Metal–Organic Frameworks

Highly Stable Copper(I)–Thiacalix[4]arene-Based Frameworks for Highly Efficient Catalysis of Click Reactions in Water

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Abstract: Environmentally friendly metal–organic frameworks (MOFs) have gained considerable attention for their potential use as heterogeneous catalysts. Herein, two Cu¹based MOFs, namely, [Cu₄Cl₄L]·CH₃OH·1.5H₂O (**1-Cl**) and [Cu₄Br₄L]·DMF·0.5H₂O (**1-Br**), were assembled with new functionalized thiacalix[4]arenes (L) and halogen anions X⁻ (X = Cl and Br) under solvothermal conditions. Remarkably, catalysts **1-Cl** and **1-Br** exhibit great stability in aqueous solutions over a wide pH range. Significantly, MOFs **1-Cl** and **1**-

Introduction

Currently, the catalytic syntheses of chemicals and pharmaceuticals through green and sustainable technologies have received considerable attention.^[1,2] To date, continuous efforts have been made to develop sustainable and effective strategies for organic catalytic reactions.^[3–6] In this regard, the use of organic solvents for chemical conversions is one of the most important issues in green chemistry, owing to their harmful influence on the environment and human health.^[7–9] Therefore, the use of less toxic solvents and the development of recycled heterogeneous catalysts are key strategies for green chemistry.^[10,11] The replacement of harmful solvents by environmentally friendly water, ionic liquids, or supercritical carbon dioxide has become one of the most desirable routes for sustainable chemistry.^[12] Water is the most green solvent, in view of environmental protection.^[13]

Click chemistry, as an important catalytic reaction type, has been extensively employed in different domains of organic synthesis, medicinal chemistry, and molecular biology.^[14–16] For example, Cu¹-catalyzed azide–alkyne cycloaddition (CuAAC) has received significant attention in many research fields, such as

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https://doi.org/10.1002/chem.201903966. It contains crystallographic data in CIF format, ¹H NMR spectra, GC spectra, tables, thermogravimetric curves, and powder XRD patterns. **Br**, as recycled heterogeneous catalysts, are capable of highly efficient catalysis for click reactions in water. The MOF structures, especially the exposed active Cu^I sites and 1D channels, play a key role in the improved catalytic activities. In particular, their catalytic activities in water are greatly superior to those in organic solvents or even in mixed solvents. This work proposes an attractive route for the design and self-assembly of environmentally friendly MOFs with high catalytic activity and reusability in water.

functional polymers, surface modification, and supramolecular chemistry.^[17–19] To date, various homogeneous Cu¹ catalysts have been studied for CuAAC reactions.^[20,21] Homogeneous copper(I) catalysts are effective, but they are difficult to separate from the reaction system, which restricts their wide use.^[22] To overcome this limitation, recycled heterogeneous catalysts have been developed accordingly.^[23–26]

Metal–organic frameworks (MOFs), as one type of promising heterogeneous catalyst, have been widely used in various catalytic reactions.^[27-31] In this regard, heterogeneous Cu^I-based MOF catalysts for click reactions exhibit some advantages, such as improved stability, easy separation, and high reusability.^[32-34] Nevertheless, the reported works directly using Cu^I MOFs as heterogeneous catalysts for click' reactions are usually conducted in organic or mixed solvents (such as ethanol and water).^[32-37] By contrast, water, as a cheap, nontoxic, safe, and green solvent, has received far less attention in CuAAC reactions with Cu^I MOFs as heterogeneous catalysts.^[38,39]

Generally, organic ligands play an important role in the rational construction of MOF catalysts featuring tunable structures.^[40,41] Calix[4]arenes, as one type of excellent candidate ligand, have attracted considerable attention from researchers due to the ease of modifying their upper and lower edges.^[42–48] Particularly, calix[4]arenes substituted by coordination hybrid atoms, such as N and S, can improve the stability of the resulting Cu^I MOFs as recycled catalysts.^[49–53]

Based on above consideration, we prepared a flexible thiacalix[4]arene with potential S and N coordination sites (L; Scheme 1).^[54] Through the self-assembly of L and CuCl₂·2H₂O (X=Cl and Br), two isostructural Cu¹ MOFs, namely, [Cu₄Cl₄L]·CH₃OH·1.5H₂O (**1-Cl**) and [Cu₄Br₄L]·DMF·0.5H₂O (**1-Br**), are afforded. In **1-Cl** and **1-Br**, the S and N atoms of the thiacalix[4]arenes and X⁻ anions bridge the Cu¹ atoms to give a layered structure. Remarkably, the Cu¹ MOFs are exceedingly

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Scheme 1. Synthetic procedure for L.

stable in aqueous solutions over a wide range of pH values. Significantly, MOFs 1-Cl and 1-Br, as recycled heterogeneous catalysts, exhibit excellent catalytic capability for click reactions in water; thus representing a new series of green and efficient catalysts.

Results and Discussion

Crystal structures of 1-Cl and 1-Br

Crystallographic analysis revealed that 1-Cl and 1-Br were isomorphic (Figure S1 in the Supporting Information) and crystallized in the same tetragonal space group, 14(1)/a. Accordingly, only the crystal structure of 1-Cl is discussed herein. The asymmetric unit of 1-Cl contains one Cl⁻ anion, a guarter of L, and one Cu¹ cation. Each Cu¹ cation shows a tetrahedral coordination geometry, coordinated by one nitrogen atom from one L ligand, a sulfur atom from one L ligand, and two Cl⁻ anions (Figure 1 a). Each pyridyl nitrogen atom is involved in coordinating with one Cu^I cation with a Cu-N bond length of 2.029 Å. Two Cl⁻ anions, as bridging nodes, link two adjacent Cu^{1} cations into a $[Cu_{2}Cl_{2}]$ unit (Figure 1 a). Meanwhile, adjacent [Cu₂Cl₂] units are bridged by L ligands through nitrogen and sulfur atoms to yield a layered structure with a Cu-S bond length of 2.3354 Å (Figure 1 b). Furthermore, neighboring layers are held together through a 3.566 Å C-H-Cl hydrogen bond (Table S2 in the Supporting Information) to afford a 3D supramolecular architecture with channel dimensions of about 6.6×10 Å² along the crystallographic *c* axis, in which the methanol and water molecules may be filled (Figure 1 c and d). The total potential solvent-accessible void volume was calculated by using PLATON to be about 16.5% (911.9 Å³/5532.1 Å³) after the removal of solvent molecules.[55]'

Catalytic studies

Samples of 1-Cl and 1-Br were immersed in organic solvents (methanol, ethanol, acetone, DMF, and dimethylacetamide) or aqueous solutions of different pH ranges for 24 h. As shown in Figures 2 and 3, the powder X-ray diffraction (PXRD) patterns indicate that the framework structures of 1-Cl and 1-Br (Fig-



Figure 1. a) Coordination environment of Cu¹ in 1-Cl (symmetry code: $^{#1}$ 1– x_r , -y, 1-z).^[68] b) Layered structure of **1-Cl**. c) The 3D hydrogen-bonding supramolecular architecture of 1-Cl. d) Packing structure of 1-Cl.

ures S2 and S3 in the Supporting Information) are well retained; thus demonstrating their high structural stability.

Based on the stability of 1-Cl and 1-Br, their catalytic properties for the azide-alkyne cycloaddition (AAC) reactions were studied. To optimize the reaction conditions, catalytic experiments were conducted with phenylacetylene and benzyl azide

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Figure 2. PXRD patterns of 1-Cl after immersion in aqueous solutions of different pH values.



Figure 3. PXRD patterns of 1-Cl after immersion in different organic solvents.

as model substrates and 1-Cl as a catalyst at varying temperatures and in different solvents. Initially, the yields of the catalytic products varied from 40 to 99% (Table 1, entries 5-7 and 13, and Figure S4e-h in the Supporting Information), with reaction temperatures changing from 30 to 60°C, water as the solvent, and 1-Cl as a catalyst (10 mg, 0.008 mmol) after 8 h. After the amounts of 1-Cl were increased from 5 to 15 mg, the corresponding product yields increased from 90 to 99% at 60°C in water (Table 1, entries 2–4, and Figure S4b–d in the Supporting Information). Notably, in the absence of catalyst 1-Cl, the yield was only up to 14% after 8 h (Table 1, entry 1, and Figure S4a) under the same conditions. If CuCl was used as a catalyst, the yield reached 46% (Table 1, entry 14, and Figure S4r in the Supporting Information). To explore the solvent effect, catalysis was carried out in various solvents, including acetonitrile, dichloromethane, methanol, acetone, and ethanol. Compared with that in acetonitrile, acetone, and dichloromethane, the

Table 1. AAC reactions of benzyl azide and phenylacetylene. ^[a]					
\bigcirc	=+	N ₃ -	catalyst 1 water	→ ⟨_>	
Entry	Cat.	Amount [mg]	T [°C]	Solvent	Yield [%] ^[b]
1	1-Cl	0	60	H₂O	14
2	1-Cl	5	60	H₂O	90
3	1-Cl	10	60	H₂O	99
4	1-Cl	15	60	H ₂ O	99
5	1-Cl	10	30	H₂O	44
6	1-Cl	10	40	H ₂ O	49
7	1-Cl	10	50	H₂O	90
8	1-Cl	10	60	MeCN	47
9	1-Cl	10	60	CH_2CI_2	45
10	1-Cl	10	60	EtOH	92
11	1-Cl	10	60	MeOH	99
12	1-Cl	10	60	acetone	46
13	1-Cl	10	60	H ₂ O	99
14	CuCl	3.2	60	H₂O	46
15	1-Br	12	60	H ₂ O	90
[a] Reaction conditions: amyl acetate (120 mg, 0.92 mmol), phenylacetyl- ene (204 mg, 2 mmol), and benzyl azide (133 mg, 1 mmol). [b] The yield					

catalytic yield was up to 99% in water under the same conditions (Table 1, entries 8–13, and Figure S4c and i–m in the Supporting Information). Therefore, water was chosen as a catalytic reaction medium for the AAC reactions. In addition, if the amount of catalysts **1-Cl** and **1-Br** was up to 0.008 mmol, the conversions reached 99 and 90%, respectively (Table 1, entries 13 and 15, and Figure S4c and s in the Supporting Information). Eventually, the catalytic AAC reaction was performed by using **1-Cl** (10 mg) in water at 60 °C.

was calculated with amyl acetate as an internal standard.

Under the optimized conditions, we conducted a kinetic study with phenylacetylene and benzyl azide as substrates. The product yield reached 97% after 6 h, and then rose slowly from 97 to 99% in the following 2 h (Figure 4 and Figure S4n– q in the Supporting Information). To further study the applica-



Figure 4. Catalytic kinetic behavior for the reaction between benzyl azide and phenylacetylene with catalyst **1-Cl** (black) and that in the filtrate after removal of **1-Cl** 2 h after catalysis (red).

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bility of the catalyst, a variety of alkynes and azides with substituted terminal groups were applied as substrates for the AAC reactions. The catalytic AAC reactions gave very high conversions for all selected substrates (Table 2); thus indicating

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that catalyst **1-CI** is effective for substrates with electron- withdrawing or -donating groups on the phenyl rings (Figure S5a-j in the Supporting Information). For example, if phenylacetylene reacts with benzyl azide derivatives, the yield can reach 99%. If the catalytic reactions of benzyl azide with various phenylacetylene derivatives were performed, slightly lower conversions of about 92 and 89% (Table 2, entries 7 and 8) were achieved for CI- and Br-substituted phenylacetylenes, respectively; this may arise due to the steric hindrance effect of the substituted groups.^[36,56]

The heterogeneous nature of the reaction for phenylacetylene with benzyl azide was studied in the filtrate (Figure S4t-v in the Supporting Information). After 2 h of the AAC reaction, catalyst **1-CI** was filtered. Notably, no clear reaction occurred in the filtrate under the same conditions (Figure 4). Further, inductively coupled plasma analysis indicates that no catalyst leaching is observed during the catalytic reaction; thus certifying the heterogeneous nature of the AAC reaction. To probe the reusability of **1-CI**, the recycled catalytic reactions were examined by using alkynes and azides as substrates. In each cycle, catalyst **1-CI** was recovered by filtration, washed with methanol, and used in the next cycle of the reaction under the same conditions. The yield of each run was almost the same (Figure 5 and Figure S6 in the Supporting Information). Notably, the PXRD patterns demonstrate that the structural integrity of **1-CI** remained after each cycle (Figure S7 in the Supporting Information). The formation of the desired 1,2,3-triazole compounds was confirmed by means of ¹H NMR spectroscopy (Figure S8–S17 in the Supporting Information).



Figure 5. Conversions obtained in recycling experiments for the AAC reaction with 1-Cl as a catalyst.

Notably, catalyst 1-Cl features efficient catalytic performances for the AAC reactions under relatively mild reaction conditions. For example, the product yield is up to 99% for the AAC reaction of benzyl azide and phenylacetylene with catalyst 1-Cl at 60 °C for 8 h. Nevertheless, for related catalysts $[Cu_4(SiW_{12}O_{40})(L1)] \cdot 6H_2O \cdot 2DMF$ (L1 = resorcin[4] arene-based ligand)^[36] and [Cu₄(SiW₁₂O₄₀)(L2)₂(DMF)₂]·2EtOH·DMF (L2=thiacalix[4]arene-based ligand),^[35b] the same AAC reaction was accomplished (99%) if the reaction temperature was elevated to 80 °C and the reaction time was prolonged to 12 h. In addition, catalyst 1-CI features a remarkable recyclability for the AAC reaction. For instance, a product yield of 97% was still retained in the fifth run, whereas the corresponding yield for the catalyst { $[Cu_6(bpz)_6(CH_3CN)_3(CN)_3Br]$ ·2OH·14CH₃CN}_n (bpz=3,3',5,5'tetramethyl-4,4'-bipyrazole) was only up to 68%.^[35a] The good catalytic recyclability of 1-CI may account for its framework stability.

Moreover, a possible catalytic reaction mechanism was assumed (Scheme 2). Cu^I-based catalyst **1-Cl** possesses a high activity for the AAC reaction because of its active Cu^I sites.^[57] The reaction process mainly involves the generation of Cu^I-acetylide product (**B**) through the interaction of the alkyne with Cu^I.^[58] Then the product (**B**; Scheme 2) attacks the azides to produce intermediate **C**.^[59] Afterward, the N3 atom in **C** interacts with the C4 atom of the alkyne, forming the Cu^I-metallacycle (**D**).^[53,60a] In the metallacycle, ring contraction results in intermediate species **E**.^[56] Finally, catalyst **1-Cl** is recovered with the formation of the target product 1,4-disubstituted 1,2,3-triazole.

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Scheme 2. Proposed mechanism for the AAC reaction with 1-Cl as a catalyst.

Based on the catalytic activity of **1-Cl** and **1-Br** for the AAC reactions, three-component epoxy ring-opening reactions of epoxy derivatives, sodium azide, and phenylacetylene were also studied. The catalytic experiments were conducted under the optimized conditions, with 2-(phenoxymethyl)oxirane, sodium azide, and phenylacetylene as substrates and **1-Cl** (10 mg) as a catalyst in water at 60 °C for 8 h (Table 3 and Figure S18a-m, r, and s in the Supporting Information). Notably, in the absence of **1-Cl**, only 13% yield was obtained under the same reaction conditions (Table 3, entry 1, and Figure S18a in the Supporting Information). If CuCl was used as a catalyst, the yield was only up to 34% (Table 3, entry 14, and Figure S18r in the Supporting Information).

The kinetic reaction was explored at different time intervals under the optimized conditions, with 2-(phenoxymethyl)oxirane, sodium azide, and phenylacetylene as substrates. As shown in Figure 6, the yields increased rapidly from 65% at



Figure 6. Catalytic kinetic curve of 2-(phenoxymethyl)oxirane, sodium azide, and phenylacetylene with 1-Cl as a catalyst (black) and the filtrate upon removing 1-Cl after 2 h of catalysis (red).

the beginning, to 95% over the next 4 h, and finally up to 99% (Figure S18n-q in the Supporting Information).

To further study the wide application of catalyst **1-Cl**, a series of epoxy and phenylacetylene derivatives were utilized as substrates for the epoxy ring-opening reactions. As listed in Table 4, for epoxides with aliphatic or aromatic substituents, the corresponding cyclic carbonates revealed excellent yields (Figure S19a–k in the Supporting Information). Phenylacetylene substrates with electron-withdrawing or -donating groups gave high conversions. However, a slightly lower conversion of about 91% was achieved if OCH_3 -substituted phenylacetylene was used as a substrate; this may arise from the steric hindrance effect of the substituted groups.^[56,60b]

As shown in Figure 6, filtration experiments for 2-(phenoxymethyl)oxirane, sodium azide, and phenylacetylene demonstrate the heterogeneity of the catalytic reaction with **1-Cl** as

Table 3. The epoxy ring-opening reaction of 2-(phenoxymethyl)oxirane, sodium azide, and phenylacetylene under various reaction conditions. ^[a]					
	\bigcirc	-= + NaN ₃ +	$\bigtriangledown \xrightarrow{\text{catalyst 1}} \qquad \qquad$		
Entry	Cat.	Amount [mg]	<i>T</i> [°C]	Solvent	Yield [%] ^[b]
1	1-Cl	0	60	H ₂ O	13
2	1-Cl	5	60	H ₂ O	90
3	1-Cl	10	60	H ₂ O	99
4	1-Cl	15	60	H ₂ O	99
5	1-Cl	10	30	H ₂ O	32
6	1-Cl	10	40	H ₂ O	50
7	1-Cl	10	50	H ₂ O	90
8	1-Cl	10	60	MeCN	32
9	1-Cl	10	60	CH ₂ Cl ₂	21
10	1-Cl	10	60	EtOH	65
11	1-Cl	10	60	MeOH	90
12	1-Cl	10	60	acetone	24
13	1-Cl	10	60	H ₂ O	99
14	CuCl	3.2	60	H ₂ O	34
15	1-Br	12	60	H ₂ O	90
[a] Reaction conditions: epoxide (1.5 mmol), NaN ₃ (97.5 mg, 1.5 mmol), and phenylacetylene (1 mmol), water (4 mL), 60 °C, 8 h. [b] The yield was deter-					

[a] Reaction conditions: epoxide (1.5 mmol), NaN₃ (97.5 mg, 1.5 mmol), and phenylacetylene (1 mmol), water (4 mL), 60°C, 8 h. [b] The yield was determined by means of GC with ethylbenzene as an internal standard.

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Table 4. Catalytic reactions of epoxide derivatives, sodium azide, and phenylacetylenes with substituted groups catalyzed by 1-Cl. ^[a]					
Entry	Azide	Alkyne	Product	Yield [%] ^[b]	
1		=-{>		99	
2		≡-{_}		99	
3		≡-{_}		95	
4		≡-{_}		99	
5	\bigcirc	≡-{_}		97	
6				97	
7		$\equiv -\langle -F \rangle$		99	
8	$\bigcirc^{\circ \sim \bigtriangledown}$	≡- √_ -ci		99	
9		≡-{_}Br		96	
10		≡-{_}-СН ₃		99	
11		≡-{_}осн ₃		91	
[a] Reaction conditions: alkyne (1 mmol), 1-Cl (10 mg, 0.008 mmol), epoxide (1.5 mmol), and NaN ₃ (97.5 mg, 1.5 mmol), water (4 mL), 60 °C, 8 h. [b] Ethylbenzene was used as an internal standard to calculate the yield.					

catalyst (Figure S18t–v in the Supporting Information). To probe the reusability of catalyst **1-CI**, recycled catalyst experiments were examined with NaN₃, epoxypropyl phenyl ether, and phenylacetylene as substrates. In each cycle, catalyst **1-CI** was recovered by filtration, washed, dried under vacuum, and then used for the next run under the same conditions (Figure 7). It is noteworthy that the product yield in the fifth run was almost the same as that in the first run (Figure S20a–e in the Supporting Information). Notably, the PXRD patterns demonstrate the framework integrity of catalyst **1-CI** after each cycle of catalysis, as shown in Figure S21 in the Supporting Information. The expected product, β -hydroxy-1,2,3-triazole was also confirmed by means of ¹H NMR spectroscopy (Figures S22–S32 in the Supporting Information).

Remarkably, catalyst **1-Cl** exhibits high catalytic activity for epoxy ring-opening reactions relative to that of the known related MOF.^[61] For example, a product yield of 95% was achieved for catalyst **1-Cl** with 2-butyloxirane, sodium azide, and phenylacetylene as substrates at 60 °C for 8 h. For the catalyst [(Cu_4I_4)₂(L3)₄]·20 DMF·3 CH₃CN (L3 = (*R*,*R*)-*N*,*N*'-bis[3-*tert*-butyl-5-

(4-pyridyl)salicylidene]-1,2-diphenylethylenediame),^[61] the corresponding yield only reached 77% with identical substrates in water at 60 °C for 24 h. The result indicates that **1-Cl** is an efficient catalyst for the epoxy ring-opening reaction.



Figure 7. Recycling experiments for the three-component epoxy ring-opening reaction catalyzed by 1-Cl.

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As shown in Scheme 3, a possible mechanism for the threecomponent epoxy ring-opening reaction is proposed. Catalyst **1-CI** presents high activity for the epoxy ring-opening reaction due to its catalytically active Cu¹ species.^[62] It is well established that the phenylacetylene first coordinates with Cu¹ to generate



Scheme 3. Possible mechanism for the epoxy ring-opening reaction with 1-Cl.

the Cu^I–acetylide product (**B**).^[63] The α -carbon of the epoxide is attacked by the N₃⁻ anion to produce the azide. Afterward, the intermediate (**F**) interacts with the product (**B**) to yield another intermediate (**G**).^[64] Intermediate **E** was achieved through C–N bond formation between the end nitrogen of the coordinated azide and the β -carbon of Cu^I–acetylide.^[50,65] Intermediate **H** results from the ring contraction of intermediate **E**. Eventually, the Cu^I catalyst was recovered after protonolysis with formation of the final product, β -hydroxy-1,2,3-triazole.

MOF 1-Cl is an effective catalyst for click reactions toward the substrates used.^[36] The open MOF structure plays a key role in the improved catalytic efficiency. To understand the catalytic reaction environment, DFT simulations were carried out for the diffusion and interaction of phenylacetylene with the Cu^I site in the channels of **1-CI** (Figures S33–S35 in the Supporting Information). Notably, the 1D channel size (ca. 6.6 Å × 10 Å; Figure S36 in the Supporting Information) of 1-Cl is much larger than that of all examined alkynes and azides. Thus, the substrates could easily diffuse into the 1D channel and react with the active Cu¹ sites. To further explore the role of the 1D channel in 1-Cl, the optimized geometries of the catalytic products for the AAC reactions in water were calculated by using Gaussian 09 at the B3LYP/6-311G(d,p) level (Table S4 in the Supporting Information).^[66] For the catalytic products of the AAC reactions, the two relatively short molecular dimensions along the y and z directions are 5.98-6.77 and 5.12-5.91 Å, respectively. These dimensions are smaller than that of the 1D channel size (6.6 Å×10 Å) of 1-Cl, and therefore, diffusion of the formed catalytic product through the 1D channels is allowed.^[67] Clearly, the 1D channels and exposed active Cu^I sites in 1-Cl support the high catalytic activities of the click reactions.

Conclusion

Two layered Cu^I MOFs were successfully assembled by using a thiacalix[4]arene-based ligand with S and N coordination sites. MOFs **1-Cl** and **1-Br** are exceedingly stable in aqueous solutions over a wide range of pH values. Most strikingly, they feature highly effective catalytic activities for click reactions as recycled heterogeneous catalysts. The exposed active Cu^I sites and 1D channels in these MOF structures play an important role in improved catalytic activities. In particular, the catalytic activities of **1-Cl** and **1-Br** in water are superior to those in organic solvents or even in mixed solvents. The results demonstrate that **1-Cl** and **1-Br** are suitable for potential applications as environmentally friendly catalysts. This work provides a new route for the development of environmentally friendly MOF catalysts for use in water.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: click chemistry · green chemistry · heterogeneous catalysis · metal–organic frameworks · thiacalixarenes

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FULL PAPER

Going green: Copper(I)–thiacalix[4]arene-based frameworks are investigated as stable, recyclable heterogeneous catalysts for the click reaction in water. The metal–organic framework structures, especially exposed active Cu¹ sites and 1D channels, play a key role in the improved catalytic activities (see scheme).



Metal–Organic Frameworks

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Highly Stable Copper(I)– Thiacalix[4]arene-Based Frameworks for Highly Efficient Catalysis of Click Reactions in Water