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Review

Copper-Based Metal–Organic Frameworks (MOFs) as an Emerging Catalytic Framework for Click Chemistry

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Abstract: In the extensive terrain of catalytic procedures for the synthesis of organic molecules, metal–organic frameworks (MOFs) as heterogenous catalysts have been investigated in a variety of chemical processes, including Friedel–Crafts reactions, condensation reactions, oxidations, and coupling reactions, and utilized owing to their specific properties such as high porosity, tuneability, extraordinary catalytic activity, and recyclability. The eminent copper-tailored MOF materials can be exceptionally dynamic and regioselective catalysts for click reactions (1,3-dipolar cycloaddition reaction). Considering the fact that Cu(I)-catalyzed alkyne–azide cycloaddition (CuAAC) reactions can be catalyzed by several other copper catalysts such as Cu (II)-β-cyclodextrin, $Cu(OAc)_2$, $Fe_3O_4@SiO_2$, picolinimidoamide–Cu(II) complex, and Cu(II) porphyrin graphene, the properties of sorption and reusability, as well as the high density of copper-MOFs, open an efficient and robust pathway for regimented catalysis of this reaction. This review provides a comprehensive description and analysis of the relevant literature on the utilization of Cu-MOFs as catalysts for CuAAC 'click' reactions published in the past decade.

Keywords: metal–organic frameworks (MOF); Cu-MOF; catalyst; 1,4-disubstituted 1,2,3-triazole; click chemistry; heterogenous catalysis

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1. Introduction

Click chemistry is one of the most robust and versatile methodologies currently known to researchers, capable of synthesizing large complex compounds from relatively smaller moieties [1,2]. Due to its advantageous features and facile pathway of synthesis, the methodology has received significant interest globally. Carolyn R. Bertozzi, Morten Meldal, and K. Barry Sharpless in 2022 were awarded the Nobel Prize in Chemistry for their ground-breaking contribution, which was a big step in advancement. The advent of click chemistry has led to the discovery of nitrogen-rich azole heterocycles, which have been shown to be fascinating compounds with broad potential significantly with their pharmacological [3] and chemosensing [4] properties. 'Click' reactions, specifically Cu(I)-catalyzed cycloaddition involving a terminal alkyne and an organic azide to synthesize 1,4-disubstituted-1,2,3-triazole, have received a large amount of consideration in the fields of material science, polymer science, peptide chemistry [5], and synthetic organic chemistry over the past few decades. However, due to the fact that alkynes are poor 1,3-dipole acceptors, this reaction cannot proceed regioselectively without a suitable catalyst. Significantly, the presence of Cu(I), which forms bonds with terminal alkynes, greatly enhances the pace, selectivity, and overall efficiency of click reactions [6].

The catalysts tailored from transition metals have the potential to act as fabricators in the assemblage of supplementary intricate structures, yielding complex organic structures with relative ease. Several metal catalysts such as Ru, Ag, and Au with enhanced catalytic activity and selectivity have been described in the scientific literature [7,8]. In the past decade, the 1,3 dipolar cycloaddition reaction for the synthesis of 1,2,3-triazole has received considerable attention and has been investigated using a variety of different types of copper catalysts including Cu(II)-β-cyclodextrin [9], Cu(OAc)$_2$ [10], Fe$_3$O$_4$@SiO$_2$ picolinimidoamide–Cu(II) complex [11], Cu(II) porphyrin graphene [12], bromotris(triphenylphosphine)copper(I) [13], and Cu(II)-supported graphene quantum dots [14]. In spite of this, the majority of the copper catalysts that were discussed before had a number of significant drawbacks, including laborious and pricey preparation processes; the utilization of hazardous solvents and reagents; and, most critically, challenging procedures for catalyst separation [15]. Furthermore, the intensifying public concern for environmental protection has prompted scientists to look for more sustainable synthetic routes to overcome the challenges of recyclability of catalysts and switching to less hazardous solvents/chemicals. To anticipate the ease of the synthesis of 1,2,3-triazole derivatives, the area of organic synthesis has focused significantly on the creation of novel and effective Cu(I)-based MOFs catalysts (Figure 1). Over the past decade, scientists have made great strides to manufacture various MOFs and explore of their use in numerous scientific domains, including energy storages [16], medicinal technology [17], environmental pollution [18], sensing platforms, catalysis, photocatalysis [19], oxidation, hydrogenation [20], drug delivery [21,22], and bioimaging [23] due to their diverse active sites [24,25].

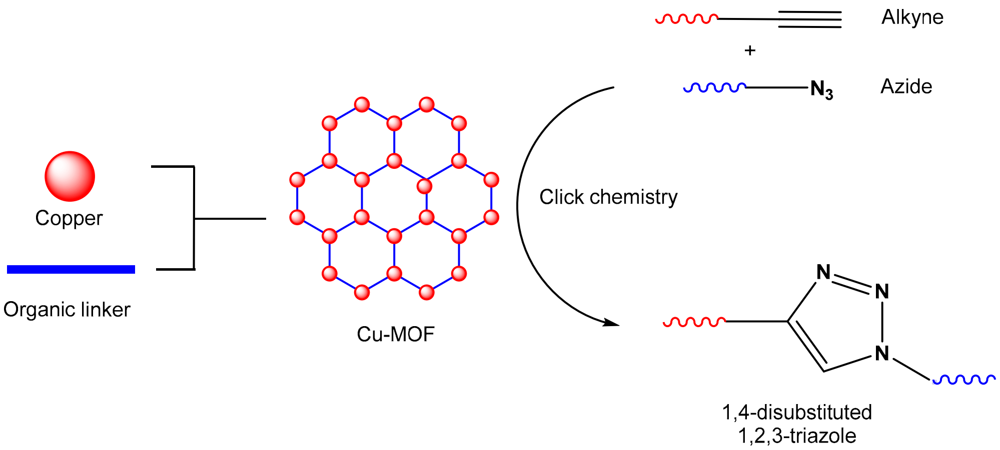


Figure 1. An illustration of MOF assembly and subsequent use in click chemistry.

Metal–organic frameworks are strong hybrid emerging materials due to their amenable physical and chemical properties [26]; porous structure consisting of inorganic/supplementary building units (atoms, molecules, and ions of metals); and organic building blocks, known as linkers/bridging ligands (carboxylates, as well as anions such as phosphonate, sulfonate, and heterocyclic chemicals) [27], as shown in Figure 2. The long organic linkers are responsible for the high porosity and great storage capacity of MOFs [28]. In addition, they have the unique capacity to intentionally alter and adjust the form and function of their pores. Moreover, due to the remarkable adaptability of MOF structures, it is possible to synthesize catalytically active sites by employing defect engineering and linker modification strategies [29,30].

The coordination number, geometry, and functional assembly in MOFs play a dominant role in shaping the structure of the framework. MOFs have been found to display a wide range of supplementary binding unit (SBU) geometries, such as the octahedron, the trigonal matrix, the square paddlewheel, and the triangle, each of which has a different number of extension points [27]. As a general rule, a connecting ligand interacts with a metal ion that has several available reactive sites [31]. SBU connections and organic linkers control the ultimate topology of any given MOF such that infinitely stretched polymers or discretely closed oligomeric structures may emerge from a given system [32,33]. This review aimed to assemble copper-embedded MOFs for the synthesis of 1,4-disubstituted-1,2,3-triazoles.

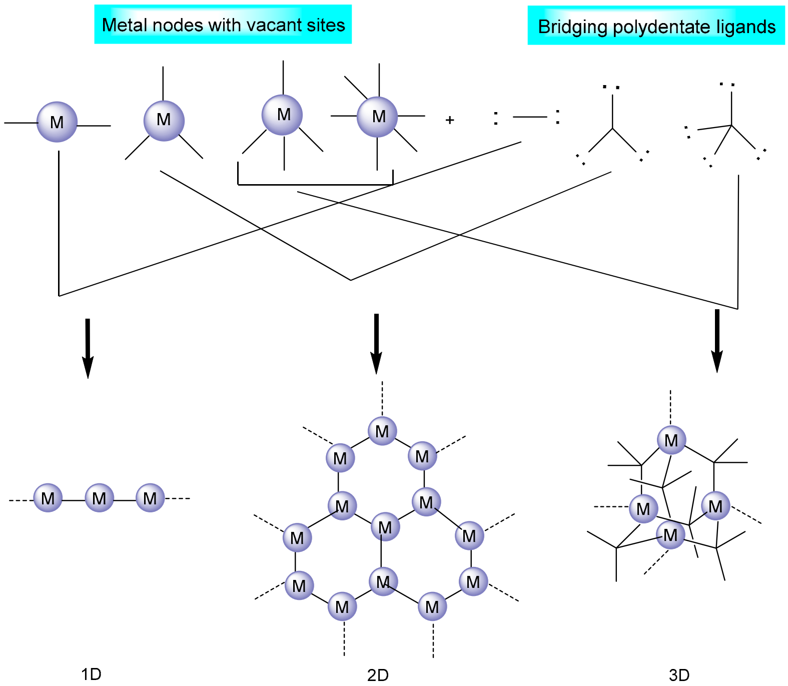


Figure 2. MOF structure based on the metal nodes and bridging ligands [31].

2. MOFs as Heterogenous Catalysts

The transition metal complexes can be utilized as homogenous catalysts due to their extraordinary catalytic action for a prevalent variety of organic reactions, showing regio- and chemoselectivity [34,35]. However, this recompense comes with some drawbacks, namely, the homogenous catalysts can be decomposed during the reaction process, making their recovery a challenging process [36]. The various techniques for heterogenizing a homogenous catalyst involve grafting of polymers, impregnation of solid carriers, introduction to zeolite cavities via the "ship in a bottle" method [37], and the formation of organized structured or non-organized structured mesoporous organic/inorganic hybrid systems [30].

Researchers have primarily concentrated on heterogeneous catalysts, as opposed to homogeneous catalysts, due to the greater reusability and the high selectivity of the heterogenous catalyst [38]. In catalyst research, the gold standard followed currently is a combination of computational methods for predicting catalytic activity and novel synthesis methodologies for creating the appropriate organized frameworks, with constant, well-defined active sites that enable good selectivity while avoiding deactivation [39,40]. A large number of recently discovered heterogeneous catalysts are based on metal–organic frameworks, an attractive new field that uses metal ions as active sites in the generated crystal-like structure, metal complexes that were part of the organic linkers, or supported metal nanoparticles. The microporous MOF (microporous co-ordination polymer) generated as an outcome grounded on metal ion action at nodes or at the ligands emerges instantaneously as a counterpart of the homogeneous catalytic system [41]. Due to their potential use as contributing templates in the production of heterogenous catalysts, metal–organic frameworks have recently been a key area of research [42].

3. Physico-Chemical Properties of MOFs

Since MOFs are composed of a metal ion bound to an organic linker chain, they have outstanding properties in terms of their size, porosity, etc. (Table 1, Figure 3), due to which MOFs can be used in a wide range of applications including catalysis, sensing, and drug delivery, among others. In addition, the MOFs may be changed via regulated integration in conjugation with one-of-a-kind and desirable functional materials, which can then impart the required characteristics onto the MOF structures [43,44]. Organic linkers with conjugated structures facilitate electron transfer between ligands and metals. For use as smart materials, MOFs with dynamic frameworks may undergo reversible structural changes that vastly increase their intended qualities.

Table 1. Physico-chemical properties of MOFs. * Reproduced from references with permission.

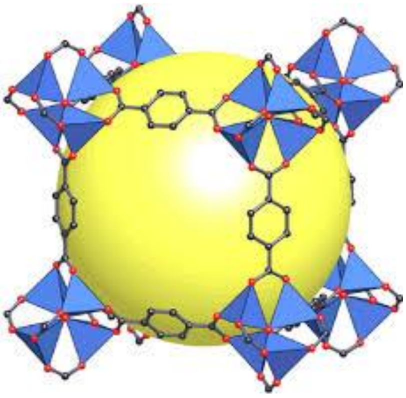
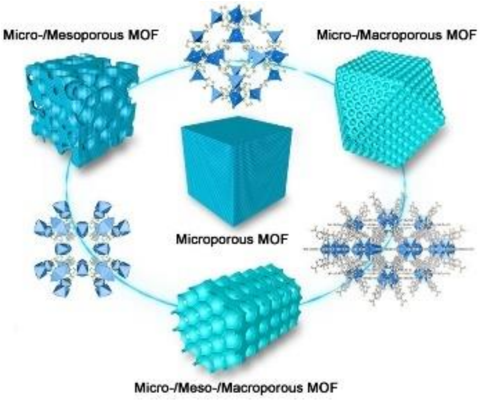
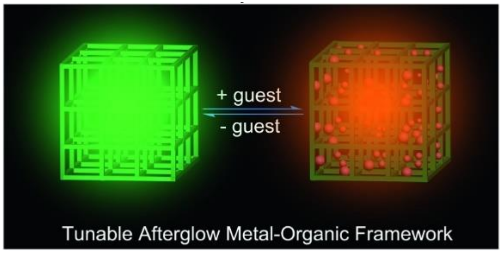
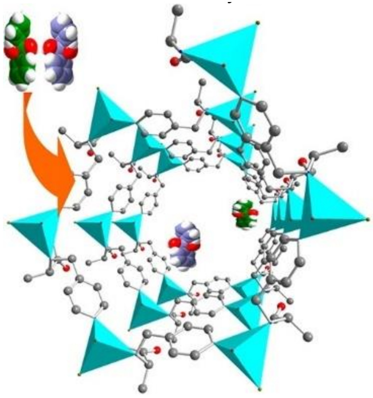
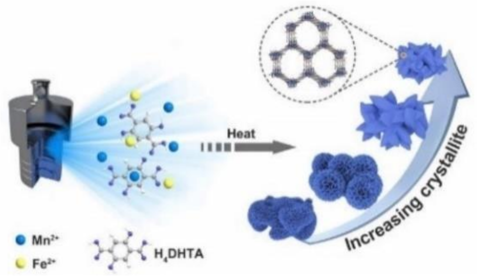
Entry	Property	Description
1.	Surface area 	• The formation of a cage due to the binding between the metal ion with the organic linker creates a hollow structure from the inside leading to the formation of a large surface area of MOFs [45]. • The sensing potential of surface-rich MOFs is intriguing. They may be used as a membrane because of their remarkable gas adsorption and separation capabilities.
2.	Porosity 	• One of the properties that lends these materials their greatest value in catalysis is that the pore size may be controlled during synthesis by altering the synthesis process and chemical precursors [44]. • Most of the MOFs described thus far, however, are microporous, which slows down mass transfer and restricts accessibility of heavier molecules to their interior surface [46]. *
3.	Structure tunability and Luminescence 	• MOFs are highly tunable due to their porous and polymeric cage-like networks. • The synthetic tunability of MOFs is opportune for multifunctional catalytic systems [43,44]. • One of the most distinguishing features of MOFs is luminescence that involves the release of light from excited molecules. • This is not only associated with the type of metal in the composition of MOFs but it may also be potentialized by organic ligands that provide excellent chromophores for luminescence [47]. *

Table 1. *Cont.*

Entry	Property	Description
4.	Chirality 	• The synthesis of chiral metal–organic frameworks (MOFs) is highly relevant for asymmetric heterogenous catalysis. Chirality can be introduced to MOFs by using chiral linkers for synthesis [45]. • MOFs can be regarded as molecular sieve-like materials as their applications include chiral recognition, chiral separation, and chiral catalysis [48]. *
5.	Crystallinity 	• MOFs have a crystalline property because the synthesis of MOFs involves the key process of crystallization. • Highly crystalline mesoporous designs are particularly promising, owing to their unique features coming from the crystallized frameworks, having a large amount of potential in energy and environment-related areas [49]. *

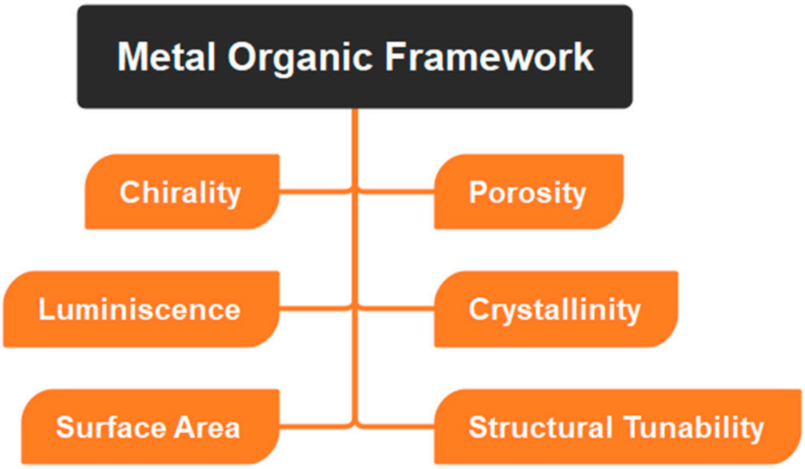


Figure 3. Depicting physicochemical properties of MOFs.

4. Methods for the Synthesis of MOFs

Numerous techniques for the manufacture of MOFs have been documented in published works. Some examples of these techniques, which are included in the table below, are microwave-assisted synthesis [50], solvothermal synthesis, sonochemical synthesis, electrochemical synthesis [51], among others (Table 2). The choice of solvent is often influenced by a variety of characteristics, such as the redox potential, reactivity, stability constant, and solubility of the compound [52,53].

Table 2. General methods for synthesis of MOFs.

Entry	Method	Description	Examples	References
1.	Electrochemical synthesis	Electrochemical synthesis involves the addition of metal ions into a reaction mixture consisting of organic linkers and electrolytes via anodic dissolution. The significant benefit of this technique is that the anions often found with metals in salts may be eliminated, resulting in very pure compounds, since less time and energy are needed for reactions to take place under more benign circumstances.	ZIF-8, HKUST-1, MIL-100 (Fe).	[51]
2.	Microwave-assisted synthesis	The use of microwaves to irradiate the reaction mixture results in the creation of nanoscale MOF crystals. There are several benefits to this synthesis, including high efficiency, shorter reaction times, phase selectivity, morphological control, and particle size reduction.	$[Cu_3(btc)_2(H_2O)_3]$, HKUST-1	[50]
3.	Mechanochemical synthesis	Mechanical forces are introduced to complete the chemical reaction. Mechanochemical synthesis has the benefit of not requiring the use of organic solvents, which may be carcinogenic, poisonous, and damaging to the environment. Metal oxides are often employed as precursors in this procedure rather than metal salts.	InOF-1, $Cu_3(BTC)_2$-MOF	[52,53]
4.	Slow evaporation method	This conventional method for MOF preparation involves the use of suitable solvents to dissolve the precursor materials and later on slow evaporation of the solvent at an adequate temperature. The synthesis of MOFs using this approach is hindered by the insolubility of the chemicals. Accordingly, a combination of solvents may be utilised to improve solubility.	$[Cu(2,3\text{-}pydc)(bpp)]\cdot 2.5H_2O$, $[Zn(2,3\text{-}pydc)(bpp)]\cdot 2.5H_2O$	[50]
5.	Solvothermal synthesis	The reaction between the organic linker and metal ion takes place in a suitable solvent at a temperature above the boiling point of the solvent used. The primary benefit of this technique is that the relatively greater yield can be obtained.	$Zn_2(bpabdc)_2(DMF)_2(H_2O)_n$, $[Cu(tdc)(H_2O)]_n.n(DMA)$	[54,55]
6.	Sonochemical synthesis	The solution mixture was subjected to ultrasonic radiations (20 kHz–10 MHz) to synthesize MOF with novel morphologies. The sonochemical technique allows for the rapid production of MOFs with a tiny crystal size in a very short reaction time. This approach has the benefits of being fast, cheap, repeatable, and eco-friendly.	HKUST-1, TMU-7, $[Zn_3(btc)_2]$	[56]

5. MOFs as Catalysts for Innumerable Reactions

MOFs are becoming an integral part of the research society since they can be utilized as a low-cost heterogeneous catalyst in many different chemical processes [57]. This can be attributed to MOFs having large peripheral areas, size, shape, enantioselectivity, persistent porosity, and multifunctional ligands, with these being some of the interesting and modifiable features of MOFs [45]. There are several benefits of using MOFs as heterogeneous catalysts, including improved catalytic reactivity, flexibility, and facile tunability [52]. However, the use of MOFs is unfavorable for reactions that need extreme conditions because of their limited chemical and thermal stability [58]. Some of the many organic processes for which MOFs were utilized as catalysts or catalyst support include Friedel–Crafts reactions [59]; Knoevenagel condensation [60]; aldol condensation [61]; oxidation [51,62]; and coupling reactions [63–65].

Nguyen et al. described a solvothermal acylation process using IRMOF-8 for the Friedel–Crafts reaction, wherein 2,6-naphthalenedicarboxylic acid and zinc nitrate tetrahydrate are dissolved in dimethylformamide (DMF) for the synthesis of IRMOF-8. Moreover, a high yield of the product was achieved when the catalyst was employed in the reaction and was recovered successfully [59]. Similarly, MOF-5 was synthesized by Phan et al.—1,4-benzene dicarboxylic acid and zinc nitrate hexahydrate were combined in dimethylformamide (DMF) under solvothermal conditions to perform a Friedel–Crafts benzylation of toluene [66]. Gascon and teammates produced MOF with non-coordinated sites with an aniline-like amino group for Knoevenagel condensation with 100% selectivity. Xamena and colleagues studied the catalytic activity of IRMOF-3 and MOF-5 on the Knoevenagel condensation reaction [67]. The alkene oxidation of α-pinene and cyclohexene in a solvent-free environment was investigated by Kholdeeva et al. using MOFs (Fe-MIL-101 and Cr-MIL-10), and the allylic oxidation products were produced. Both Cr-MIL-101 and Fe-MIL-101 exhibited selectivity, with Cr-MIL-101 favoring the formation of α,β-unsaturated ketones, and Fe-MIL-101 forming 2-cyclohexen-1-ol as the desired product [51]. Under ideal circumstances, both catalysts demonstrated improved reusability. Torbina et al. determined the catalytic activity of chromium-based MOFs as a heterogenous catalyst for the oxidation reaction of propylene glycol with tert-butyl hydroperoxide [68]. In another example, Phan et al. employed the very porous metal–organic framework MOF-199 as a heterogeneous catalyst for the Ullmann reaction between phenols and aryl iodides to generate diaryl ethers. After six hours at 120 °C, the product yield was 82%. It was shown that the MOF-199 catalyst may be used several times without significantly losing its catalytic efficiency [69]. Several MOFs are used to catalyze the different reactions reported (Table 3). From this perspective, we focused on a few noteworthy instances that provide a balanced comparison to currently available copper-based MOFs over other MOFs to catalyze a wide variety of reactions.

Table 3. Several reactions catalyzed by MOF-based catalysts.

Entry	Reaction Catalyzed	MOF Type	Metal in MOF	Reference
1.	Friedel–Crafts reaction	HPW@Zr-BTC	Zirconium	[70]
		Cu-MOF-74	Copper	[71]
		Urea containing 2D MOF	Copper	[72]
4.	Suzuki coupling	Cu-BDC MOF	Copper	[63]
5.	Heck coupling	Pd(II)-porphyrinic MOF	Palladium	[73]
6.	Suzuki–Miyaura coupling	NPC-Pd MOF	Palladium	[74]
7.	Knoevenagel condensation	Al-MIL-101-NH_2	Aluminium	[75]
8.	Aldol condensation	Basolite F300	Iron	[61]
9.	CuAAC reaction	Fe_3O_4@HKUST-1	Copper	[76]

6. Reactions Catalyzed by Cu-Tailored MOFs

Cu-MOFs have gained a great deal of popularity in the area of study as a result of their high catalytic activity, a wealth of resources, and ease of synthesis, all of which are facilitated by the excessive natural abundance of copper. Copper-containing catalysts provide a promising route for activating starting materials while maintaining reaction selectivity under tunable conditions, allowing for the generation of complex scaffolds from easily accessible building pieces [77,78]. A few of the reaction methodologies that are promoted by Cu(I) scaffolds are CuAAC, oxidation, coupling reactions, and Friedel craft acylation reactions, among others.

Maleki et al. employed the hydrothermal synthesis of Cu-MOF, presenting an effective and environmentally friendly technique of synthesizing tetrazole derivatives using Cu-MOF as a catalyst due to the high crystallinity and purity of HKUST-1 (Cu-MOF) (Figure 4). The structure's face-centered cubic symmetry can be ascribed to the detail that three-dimeric copper wheels are covalently bonded to each BTC ligand. However, two copper atoms are octahedrally bonded to eight oxygen atoms. As a consequence of activation of the carbonyl and ethoxy groups during synthesis, Cu-MOF demonstrated good catalytic activity in three- and four-component processes involving aldehydes, amines, triethyl orthoformate, -keto-esters, and 2-cyano-guanidine [79]. Using aromatic aldehydes, malononitrile, 2-hydroxynaphthalene-1,4-dione, and cycloketone in a one-pot domino four-component reaction using a copper-based MOF as a heterogeneous catalyst and aluminum chloride as a Lewis acid, Taheri and co-workers examined the synthesis of tacrine derivatives. The reaction for the synthesis of MOF was completed at room temperature in the presence of a Cu(II) nitrate trihydrate and 1,4-benzenedioic acid in DMF. The use of Cu-MOF as the Lewis acid catalyst might facilitate the production of pyranic intermediates, which would then be followed by the Friedlander quinoline reaction being supplemented with $AlCl_3$ in order to produce the desired products. In addition to higher yields, utilizing Cu-MOF as a heterogeneous catalyst for the production of the required products (Figure 4) also eliminates the need for a tremendous separation procedure for pyranic intermediates [80].

Ghasemzadeh et al. reported a condensation process between curcumin, aromatic aldehydes, and barbituric acid, used to efficiently synthesize novel pyrano [2,3-d] pyrimidine2,4-diones in a single step. The magnetic $CoFe_2O_4$@OCMC@Cu(BDC) showed superior catalytic activity in the generation of heterocyclic compounds (Figure 4) and had a remarkable degree of reusability through at least six cycles. The $CoFe_2O_4$@OCMC@Cu(BDC) catalyst may play a crucial role in promoting the reactions with high efficiency due to its abundance of Lewis acid sites (Co^{2+}, Fe^{3+}, and Cu^{2+}) [81]. Moreover, a green three-component reaction carried between aldehydes, dimedone, and aryl amines/2-naphthol/urea to produce a wide range of substituted xanthene derivatives catalyzed by $CoFe_2O_4$@OCMC@Cu(BDC) MOF is reported by Ghasemzadeh and Ghaffarian. A metal–organic framework was shown to have a flower-like shape with surface area, total pore volume, and average pore diameters of 64,933 m^2g^{-1}, 0.186 cm^3g^{-1}, and 11.46 nm, respectively. This approach had several benefits, including good yields, clean and ecologically friendly settings, minimal catalyst loading, simple catalyst separation, and a short reaction time [82].

Three-component coupling and cyclization processes for the synthesis of propargylamines, indoles, and imidazopyridines were developed by Corma et al. via copper-containing MOF [Cu(2-pymo)$_2$]. These crystal structures show that copper ions interact with adsorption substrates more efficiently attributable to a highly deformable, three-dimensional sodalite-like framework consisting of two Cu^{2+} ions attached to each heterocyclic ligand (pyrimidine, imidazole, or benzene). The MOFs possessed this characteristic, making them superior and more active than conventional N-heterocyclic copper coordination complexes. Using a three-component coupling process of amines, aldehydes, and alkynes catalyzed by [Cu(2-pymo)$_2$], the propargylamine derivatives were synthesized with good yield and selectivity. On the other hand, the [Cu(BDC)] catalyst performed admirably in the 5-exo-dig cyclization of 2-aminopyiridine, aldehydes, and terminal alkynes to produce imidazopyridines (Figure 5) [79].

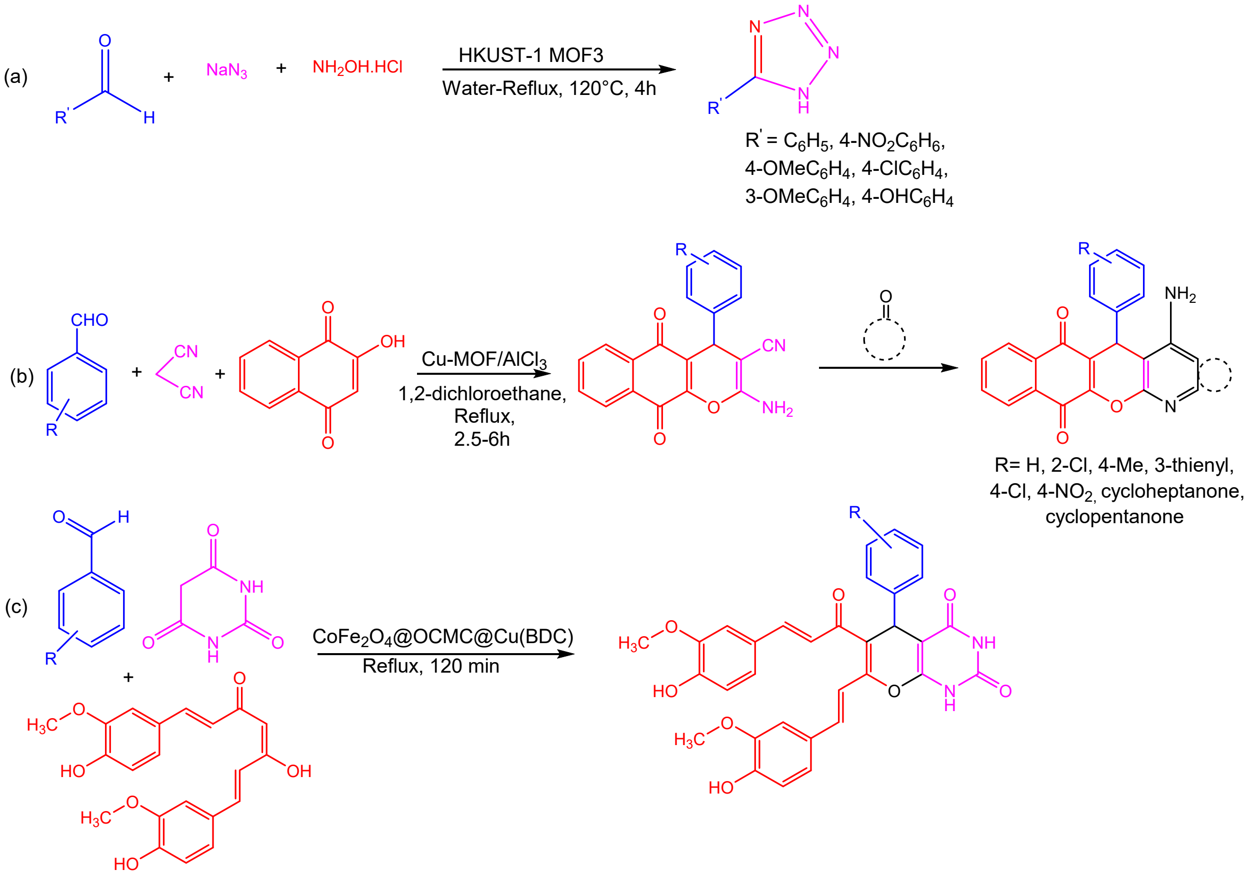


Figure 4. Different reactions catalyzed by Cu-MOFs (**a**) formation tetrazole from HKUST-1 MOF3 (**b**) three component coupling and cyclization reaction using Cu-MOF (**c**) single step three component coupling and cyclization reaction using $CoFe_2O_4$@OCMC@Cu(BDC) [82].

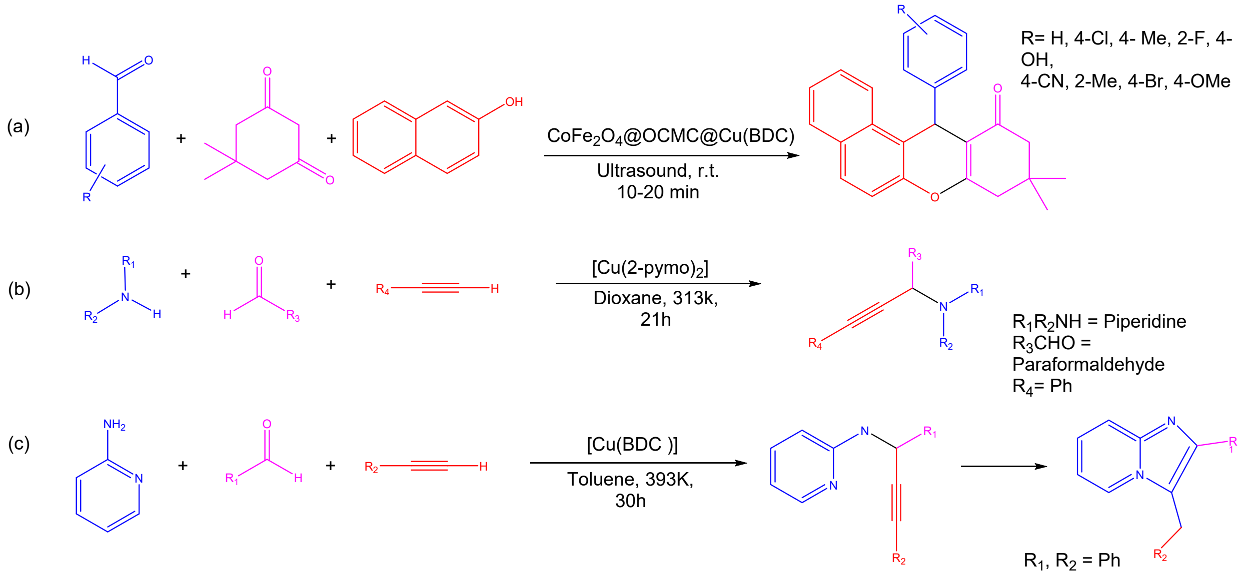


Figure 5. Schematic representation of the synthesis of (**a**) xanthene, (**b**) propargylamines, and (**c**) imidazopyridines using various copper MOFs as the catalysts [79].

The use of copper-tailored metal–organic frameworks has attracted a large amount of interest in a wide variety of processes such as condensation reactions, coupling reaction, and oxidation, but especially in click reactions [83]. It can be concluded that the reactions catalyzed by Cu-MOFs are significantly more versatile and robust than other metal catalysts, as well as the fact that Cu-MOFs have high recyclability, as depicted in Table 4. Furthermore, Cu(I) may coordinate with both hard and soft donor ligands in its coordination sphere, facilitating interactions between ligands of varying compositions [84,85].

Table 4. Comparison of Cu-based MOF over other catalysts used to catalyze an alkyne azide cycloaddition reaction.

Entry	Catalyst	Metal	Reaction Conditions	Solvent	Recyclability	References
1.	$Cu(INA)_2$-MOF	Cu(I)	1.5 h, 80 °C	solvent free	5 times	[86]
2.	$[Cu(CPA)(BDC)]_n$	Cu(I)	7 h, 90 °C	H_2O-MeOH (1:4)	4 times	[60]
3.	$Cu_2(BDC)_2(DABCO)$	Cu(I)	45 min, 60 °C	ethanol	5 times	[87]
4.	CuI	Cu(I)	rt	no solvent	NA	[84]
5.	$CuBr(PPh_3)_3]$	Cu(I)	60 °C, 5 h	THF/TEA	NA	[88]
6.	sf-CuS	Cu(I)	rt, 30 min	H_2O	NA	[89]
7.	$AgN(CN)_2$	Ag(I)	rt	DIPEAH $_2O$/ethylene glycol	NA	[90]
8.	$ZnEt_2$	Zn(II)	rt, 18 h	THF	NA	[91]
9.	Au(RD32)	Au(III)	60 °C, H_2O	EtN_3	NA	[92]
10.	$RuH_2(CO)(PPh_3)_3$	Ru(II)	80 °C, 2 h	PTC, H2O	NA	[93]
11.	Pd@PR	Pd(0)	8–12 h, 100 °C	DMF	NA	[94]

7. Reaction Mechanism for CuAAC Using MOF Catalyst

The CuAAC reaction stands out from other click reactions, owing to its remarkable process that involves the rapid devising of a super-reactive coordination complex of alkynes and azide utilizing a copper(I) catalyst [95]. However, the catalyst in CuAAC triggers the reaction and brings the reactants together even at extremely low concentrations that are physiologically relevant, while without the catalyst, the reaction rate and selectivity are poor [84]. Since the deprotonation of terminal alkynes is required in the CuAAC reaction process, to produce the Cu–alkynyl intermediate, the procedure can only be carried out using terminal alkynes. This intermediate makes a connection with azide during the subsequent step, which results in the formation of a six-membered cyclic intermediate that rapidly converts into a stable triazole.

The chemical mechanism demonstrating the synthesis of 1,4-disubstituted 1,2,3-triazole using Cu alkynyl intermediate was suggested by Sharpless and colleagues. However, in addition to increased regioselectivity, a strong yield and rapid kinetics of the reaction are also two of the most significant advances that have been documented by a variety of scientists. Cu in the +1 oxidation state can be generated in situ from $CuSO_4.5H_2O$ and sodium ascorbate or utilized directly as CuI, $[Cu(PPh_3)_3Br]$, CuBr, Cu_2O, and other compounds [96–98]. A mononuclear mechanism for the reaction's progression was initially reported by Sharpless and colleagues; however, as scientific knowledge expanded, a binuclear mechanism was discovered and reported by Finn and Folkin. This mechanism involves two copper atoms binding to the alkyne in different positions to form a complex, which is then attacked by the nucleophilic azide to form a six-membered ring. The creation of a new C-N bond then yields the desired result, as highlighted in Figure 6.

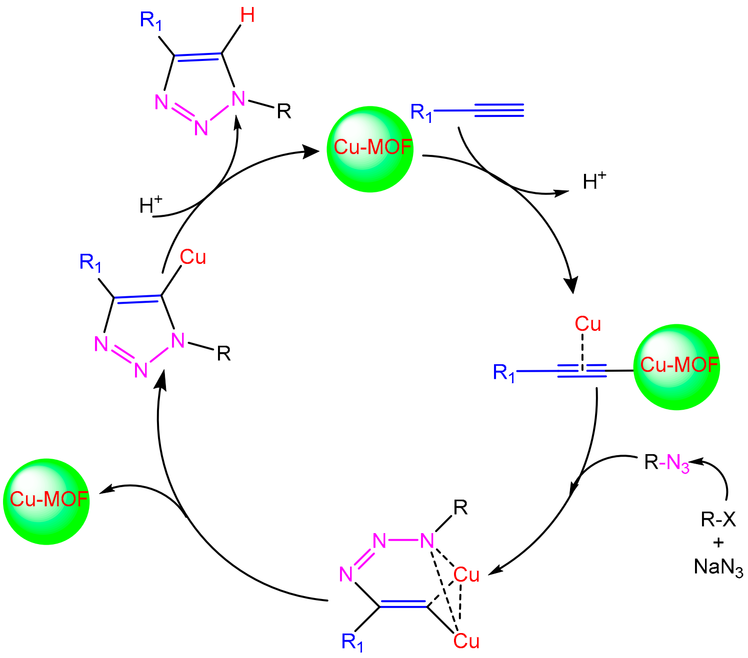


Figure 6. Plausible reaction mechanism for CuAAC using Cu-MOF as a catalyst [95].

In fact, over the past several decades, A3 coupling reactions, synthesis of tetrazoles, and condensation reactions have garnered a large amount of attention. The mechanism for the A3 coupling reaction involves the activation of the C-H bond by the metal catalyst, which is a key step in the reaction process for A_3 coupling. The terminal alkyne is made more acidic due to the formation of a metal complex with the alkyne proton. With a weak base, the amines in the reaction medium deprotonate the terminal alkyne to produce the alkynyl nucleophile. Metal acetylide interacts with iminium ions to make propargylamine, while simultaneously the catalyst is regenerated for use in a subsequent reaction cycle [99], as illustrated in Figure 7.

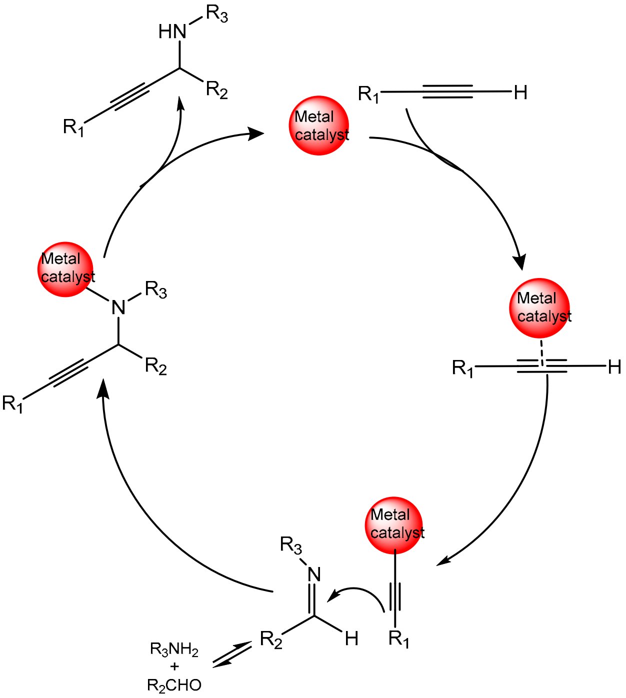


Figure 7. Plausible reaction mechanism for A3 coupling reactions [99].

Tetrazoles are a family of synthetic organic heterocyclic compounds that are made up of a five-member ring that contains four nitrogen atoms and one carbon atom. The formal [3 + 2] cycloaddition of azides and nitriles is the simplest and most efficient way to produce tetrazoles, which are finding widespread use in pharmaceuticals as bioisosteres, information recording systems, etc. Since the nitrile group is activated in the tetrazole synthesis by its coordination with nitrogen and the triple bond, increasing the electrophilic character of the cyanide group, these intermediates speed up the 3 + 2 cycloaddition process. The complex is subsequently exposed to sodium azide, resulting in the formation of a second intermediate that is acidified to provide the final tetrazole product (Figure 8) [100].

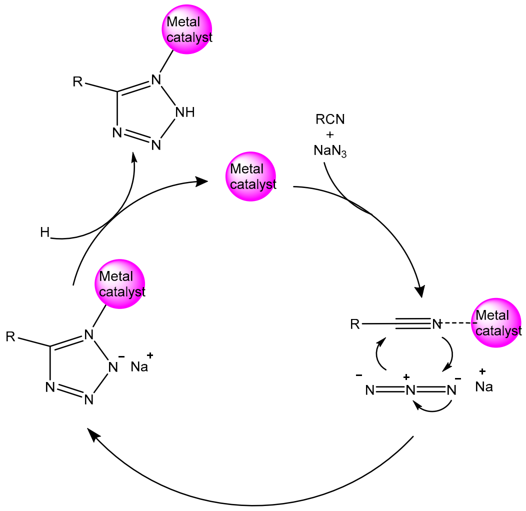


Figure 8. Plausible reaction mechanism for tetrazole synthesis [100].

The condensation reaction mechanism proceeds with the formation of Lewis acid sites in the vacant orbitals of Zn-MOF caused by Zn(II). This is due to the interaction of Zn(II) with the unpaired electrons on the carbonyl oxygen, suggesting that the O atom's positive charge may promote further polarization of the carbonyl group. Meanwhile, the hydroxyl O atom connected to the Zn(II) ion acted as the central Lewis basic site, stimulating the active methylene of malononitrile to donate protons and create a carbon anion near the benzaldehyde. The carbonyl C atom of benzaldehyde was then reacted with malononitrile to generate the final product (Figure 9) [101].

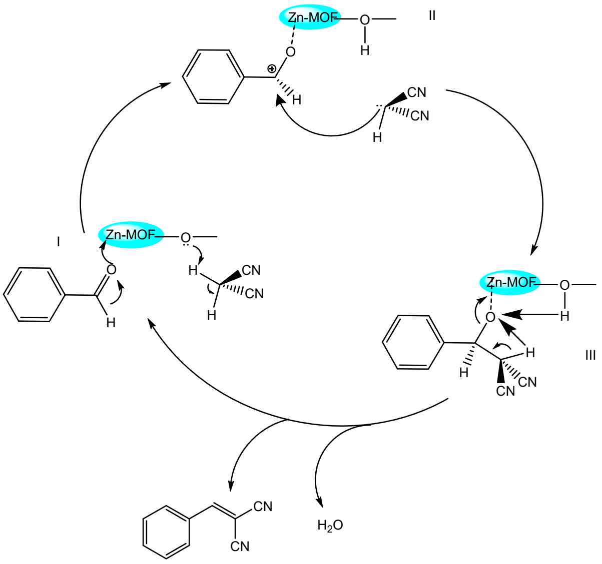


Figure 9. Plausible reaction mechanism for condensation reaction. [101].

8. Copper-Based MOFs as Click Catalysts for Spectacular CuAAC

The Cu(I)-catalyzed azide-alkyne cycloaddition (CuAAC) process is one of the finest procedures for the regioselective production of 1,4-disubstituted-1,2,3-triazoles (Figure 10) in either aqueous or organic media. The wide variety of uses for 1,2,3-triazoles—as pharmaceuticals, agrochemicals, and photographic materials—have attracted a large amount of attention [95]. Furthermore, the copper (II) complex is reduceable to copper(I) in situ in the presence of a reducing agent such as sodium ascorbate, which is one of the most communal and unswerving methodologies used in the click reaction that occurs during the assembly of diverse compounds. Several researchers have discovered and reported the uses of Cu-MOFs that make them one of the great catalysts, but not much work has been done on this topic thus far. The HKUST-1 MOF has been found to contain both Cu(II) and Cu(I) ions, proving the existence of a mixed valence state. More importantly, many scientists have demonstrated that the CuMOF exhibited a distribution of double pore sizes and had excellent water stability. Indeed, these researches show the way toward a better understanding of the catalytic activity of Cu-based MOFs [80].

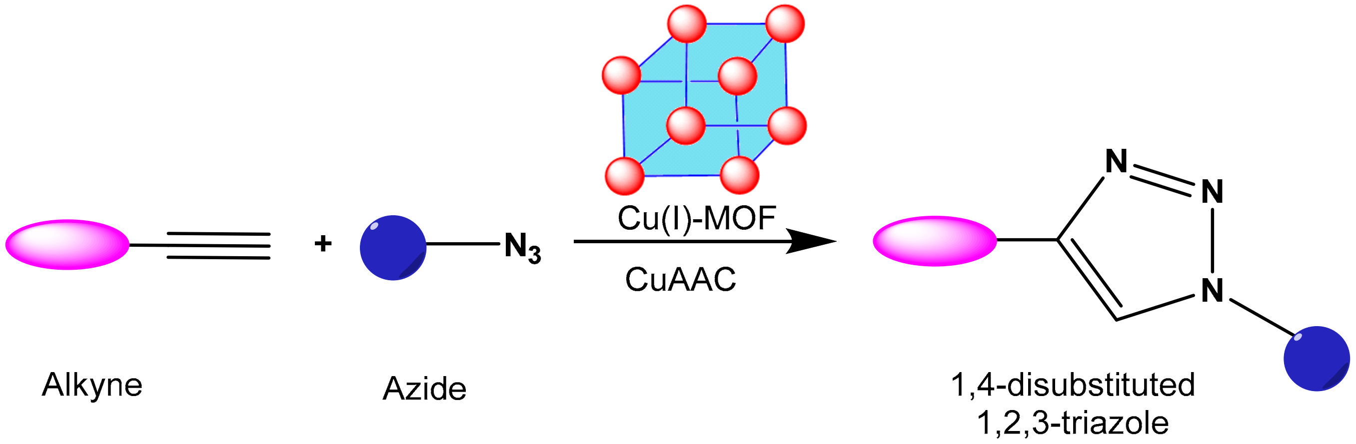


Figure 10. General reaction scheme depicting the formation of 1,4-disubstituted 1,2,3-triazole.

A novel and highly efficient copper-containing metal–organic framework has been reported by Li et al. for the regioselective synthesis of 1,2,3-triazoles without the use of solvents, yielding an excellent quantity of product, with catalyst loading being comparatively low. However, little efforts were required to recover the catalyst and it was further used for up to five cycles without appreciably diminishing its reactivity (Table 5) [102]. The catalytic activity of CuBTC–PyDC by Fan et al. [103] (Table 5) was investigated in the CuAAC reaction between benzyl azide and phenylacetylene to form 1-benzyl-4-phenyl 1,2,3-triazole. Lu et al. synthesized a unique copper(I)-based metalorganic framework (MOF), exhibiting an intriguing 3D architecture using Keggin-type polyoxometalate anions and a wheel-like resorcin [4]arene-based ligand (Table 5). With an abundance of solvent-accessible empty space and possible active Cu(I) sites, Xu et al. described the Cu-MOF (Table 5) as a catalyst from a three-anion-dependent Cu(I) coordination network (Figure 11). The catalyst's structure, recycling potential, and catalytic activity may be studied in relation to anions, allowing for fine-tuning of the catalyst's porosity and potential active metal sites [104].

Table 5. Copper-based MOFs for the synthesis of 1,2,3-triazole via CuAAC reaction.

Entry	MOF	Catalytic Amount (mol %)	Reaction Conditions	Solvent	Yield of Triazole	Recovery of Catalyst %	Catalytic Runs	References
1.	Cu-MOF	5 mol %	7 h, rt	CH_2Cl_2	94	87	5	[102]
2.	CuBTC–PyDC	5 mol %	3 h, 70 °C	Ethanol	-	76	4	[103]
3.	$\{[Cu_6(bpz)_6(CH_3CN)_3(CN)_3Br]\cdot 2OH\cdot 14CH_3CN\}_n$	10 mol %	2 h, 60 °C	DMF and DMSO solution	99	70	6	[104]
4.	Cu-MOF	5 mol %	12 h, rt	EtOH/ H_2O (2:1)	95	88	5	[105]
5.	CuI@UiO-67-IM	2 mol %	80 °C, 2 h	Water, under air atmosphere	90		5	[106]
6.	MOF-Cu (BTC)-[Pd]	2 mol %	2 h, 50 °C	DMF	100	85	2	[107]
7.	$Cu_2O@\{[Zn(Himdc)(bipy)_{0.5}]\cdot DMF\}$ MOF	0.5 mol %	7 h, 50 °C	t-BuOH–H_2O (2:1), Et_3N	98	-	3	[108]
8.	$Cu(INA)_2$-MOF	1 mol %	1.5 h, 80 °C	Solvent free	98	90	5	[86]
9.	$[Cu(I)_6I_6(Cu(II)\text{-}TPPP)].2DMF$	1 mol %	12 h, 50 °C	Methanol and water (4:1)	100	90	5	[109]
10.	Fe_3O_4@HKUST-1	1.8 mol %	2 h, reflux	H_2O	92	87	5	[76]
11.	$Cu@Cu_2O$	2.3 mol %	5 h, 50 °C	Water, t-BuOH (2:1)	100	-	-	[110]
12.	Cu@MOF-5	2 mol %	30 min, 79–80 °C	Ethanol	98	-	-	[111]
13.	$[Cu(CPA)(BDC)]_n$	10 mol %	7 h, 90 °C	H_2O-MeOH (1:4)	93	70	4	[60]

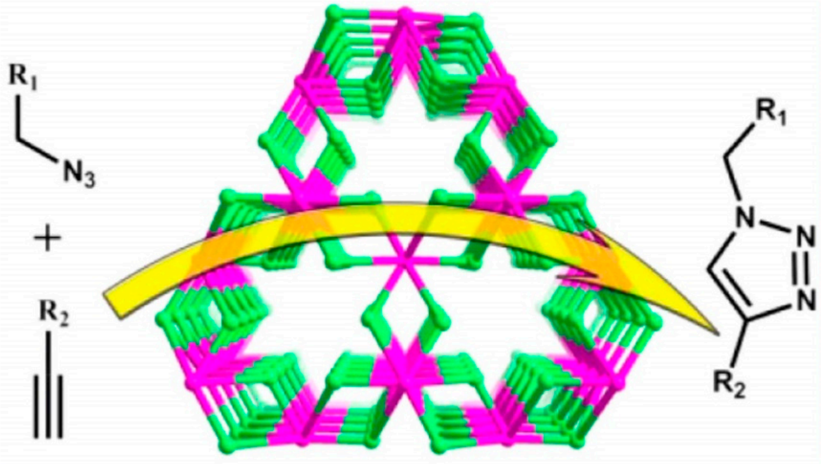


Figure 11. Schematic representation of the simplified 3D network of Cu-MOF. Reproduced from [104] with permission from the American Chemical Society, copyright year: 2015.

Murugan et al. reported the synthesis of a metal–organic framework (Cu-MOF) (Table 5) based on ultrasmall cubic copper nanoclusters with relative ease to catalyze the CuAAC reaction in an efficient and chemoselective manner. Selective stepwise conversion of the terminal azide afforded the highest yields in the 70–88% range for the unsymmetric bistriazoles arising from the click reaction of bifunctional azides and alkynes in the presence of Cu-MOFs (Figure 12). The bifunctional terminal contacts through thiol and sulfonate groups supplied the site-isolation-based active sites for selective catalysis, which explains how Cu-MOFs may perform selective mono-click reactions. Because Cu-MOFs may be recovered easily and reused up to five times without substantial loss of activity, they have great potential for selective organic conversions in medicinal and industrial formulations [105].

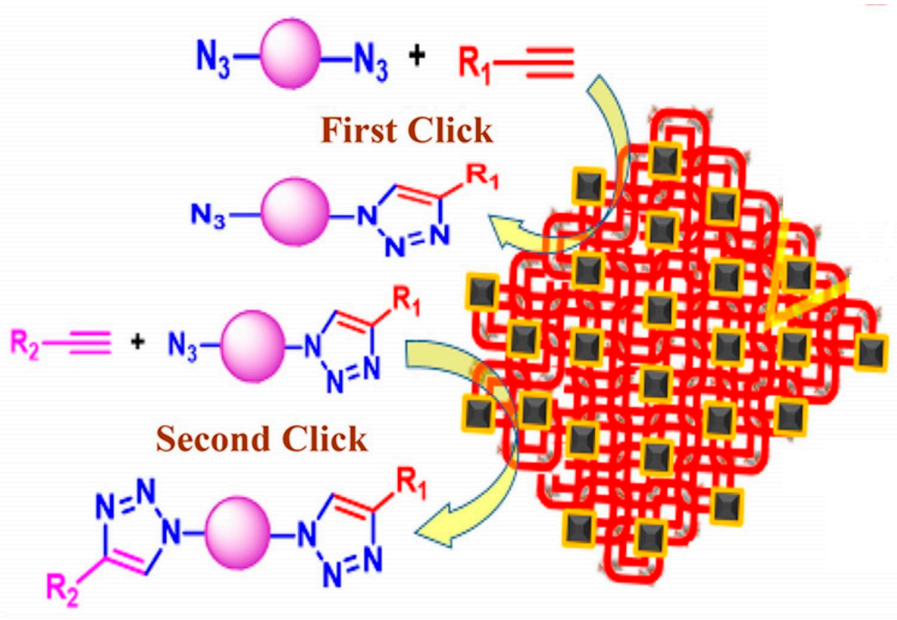


Figure 12. Synthesis of a metal–organic framework (Cu-MOF) to catalyze the CuAAC reaction in an efficient and chemoselective manner. Reproduced from [105] with permission from the American Chemical Society Copyright (2020).

In order to accomplish the tandem click reactions with excellent yield under optimal circumstances, Arnanz et al. created a bifunctional metal–organic framework catalyst incorporating palladium and copper(II) benzene-1,3,5-tricarboxylate MOF-Cu(BTC)-[Pd] (Table 5). The development of thermally stable pyridine species grafted on the surface is attributed to the CuBTC's inherent chelating capability, which is due to its electron-rich functional groups. A pyridine-Pd-grafted bifunctional catalyst with high activity for one-pot click reactions was prepared [107]. In a recent study, Jayaramulu and colleagues revealed a straightforward approach for stabilizing Cu_2O nanoparticles of size 2–4 nm on the polar pore surface of a 2D layered metal–organic framework $[Zn(Himdc)(bipy)_{0.5}]DMF$ (Table 5). The 1,3,-dipolar cycloaddition reaction of terminal alkynes and aliphatic/aromatic azides to produce 1,2,3-triazoles has been catalyzed by a Cu_2O@MOF composite (Figure 13), which will be recycled after use [108].

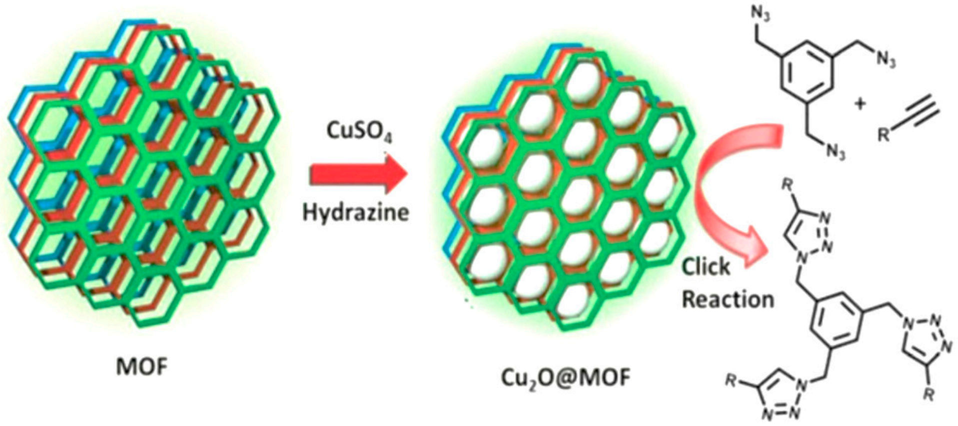


Figure 13. A schematic showing the stabilization of Cu_2O nanoparticles in 2D layers and the catalytic azide–alkyne cycloaddition reaction. Reproduced from [108] with permission from RSC, copyright: 2015.

The catalytic activity of $Cu(INA)_2$-MOF in CuAAC (copper-catalyzed azide-alkyne cycloaddition) was reported by Wiling and colleagues. The simple procedures enabled 1,2,3-triazoles to be prepared in a solvent-free environment. Even after five catalytic cycles, the $Cu(INA)_2$-MOF crystal structure remained constant if the reaction could be carried out on a gramme scale at the optimized conditions to better understand the synthetic applicability of the catalyst [86]. On the basis of a novel premodified ligand (n-pentadecyl-attached imidazolium (IM) decorated dicarboxylic acid) (Table 5) and ZrCl4, Hu et al. reported the formation of a CuI-loaded and n-pentadecyl-attached, imidazolium-salt decorated, UiO-67-type metal–organic framework (CuI@UiO-67-IM) (Figure 14) [106].

Jiang et al. described the azide–alkyne cycloaddition reactions carried out with the help of Cu(I,II)–porphyrin networks as heterogenous catalysts that were produced and effectively implemented. It is anticipated that the efficiency of the mixed valent MOFs as catalysts would increase when they are implied directly. To our astonishment, however, analogous azide–alkyne cycloaddition studies employing porphyrin-based MOFs were investigated and were found to be the effective methodology for the synthesis of various triazole derivatives with high yield (Table 5) [109].

Arefi et al. reported the development of a core–shell magnetic MOF catalyst by the combination of Fe_3O_4 MNPs (magnetic nanoparticles) covered with metal–organic frameworks (MOFs) composed of copper nodes and 1,3,5-benzenetricarboxylic acid linkers (Table 5, Figure 15). Good-to-exceptional yields may be achieved when using water as the green solvent together with the Cu moieties in MOF and shell structures to catalyze the production of 1,2,3-triazole derivatives. In addition, the superparamagnetic characteristics of this catalyst indicated a high degree of reusability [76].

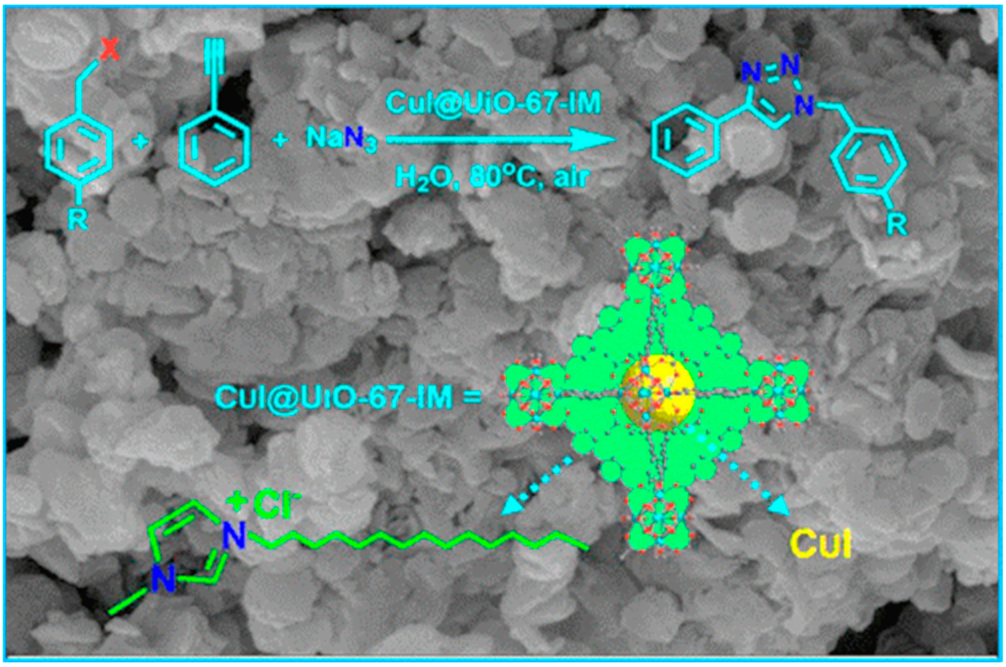


Figure 14. Copper-based MOF (CuI@UiO-67-IM) as a catalyst for alkyne azide cycloaddition reaction. Reproduced from [106] with permission from the American Chemical Society, copyright year: 2017.

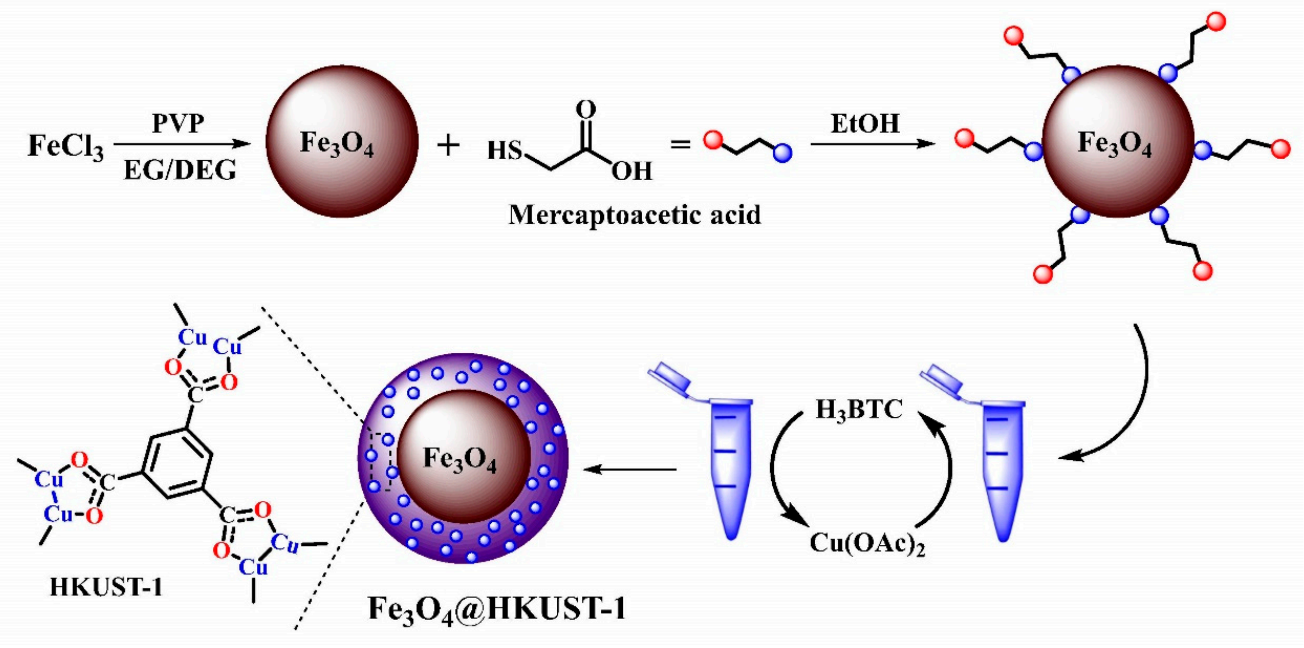


Figure 15. Synthesis of the catalyst Fe_3O_4@HKUST-1. [76].

A mesoporous 2D Cu-MOF (Figure 16) comprising a 2D sheet with a square grid structure (Table 2) was created by Naskar et al. and supported by structural investigations. This porous grid effectively enables organic transformations including click reactions in the aqueous methanolic media by acting as a heterogeneous green catalytic agent with superficial recovery and heat resistance [60].

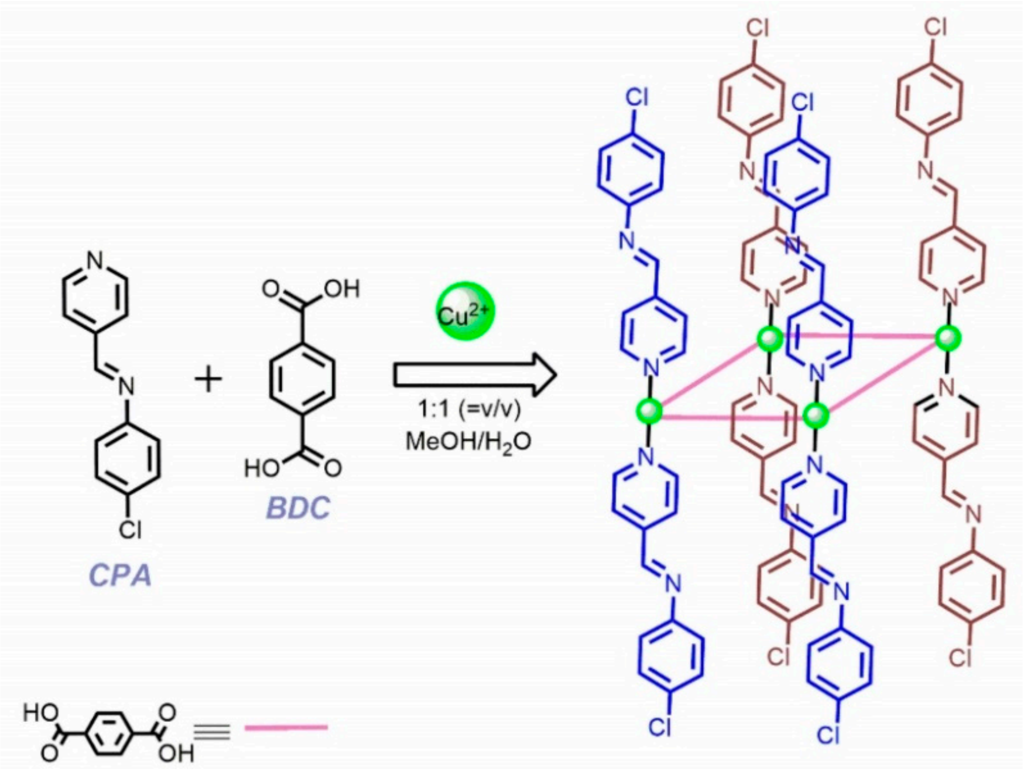


Figure 16. Schematic representation of synthesis of Cu-MOF [60].

The Cu(II) coordination polymer synthesized by Bikas and colleagues had an azido bridge and a 1,3-oxazolidine-based ligand. The molecule was then used as a catalyst in a one-pot, three-component cycloaddition process that combined epoxide, azide, and an alkyne to generate -hydroxy-1,2,3-triazoles by employing water as the solvent in their catalytic processes because of its non-toxic nature, inexpensive cost, and negligible effect on the environment. The synthesized 1D azido-bridged Cu(II) coordination polymer (Table 6) was found to be an effective catalyst for the synthesis of hydroxy-1,2,3-triazoles [112]. Likewise, another 3D Cu-based MOF (Figure 17) was reported for the smooth synthesis of 1,4-disubstituted 1,2,3-triazole [113].

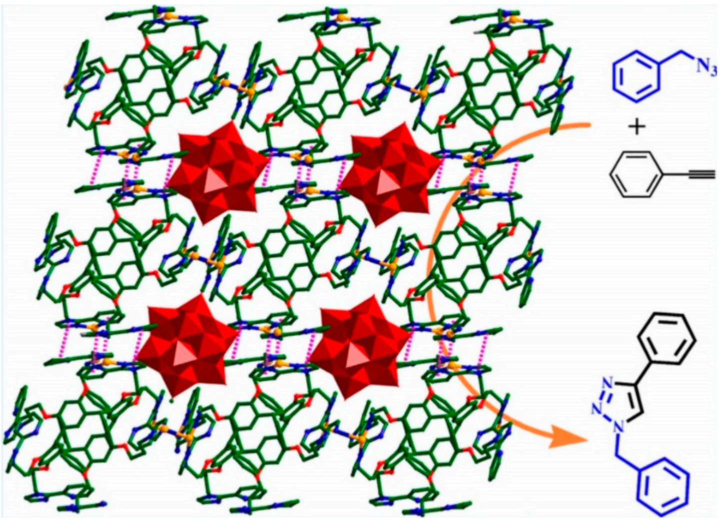


Figure 17. Three-dimensional copper-based MOF for the synthesis of 1,2,3 triazole. Reproduced from [112] with permission from the American Chemical Society, copyright year: 2018.

Table 6. Copper-based MOFs for the synthesis of 1,2,3-triazole via the CuAAC reaction.

Entry	MOF	Catalytic Amount (mol %)	Reaction Conditions	Solvent	Yield of Triazole	Recovery of Catalyst %	Catalytic Runs	References
1.	$[Cu^{I}_4(SiW_{12}O_{40})(L)]\cdot 6H_2O\cdot 2DMF$	30 mg	12 h, 80 °C	Methanol	99	99	5	[114]
2.	$[Cu_4Cl_4L]\cdot CH_3OH\cdot 1.5H_2O$	10 mg	8 h, 60 °C	Water	99	-	5	[113]
3.	Cu(BTC)-MOF	10 mg	16 h, RT	CH_3OH	91	87	3	[115]
4.	$Cu_2(BDC)_2(DABCO)$	20 mg	45 min, 60 °C	Ethanol	98	92	5	[87]
5.	Cu@N-C(600)	5 mg	12 h, 50 °C	t-BuOH/H_2O (3/1)	98	93	4	[116]
6.	$[Cu(H_3L)(\mu_{1,3}\text{-}N_3)(N_3)]_n$	4 mg	3.5 h, 40 °C	Water	93	-	-	[112]
7.	IRMOF-3-PI-Cu	2 mg	20 h, 90°C	DMSO	90	80	5	[117]
8.	$[Cu_4Cl_4L]\cdot CH_3OH\cdot 1.5H_2O$	10 mg	8 h, 60 °C	Water	99	97	5	[118]
9.	Cu-BTC	10 mg	1 h, 60 °C	1,4-Dioxane, TEA	-	-	-	[119]
10.	rCu-MOF	0.2 mg	4 h, 60 °C	H_2O, N_2 for 20 min	-	-	3	[120]

In a Huisgen 1,3-dipolar cycloaddition method, the porous MOF [$Cu_2(BDC)_2(DABCO)$] was employed as a catalyst to create a wide range of 1,2,3-triazole derivatives. This was done so that the technology could be used to its fullest potential, allowing the reaction to be completed successfully. In this work, $Cu_2(BDC)_2(DABCO)$ was synthesized using 1,4-benzenedicarboxylic acid, diacetyl bis(2-aminoethyl) ketone, and copper(II) acetate as reactants. This method was executed at room temperature a in solvent-free environment. The catalyst has a large surface area (1012 m^2g^{-1}) and a small average pore size (3.9 nm), making it very effective for the synthesis of 1,2,3-triazole analogues with good regioselectivity (Table 6). By using the microdilution approach, the determination of the synthesized triazoles as useful skeletons was performed in order to demonstrate adequate antibacterial and antifungal properties against a variety of pathogenic organisms, including *S. aureus*, *E. coli*, and *C. albicans* [87].

Wang et al. reported a novel functionalized thiacalix [4]arenes (L), and halogen anions were used in a solvothermal assembly of CuI-based MOFs [Cu_4Cl_4L]$CH_3OH1.5H_2O$ (1-Cl). In addition, the synthesized MOF has the potential to be a reusable heterogeneous catalyst that can catalyze click reactions in water at very high efficiency (Table 6, Figure 18). The enhanced catalytic activity may be attributed in large part to the MOF structures, particularly the exposed active CuI sites and 1D channels [118].

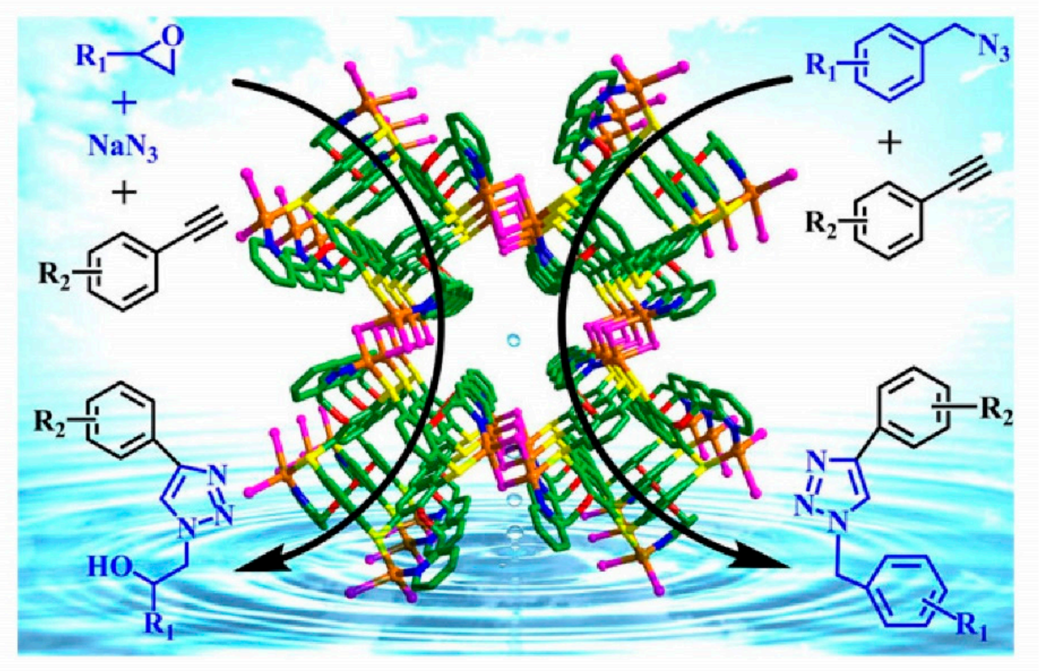


Figure 18. The metal–organic framework structures with exposed active CuI sites and a depiction of the catalytic activity for the formation of 1,2,3-triazole. Reproduced from [118] with permission from Wiley, copyright year: 2019.

Yamane et al. reported the synthesis of metal nanoparticles that are supported on MOF-derived carboniferous substances using the HPHT synthesis procedure (Table 6). Cu-BTC was modified for conversion into Cu@C (copper carbon composite) at low temperatures, and the composites were pyrolysed HPHT methods. After HPHT treatment, the composite samples were analysed for their catalytic activity in cycloaddition reactions. Phenyacetylene and benzyl azide were reacted in the presence of 1,4-dioxane as a solvent and triethylamine as a base using Cu@C as the catalyst, obtaining the desired stereoselective product with good yield (Figure 19) [119].

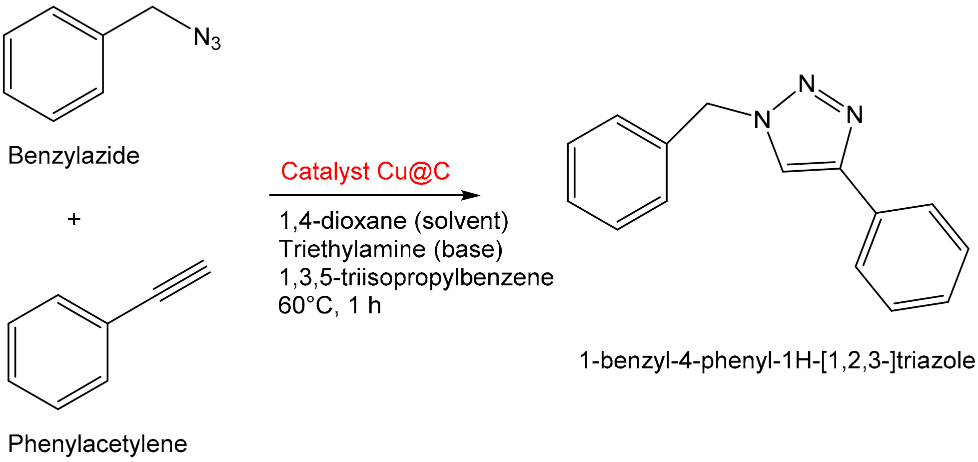


Figure 19. Cycloaddition reaction depicting the catalytic performance of Cu@C [119].

Fu et al. created a copper MOF in reduced form (rCu-MOF). Many 'click' reactions were carried out with high yield using this reduced Cu-MOF (Figure 20). The rCu-MOF catalyst was shown to be more active than the traditional copper halide catalyst, with the added benefit of being easily recyclable (Table 6). rCu-MOF is appealing as a catalytic material for industrial applications due to these features as well as due to its simplicity of synthesis, absence of metallic contamination, and great mechanical constancy. This research paves the way for further exploration of rCu-MOFs in polymer chemistry [120].

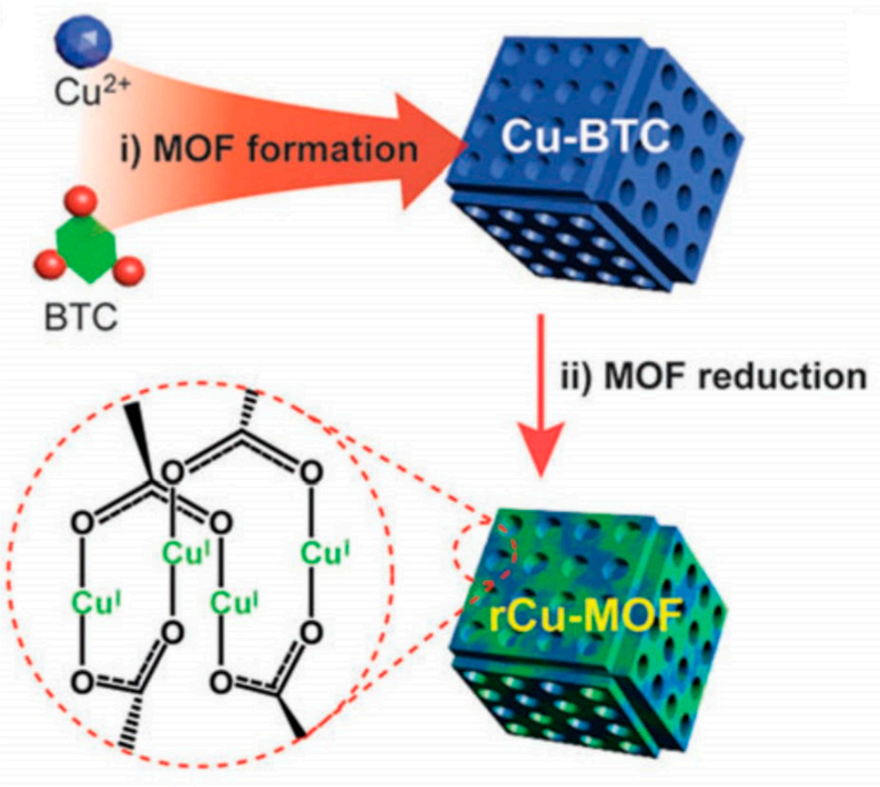


Figure 20. A simplified depiction of the steps required to make a reduced copper metal–organic framework (rCu-MOF). (i) Benzene 1,3,5-tricarboxylate (BTC) undergoes a coordination reaction with $Cu^{2+.}$ and (ii) a hydroquinone-induced Cu-BTC reduction at 150 °C. Reproduced from [120] with permission from RSC, copyright year: 2016.

The one-pot click reaction was reported by Luz et al. using $[Cu(2\text{-pymo})_2]$ MOF as a catalyst for the 1,3-dipolar cycloaddition reaction between benzyl azide and phenylacetylene at 70 °C in ethanol [30]. The 3-propargyl-4H-pyrano[2,3-d] pyrimidine compounds were synthesized through a click synthesis involving azide (tetra-O-acetyl—D-glucopyranosyl) and the metal–organic framework Cu@MOF-5 (Table 7). The resulting 1,2,3-triazole product was tested for its ability to inhibit the protein tyrosine phosphatase B (MtbPtpB) activity of Mycobacterium tuberculosis. The most active compound's kinetic experiments revealed competitive inhibition of the MtbPtpB enzyme. The strong inhibitory effect against MtbPtpB was believed to depend on the interaction of Arg63 amino acids with an anion-type para-hydroxyl group through a salt bridge of iminium cation, according to an extensive structure–activity relationship (SAR) in vitro and in silico investigations. The experimental evidence obtained by cross-docking showed that the chemical synthesized was more potent against the mycobacterium TB protein tyrosine phosphatase B. It was found by docking that the amino acids were inside the obligatory site and were likely hotspots for ligand binding (Figure 21) [121].

Table 7. Copper-based MOFs for the synthesis of 1,2,3-triazole via the CuAAC reaction.

Entry	MOF	Catalytic Amount (mol %)	Reaction Conditions	Solvent	Yield of Triazole %	Catalytic Runs	References
1.	Cu-Bis-NHC- MOF	10 wt %	-	THF/MeOH	-	-	[122]
2.	{[Cu_2(L)(H_2O)$_2$]·(5 DMF)(4 H_2O)}$_n$	5 wt %	4 h, 50 °C	CH_2Cl_2	96	-	[123]
3.	[Cu(2-pymo)$_2$]	-	4 h, 70 °C	Ethanol	-	6	[30]
4.	MOF-Cu-TPP	-	-	-	-	10	[124]
5.	MSNs@Cu- MOF	-	-	-	-	-	[125]
6.	Cu@MOF-5	-	4–5 h, 79−80 °C	abs. EtOH	94	-	[121]

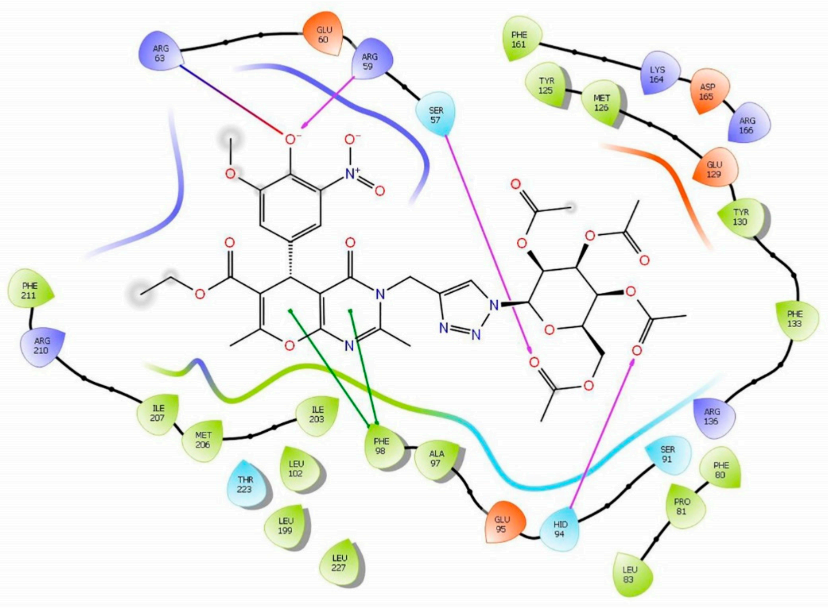


Figure 21. Amino acids involved in the intermolecular interactions of 1H-1,2,3-triazole. Reproduced from [121] with permission from Elsevier, copyright year: 2019.

Click chemistry has developed into a highly effective toolbox for manipulating biological processes in their native settings. The copper(I)-catalyzed azide–alkyne cycloaddition (CuAAC) reaction is a common click process utilized in drug production and design. For in vivo tumor treatment, Wang et al. built a heterogeneous copper catalyst using metal–organic frameworks (Table 7) that preferentially accumulated in the mitochondria of live cells and showed significant catalytic activity, as illustrated in Figure 22. To execute the targeted drug production in mitochondria, the catalyst may be employed to activate the profluorophobic unit. There is no better way to reduce cytotoxic medications' deleterious side effects while increasing their effectiveness than the in situ synthesis of active pharmaceuticals from inert prodrugs in subcellular organelles [123].

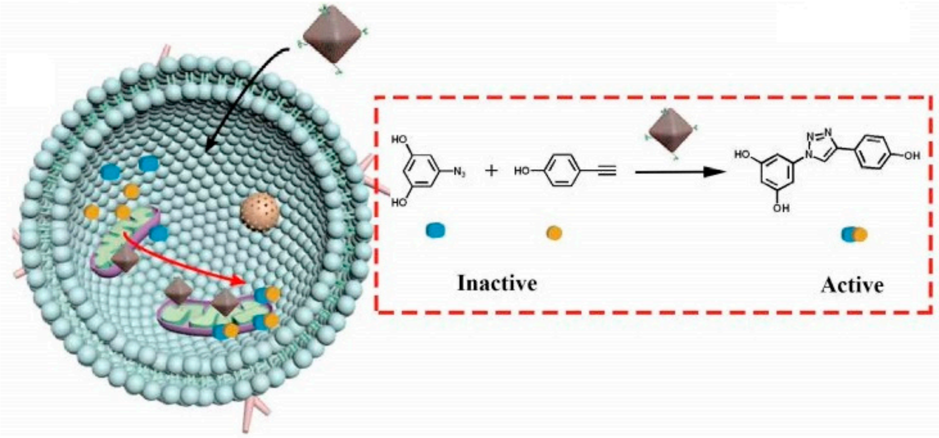


Figure 22. Intracellular bioorthogonal reaction for in situ drug synthesis under mitochondria catalyzed by MOF-Cu-TPP. Reproduced from [123] with permission from Wiley, copyright year: 2019.

The reported copper metal–organic frameworks for the synthesis of 1,2,3-triazole appended probes via CuAAC are often recyclable and have a high reusability of up to four or five times. Additionally, the catalysts are also recoverable at an astounding pace [111,113–116]. Depending on the reactants and the reaction conditions, the quantity of MOF catalysts may be anywhere ranging from 0.5 mol % to 10 mol % or 0.2 mg to 30 mg. The desired products were obtained with excellent yields of more than 90%, and in some cases, an exceptional yield of 100% was reported, as highlighted in Table 5 (entries 6, 9, and 11) [105,107,109]. Cu-MOFs have relatively outstanding chemical stability, particularly in organic solvents and aqueous solutions, due to the involvement of Cu(I) sites, making the MOF a heterogeneous catalyst for the azide–alkyne cycloaddition (AAC) process [7,8].

9. Challenges in the Synthesis and Applications of Cu-Based MOFs

The challenges in the synthesis of Cu-based MOFs emerge from the need to comprehend and manage the inherent complexity of the many different topologies and compositions of MOFs. However, Cu has dynamic stability and requires more basic compounds, which often leads to the carboxylate products and waste disposal issues and separation challenges [120]. Moreover, due to the microporous structure of Cu-MOFs and MOF-based materials, mass transfer constraints occur in large molecules, which limits researchers from advancing the field of Cu-MOF synthesis. Hierarchical porosity can be introduced to resolve the problem of mass transfer. The key challenges in the application of Cu-MOFs are that they are not very mechanically stable due to their increased pore size, which sometimes hinders their use as catalysts in practical catalytic reactions [102]. This makes it necessary to focus on increasing their mechanical and chemical stability to preserve catalytic efficacy and selectivity [111]. After reviewing the relevant literature, we conclude that MOFs and MOF-derived materials are promising starting points for investigating catalytic applications, even though they provide both challenges and opportunities.

10. Conclusions and Future Aspects

There has been exponential growth in recent years in the synthesis and application of novel MOFs with exciting new architectures and functionalities. Thus, it is reasonable to anticipate that MOFs will continue to provide increasingly more efficient responses to issues in contemporary organic chemistry and modern organometallic catalysis, since the catalytic processes they mediate have grown more pervasive over the previous years. Copper-tailored metal–organic frameworks have gained a large amount of attention in the diversity of reactions, especially in CuAAC, since the MOF catalysts can be easily recovered and used multiple times, owing to their structure, durability, and porosity. This review focused on the copper-based MOFs that have been widely employed for the synthesis of 1,2,3-triazoles across a wide range of reaction conditions, with benefits including improved yield and reduced reaction time, as well as the effective recovery of the catalyst. MOF catalysts enhance the synthesis of such compounds that would otherwise be difficult to produce without the aid of a catalyst, or for which reaction improvements would be beneficial. Since MOFs are capable of catalysis, future research and industrial development stand to benefit from the synthesis of ever more creative and recyclable MOFs in the forthcoming years.

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Abbreviations

MOF	Metal–organic framework
Im	Imidazolate
BTC	Benzene tricarboxylate
BDC	Benzene dicarboxylate
PyDC	Pyridine-3,5-dicarboxylate
TPP	Triphenylphosphonium
CPA	4-Chloro-phenyl)-pyridin-4-ylmethylene-amine
Himdc	4,5-Imidazoledicarboxylate
Bipy	4,4′-Bipyridine
DABCO	1,4-Diazabicyclo [2.2.2] octane
2-pymo	2-Hydroxypyrimidinolate
SBU	Supplementary building units
OCMC	O-Carboxymethyl chitosan
IM	Imidazolium
HPHT	High pressure and high temperature
MtbPtpB	Mycobacterium tuberculosis protein tyrosine phosphatase B

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