99%
2	Ph≡	—SO$_2$N$_3$	isopropylamine	18%	97%
3	Ph≡	—SO$_2$N$_3$	NH$_2$	39%	94%
4	Ph≡	—SO$_2$N$_3$	NH	8%	92%
5	Ph≡	—SO$_2$N$_3$	NH$_2$	37%	93%
6	Ph≡	—SO$_2$N$_3$	NH$_2$	2%	76%
7	Ph≡	—SO$_2$N$_3$	NH$_2$	11%	91%

[a] The reaction was conducted at room temperature for 1 h in THF in the presence of catalytic amount of MOF$_{CuI}$ and IPrCuI (Iodo[1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene]copper(I)).

and propylamine was measured by 0.08% and 0.04%, respectively. According to these results, MOF$_{CuI}$ with a pore size of 0.8 nm also showed size selectivity in MCR.

## Catalytic studies of MOF$_{AuCl}$ in Au-catalyzed hydroamination

Gold catalyzed hydroamination is the reaction of alkyne with aniline, in which the N–H fragment of an amine is added to the C–C triple bond, with cleavage of the N–H bond and formation of a new C–N bond. This reaction has attracted considerable interest due to the central role of amino compounds in organic chemistry.[13-15] The resulting imines are key synthons in the synthesis of bioactive or naturally occurring products. As hydroamination is an atom economic coupling of amines and alkynes, this reaction is of high importance to the chemical industry.[16e]

Table 7. Catalyst screening for Au-catalyzed hydroamination by homogeneous catalysts (entries 1-3) and heterogeneous catalysts (entries 4-5).[a]

Ph—≡ + PhNH$_2$ →[Au catalyst (3 mol%) / AgOTf (6 mol%) / Dioxane, 70 °C] product

Entry	Catalyst	Time (h)	Isolated yield (%)
1	AgOTf	4 h	6%
2	IPrAuCl	4 h	5%
3	IPrAuCl/AgOTf	4 h	97%
4	MOF$_{AuCl}$	5 h	23%
5	MOF$_{AuCl}$/AgOTf	5 h	99%

[a] The reaction was conducted at 70 °C for 5 h in dioxane.
Conditions; Phenyl acetylene (1 eq), aniline (1.2 eq), Au catalyst (3 mol%), AgOTf (6 mol%) at 70 °C.
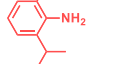
Table 8. Au-catalyzed hydroamination of alkynes and anilines in the presence of MOF$_{AuCl}$ as a heterogeneous catalyst.[a]

93%	32%	53%	92%
94%	91%	90%	80%
62%	24%	21%	20%

[a] The reaction was conducted at 70 °C for 5 h in dioxane in the presence of catalytic amount of MOF$_{AuCl}$ and AgOTF. Isolated yields. Conditions; Phenyl acetylene (1 eq), aniline (1.2 eq), Au catalyst (3 mol%), AgOTf (6 mol%) at 70 °C.

To find out the possibility of the catalytic utilization of MOF having NHC gold complex (MOF$_{AuCl}$), hydroamination between alkyne and aniline catalyzed by MOF$_{AuCl}$ was studied. According to the result for the hydroamination between phenylacetylene and aniline catalyzed by NHC ligand having AuCl (IPrAuCl) as a homogeneous catalyst

Table 9. Hydroamination of bulky substrates catalyzed by MOF$_{AuCl}$ as a heterogeneous catalyst and NHC ligand having AuCl (IPrAuCl) as a homogeneous catalyst.[a]

Entry	Alkyne	Aniline	Isolated yield (%, MOF$_{AuCl}$)	Isolated yield (%, IPrAuCl)
1			93%	99%
2			24%	96%
3			21%	88%
4			20%	97%

[a] The reaction was conducted at 70 °C for 5 h in dioxane in the presence of catalytic amount of MOF$_{AuCl}$ and IPrAuCl (Chloro[1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene]silver(I)) and AgOTF..
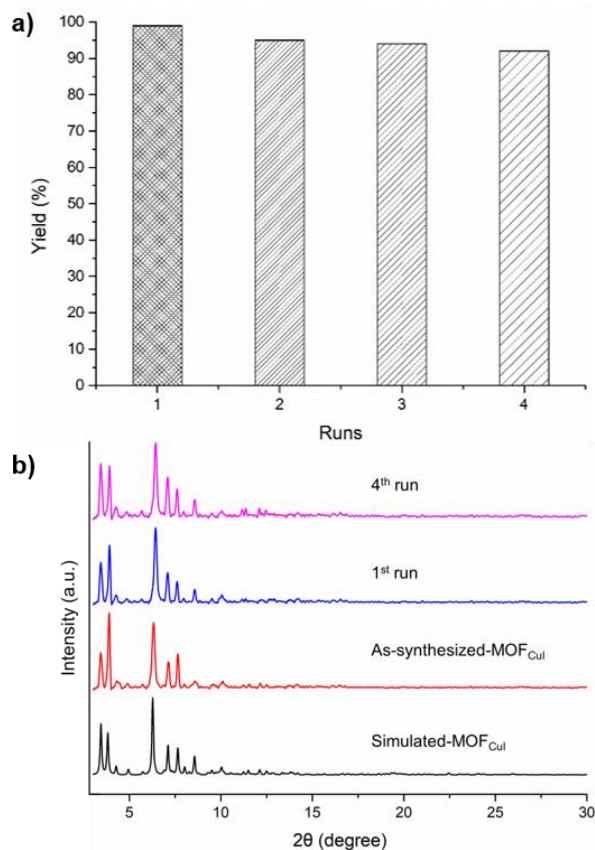

Figure 4. (a) Recycling experiments of MOF$_{CuI}$ in multicomponent reaction, (b) Powder X-ray diffraction (PXRD) profiles of as-synthesized MOF$_{CuI}$ (red), after multicomponent reaction between phenylacetylene, tosyl azide and propylamine (blue) and after 4th run (magenta).

(Table 7), the presence of a catalytic amount of silver triflate led to a dramatic increase in yield of hydroamination (entry 3). Au-NHC MOF (MOF$_{AuCl}$) as a heterogeneous catalyst also exhibited similar catalytic activity in the hydroamination (entry 5). The use of AgOTf as cocatalyst led to the chloride abstraction and activation of gold catalyst for acceleration of hydroamination.[15e]

The hydroamination was studied by utilizing the alkyne and aniline derivatives in the presence of MOF$_{AuCl}$ as a heterogeneous catalyst (Table 8). The reaction proceeds smoothly with electron-rich alkynes and electron-deficient anilines. This reactivity trend is similar to that previously reported journal covering hydroamination catalyzed by gold(I) complex.[13a] In addition, the presence of bulky substituents in anilines such as tert-butyl, isopropyl, and naphthyl groups caused severe drops in the yield (Table 9). Interestingly, when NHC gold(I) complex (IPrAuCl) was utilized as a homogeneous catalyst, similar to the previous examples of gold-catalyzed hydroamination,[13a] the steric hindrance in the aniline as well as alkyne derivatives does not significantly hamper this reaction. The low leaching of Au (0.05%) and Zn (0.08%) from MOF$_{AuCl}$ during the hydroamination between phenylacetylene and aniline was observed by ICP-OES. According to these results, MOF$_{AuCl}$

having 0.8 nm of the pores also showed size selectivity behavior in hydroamination, indicating the reaction takes place inside the pores with well-located NHC catalyst in the pores rather than outside the MOF.

NHC metal complex embedded MOFs (Cu-NHC MOF and Au-NHC MOF) exhibited high catalytic activity and size selectivity in CuAAC, MCR, and hydroamination. As a heterogeneous catalyst, MOF$_{CuI}$ and MOF$_{AuCl}$ can be easily isolated from the reaction mixture by simple filtration and reused at least 4 times without a significant decrease in yield (Figure 4a, S3, S9). In the recycling experiment, crystallinity and porosity of MOF$_{CuI}$ and MOF$_{AuCl}$ were entirely retained after the 4th cycle of CuAAC, MCR, and hydroamination, characterized by powder X-ray diffraction (PXRD) (Figure 4b, S4, S10) and nitrogen sorption experiments (Figure S5, S8, S11). From these results, MOF$_{CuI}$ and MOF$_{AuCl}$ presented high selectivity and great recyclability.

CONCLUSION

We report the preparation of metal-organic frameworks having copper halides and gold chloride from NHC metal complexes by utilizing a bottom-up approach. Even though the types of metal complexes in MOFs were different, the structures of resulting MOFs were preserved as a four-fold interpenetrated 3D structure. Because NHC metal complex embedded MOFs have well-bounded catalysts in the pores of MOFs, high porosity despite interpenetrated structure, and high stability in various organic solvents, these MOFs exhibit high catalytic activity and size-selective behavior in organic reactions such as Cu-catalyzed alkyne-azide cycloaddition, Cu-catalyzed multicomponent reaction, and Au-catalyzed hydroamination. As an efficient heterogeneous catalyst, these MOFs can be reused at least four runs without the significant loss of catalytic activity and crystallinity. Because NHC tends to be strongly bound to metal complexes,[8] MOFs bearing NHC metal complexes also show the low leaching of metal species from these MOFs in the organic reactions we demonstrated. The platform we presented in which NHC metal complexes were inserted into the interior of the MOFs as organic linkers, opens the way for the preparation of well-defined functional MOFs and the practical applications as heterogeneous catalysts.

EXPERIMENTAL SECTION

Materials and Methods. All the reagents and solvents were commercially available and used as supplied without further purification. Elemental analysis (EA) for C, H, and N were carried out using Flash 2000 (Thermo Fisher Scientific Inc.). NMR spectra were recorded by Bruker AVANCE III spectrometer operating at 400 MHz for ¹H, 100 MHz for ¹³C. Single crystal X-ray diffraction (SXRD) analysis were carried out at synchrotron radiation of 2D-SMC Crystallography at the Pohang Accelerator Laboratory (PAL, Korea). The powder X-ray diffraction patterns were obtained on a

Rigaku Smartlab system equipped with Cu sealed tube. Purified compounds were further dried under high vacuum (0.01–0.05 Torr). Nitrogen sorption isotherms were measured with Autosorp-iQ volumetric adsorption equipment. In HRMS, two types of analyzers such as magnetic sector-electric sector double focusing mass analyzer and Q-TOF mass spectrometer. The metal contents of the reaction mixture in organic reactions catalyzed by MOF$_{CuI}$ and MOF$_{AuCl}$ were determined by inductively coupled plasma (ICP) measurements conducted on iCAP7600 spectrometer.

Synthesis of metalated ligands. A flask was charged with 1,3-bis(4'-carboxy-3,5-diisopropyl-[1,1'-biphenyl]-4-yl)-1H-imidazol-3-ium chloride (100 mg, 0.15 mmol), potassium tert-butoxide (61 mg, 0.54 mmol), and corresponding metal salts (copper(I) chloride (22.3 mg, 0.23 mmol), copper(I) bromide (32.3 mg, 0.23 mmol), copper(I) iodide (42.9 mg, 0.23 mmol), dimethylsulfide gold(I) chloride (66.4 mg, 0.23 mmol)). To the flask, dry THF (4 mL) was added and stirred for 48 h under nitrogen atmosphere. The mixture was filtered through Celite. The filtrate was acidified with 1 N HCl. The crude material was washed with water and recrystallized from methanol. **1,3-bis(4'-carboxy-3,5-diisopropyl-[1,1'-biphenyl]-4-yl)-2,3-dihydro-1H-imidazol-2-yl copper(I) chloride (NHC-CuCl)** (54 mg, 48% yield). ¹H NMR (400 MHz, CD₃OD): δ 8.07-8.05 (d, 4H), 7.69-7.66 (m, 6H), 7.62 (s, 4H), 2.75-2.67 (sept, 4H), 1.40-1.37 (d, 12H), 1.35-1.33 (d, 12H); ¹³C NMR (100 MHz, CD₃OD): δ 175.10, 147.61, 144.36, 143.56, 138.69, 135.54, 130.98, 127.59, 125.63, 124.09, 30.22, 25.14, 24.16; Anal. Calcd. for $C_{41}H_{44}N_2O_4CuCl$: C, 67.66; H, 6.09; N, 3.85. Found: C, 67.59; H, 5.91; N, 3.90. **1,3-bis(4'-carboxy-3,5-diisopropyl-[1,1'-biphenyl]-4-yl)-2,3-dihydro-1H-imidazol-2-yl copper(I) bromide (NHC-CuBr)** (62 mg, 53% yield). ¹H NMR (400 MHz, CD₃OD): δ 8.08-8.06 (d, 4H), 7.70-7.65 (m, 6H), 7.62 (s, 4H), 2.75-2.68 (sept, 4H), 1.39-1.37 (d, 12H), 1.35-1.33 (d, 12H); ¹³C NMR (100 MHz, CD₃OD): δ 175.13, 147.59, 144.30, 143.61, 138.63, 135.47, 130.96, 127.63, 125.56, 124.05, 30.18, 25.17, 24.17; Anal. Calcd. for $C_{41}H_{44}N_2O_4CuBr$: C, 63.77; H, 5.74; N, 3.63. Found: C, 63.87; H, 5.56; N, 3.30. **1,3-bis(4'-carboxy-3,5-diisopropyl-[1,1'-biphenyl]-4-yl)-2,3-dihydro-1H-imidazol-2-yl copper(I) iodide (NHC-CuI)** (58 mg, 47% yield). ¹H NMR (400 MHz, CD₃OD): δ 8.08-8.06 (d, 4H), 7.65-7.62 (m, 6H), 7.62 (s, 4H), 2.75-2.69 (sept, 4H), 1.40-1.38 (d, 12H), 1.35-1.33 (d, 12H); ¹³C NMR (100 MHz, CD₃OD): δ 175.15, 147.57, 144.30, 143.64, 138.61, 135.40, 130.96, 127.64, 125.43, 124.03, 30.18, 25.23, 24.19; Anal. Calcd. for $C_{41}H_{44}N_2O_4CuI$: C, 60.11; H, 5.41; N, 3.42. Found: C, 60.03; H, 5.53; N, 3.32. **1,3-bis(4'-carboxy-3,5-diisopropyl-[1,1'-biphenyl]-4-yl)-2,3-dihydro-1H-imidazol-2-yl gold(I) chloride (NHC-AuCl)** (67 mg, 52% yield). ¹H NMR (400 MHz, CD₃OD): δ 8.08-8.06 (d, 4H), 7.74-7.68 (m, 6H), 7.62 (s, 4H), 2.74-2.70 (sept, 4H), 1.44-1.42 (d, 12H), 1.34-1.33 (d, 12H); ¹³C NMR (100 MHz, CD₃OD): δ 175.11, 147.60, 144.52, 143.58, 138.66, 135.08, 130.98, 127.63, 125.61, 124.15, 30.28, 24.76, 24.33; Anal. Calcd. for $C_{41}H_{44}N_2O_4AuCl$: C, 57.18; H, 5.15; N, 3.25. Found: C, 57.10; H, 5.27; N, 3.18.

Synthesis of MOFs containing immobilized copper and gold NHC complexes. NHC ligands bearing metal

complexes (0.040 mmol) and $Zn(NO_3)_2 \cdot 6H_2O$ (0.16 mmol, 49 mg) were added to 4-mL vial with mixture of *N*-methyl-pyrrolidone (1 mL) and *p*-xylene (2 mL). The vial was placed at 80 °C. After 72 h, block shaped crystals were washed with DMF and THF and dried under vacuum. **MOF$_{CuCl}$** (28 mg, 75% yield) Anal. Calcd for $C_{128.25}H_{139.25}N_{9.75}O_{21.25}Zn_4Cu_3Cl_3$: $\{Zn_4L_3(NO_3)_2(C_3H_7NO)_{1.75}(H_2O)_{0.5}\}$ C, 56.72; H, 5.17; N, 5.03. Found: C, 56.58; H, 5.12; N, 5.04. **MOF$_{CuBr}$** (30 mg, 82% yield) Anal. Calcd for $C_{126}H_{134.5}N_9O_{20.75}Zn_4Cu_3Br_3$: $\{Zn_4L_3(NO_3)_2(C_3H_7NO)(H_2O)_{0.75}\}$ C, 54.07; H, 4.84; N, 4.50. Found: C, 54.12; H, 4.92; N, 4.59. **MOF$_{CuI}$** (29 mg, 77% yield) Anal. Calcd for $C_{130.5}H_{144.5}N_{10.5}O_{22}Zn_4Cu_3I_3$: $\{Zn_4L_3(NO_3)_2(C_3H_7NO)_{2.5}(H_2O)_{0.5}\}$ C, 51.47; H, 4.78; N, 4.83. Found: C, 51.45; H, 4.59; N, 4.77. **MOF$_{AuCl}$** (26 mg, 73% yield) Anal. Calcd for $C_{129}H_{142}N_{10}O_{22}Zn_4Au_3Cl_3$: $\{Zn_4L_3(NO_3)_2(C_3H_7NO)(H_2O)\}$ C, 49.29; H, 4.55; N, 4.46. Found: C, 49.13; H, 4.61; N, 4.38.

Cu-catalyzed azide-alkyne cycloaddition. MOF$_{CuI}$ (4.3 mg, 4.6 µmol, 5 mol%), alkyne (0.091 mmol, 1 eq), TEA (15.2 µL, 0.11 mmol, 1.2 eq), and azide (0.11 mmol, 1.2 eq) were added to THF (0.1 mL) in a vessel. The reaction mixture was stirred at room temperature for 5 h. The crude compound was isolated by silica column chromatography and dried under vacuum.

Cu-catalyzed multicomponent reaction. To THF (0.18 mL) was added MOF$_{CuI}$ (8.7 mg, 9.1 µmol, 10 mol%), alkyne (0.091 mmol, 1 eq), amine (0.11 mmol, 1.2 eq), TEA (15.2 µL, 0.11 mmol, 1.2 eq) under N_2 atmosphere, and then, sulfonyl azide (0.11 mmol, 1.2 eq) was added slowly. The reaction mixture was stirred at room temperature for 1 h. The crude compound was isolated by silica column chromatography and dried under vacuum.

Au-catalyzed hydroamination. MOF$_{AuCl}$ (2.7 mg, 2.7 µmol, 3 mol%), AgOTf (1.5 mg, 5.5 µmol, 6 mol%), alkyne (0.091 mmol, 1 eq), and anline (0.11 mmol, 1.2 eq) was added to dioxane (0.18 mL). The reaction mixture was stirred at 70 °C for 5 h. The crude compound was isolated by silica column chromatography and dried under vacuum.

Single Crystal X-ray Diffraction Analysis. The single-crystal X-ray diffraction data of MOF$_{CuCl}$ was collected at 100 K on a Bruker APEX II QUAZAR diffractometer equipped with graphite monochromatic Mo Kα radiation (λ = 0.71073 Å) and the diffraction data of MOF$_{CuBr}$, MOF$_{CuI}$, and MOF$_{AuCl}$ were collected at 100 K on an ADSC Quantum 210 CCD diffractometer with synchrotron radiation (λ = 0.70000 Å) at Supramolecular Crystallography 2D, Pohang Accelerator Laboratory (PAL), Pohang, Korea. In the case of MOF$_{CuCl}$, frame integration was carried out using SAINT.[17a] The raw data was scaled and absorption corrected using a multi-scan averaging of symmetry equivalent data using SADABS.[17b] The raw data of MOF$_{CuBr}$, MOF$_{CuI}$, and MOF$_{AuCl}$ were processed and scaled using HKL3000 program. Contributions from the disordered solvent molecules were removed by the SQUEEZE routine (PLATON)[17c,17d] and the outputs from the SQUEEZE calculations were attached to CIF files. The structure was solved by direct method (SHELXS-97) and refined by full-matrix least-squares method based on F^2 utilizing SHELXL-

2018/3.[17e] Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed to their geometrically ideal positions.

CCDC 1965351, 1965352, 1965353, and 1965354 contain the supplementary crystallographic data for MOF$_{CuCl}$, MOF$_{CuBr}$, MOF$_{CuI}$ and MOF$_{AuCl}$, respectively. These data can be obtained free of charge via www.ccdc.cam.ac.uk/cgi-bin/catreq.cgi (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

ASSOCIATED CONTENT

Experimental details of ligand synthesis, MOF construction, recycle experiments and catalyzed reactions, crystal structures, nitrogen sorption isotherms, NMR spectra, and PXRD patterns and can be found in the supporting information.
 This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
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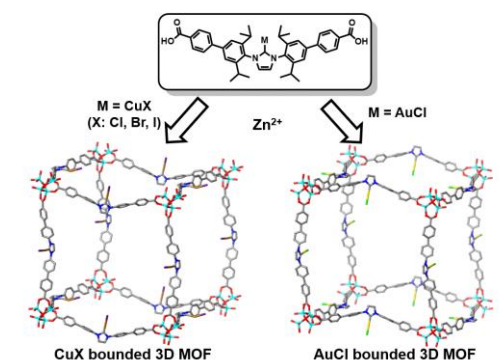
MOFs bearing copper and gold NHC complexes were prepared by bottom-up approach. Regardless of the different types of catalysts, the structures of resulting MOFs were maintained and exhibited a four-fold interpenetrated 3D structure. These MOFs possess good stability in various solvents. Due to the presence of the catalytic active copper halide and gold chloride inside pores, MOFs havning copper and gold NHC complexes showed high size selectivity of substrates in various reactions.