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A Mechanochemically Active Metal-Organic Framework (MOF) Based on Cu-Bis-NHC-Linkers: Synthesis and Mechano-Catalytic Activation

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Porous coordination polymers, more commonly known as metal-organic frameworks (MOFs), are constructed from metal ions and organic linkers which form a robust network-like structure similar to very dense polymeric networks. In this work the mechanochemical activation of a MOF is reported, based on the previous results on the mechanochemical activation of latent Cu(I)-based *N*-heterocyclic carbenes (NHCs) embedded covalently in various polymers. A mechanochemically triggered copper-catalyzed azide-alkyne cycloaddition (CuAAC) is achieved using an NHC-MOF, constructed from 1,3-bis(4-carboxyphenyl)imidazolium chloride as organic linker. A Cu(I) bis(NHC) is embedded into the MOF analogous to ($[Zn_4O\{Cu(L)_2\}_2]$) using the organic bis-NHC ligand, in turn generating a largely amorphous MOF. On activation by ultrasound, the MOF containing 4.66% of Cu shows mechanochemical activation to obtain Cu(I), subsequently triggering a CuAAC with conversions up to 26.5% as monitored by the reaction of benzylazide and phenylacetylene to yield 1-benzyl-4-phenyl-1*H*-1,2,3-triazole over a period of 20 sonication cycles. With this knowledge in solution, there are prospects to transfer this mechanochemical activity into polymer networks with embedded MOFs to detect stress in hybrid materials.

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1. Introduction

Covalent chemical bonds in both thermoplastic and thermoset polymers can be broken by mechanical fields, leading to a reduction in either molecular weight and order, as reported by Staudinger as early as 1930s.[1] This behavior is related to the area of mechanochemistry, where the activation and rupturing of covalent chemical bonds is induced by mechanical energy, resulting in novel reaction pathways, not known from thermal or photochemical activation.[2–9] Thus, similar to solid-state chemistry, where intramolecular bonds are mechanically broken[10] by an external force, this also can induce chemical transformations[11] of functional groups, such as in 1,2-dioxetanes,[7,12,13] spiropyrans,[14–17] cyclopropanes,[18,19] or rotaxanes.[20] Such specific chemical bonds are prone to activation by force, depending on their strength, geometry, and location within a polymeric material. In addition to the above-mentioned chemical transformations in polymeric compounds, mechanochemistry with metal complexes has also been reported in a variety of different metal-complexes, including Fe,[21] Ag,[22–25] Ru,[26] Pd,[27–29] and Pt,[30] many of them linked to metal-*N*-heterocyclic carbene (NHC)-complexes. Metal-NHC complexes have been evaluated as an especially promising group of mechano-catalysts, since significant catalytic effects can be observed following the mechanical activation of such complexes. Thus, e.g., a ruthenium based Hoveyda–Grubbs catalyst has been used to obtain high yields of cross metathesis- or ring-closing metathesis reaction products via milling or liquid-assisted grinding (LAG).[31] A copper-catalyzed azide-alkyne cycloaddition (CuAAC) with high conversions using $Cu(OAc)_2$ was observed within minutes via ball-milling of different alkynes and azides.[32] Besides the mechanochemical activation of metal complexes with milling or grinding, also sonication[33] has been reported, being especially efficient in polymers by placing mechanophores[23,34] in the middle of a polymer chain.
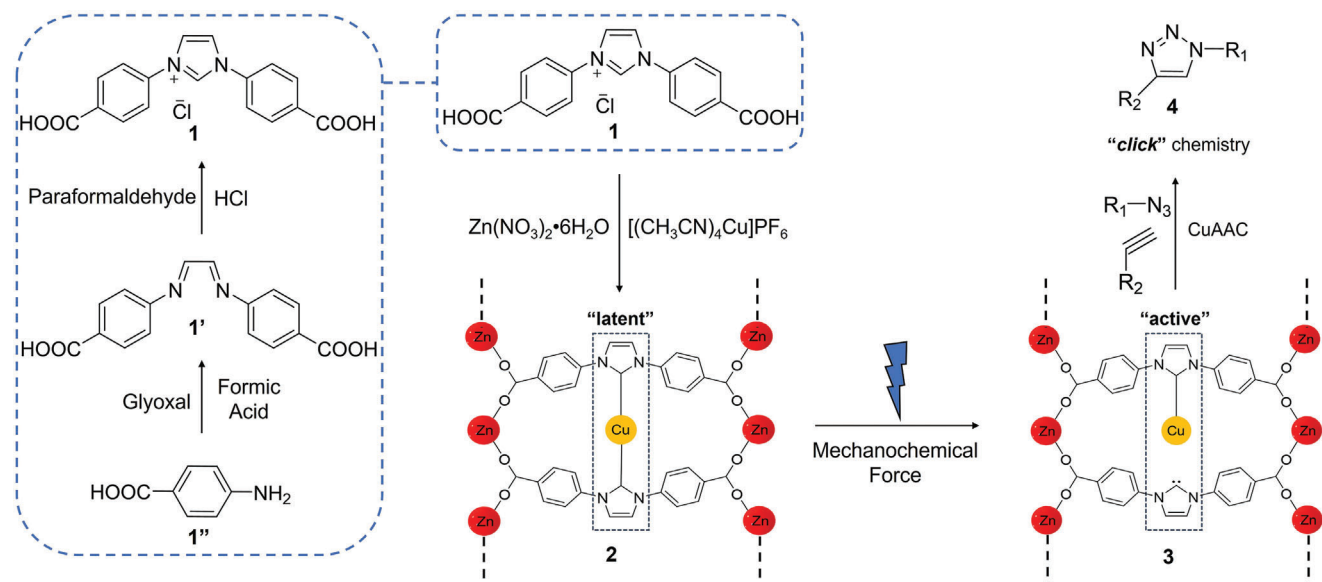
We previously have developed a latent Cu(I)-based system as a mechanophore, capable of activation by mechanical forces transmitted via covalently attached polymer chains. Therein we have used a metal complex based on NHC's in the form of Cu(I) bis(NHC) complexes,[35,36] embedded into polymer- and

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Scheme 1. Schematic concept for the synthesis of a latent NHC-MOF (2) before mechanochemical activation to yield the mono(NHC)-MOF (3) to catalyze a subsequent copper-catalyzed click chemistry (CuAAC).

peptide-backbones[37,38] to develop stress-sensing materials.[39–41] These complexes can be activated by either sonochemical activation (ultrasound), or directly by mechanical stress exerted onto the material they are embedded into.

Herein, we probe the embedding of mechanochemistry into metal-organic frameworks (MOFs) by introducing mechanochemically active metal-based NHC-complexes inside the structure of a MOF. Metal-organic frameworks (MOFs) consists of transition-metal cations or clusters, together with organic components, linked via coordination bonds.[42] Based on their 3D-extended structure they can also be regarded as highly ordered polymers, where repetitive elements are arranged in all three dimensions, thus forming a crystalline polymer-like structure, as a polymer chemists' definition could be. As MOFs are able to undergo both, reversible elastic and irreversible plastic deformations, mechanochemistry in MOFs is an attractive perspective, as force should be transmitted efficiently from nodes inside the MOF, wherein the mechanochemically active metal-NHC-bonds are placed into. It is known that plastic deformations in MOFs can be initiated by mechanical treatments (bulk compression,[43–46] shock impact,[47,48] delamination by sonication[49–51]) to alter the chemical bonds and the crystal structures of the MOFs, resulting in permanent modifications.[52]

In the past only few MOFs displaying N-heterocyclic carbenes (NHCs) as linkers have been reported. Kong et al.[53] have described the NHC 1,1′-methylenebis(3-(4-carboxyphenyl)-1H-imidazol-3-ium) to prepare the MOF [Cu$_2$L$_2$(MeOH)$_2$]·4NO$_3$·H$_2$O to quantitatively catalyze the cross-coupling of phenylhalides with phenylboronic acids via the Suzuki–Miyaura reaction, depending on the electron-withdrawing or donating properties of the precursors. Lee et al.[54] described a MOF [Cu^{II}(L$_{NHC}$–Cu^{I}Cl)(NMP)]·(NMP)$_2$·(H$_2$O) (Im-MOF-3) containing a Cu(I) mono(NHC) Cl, catalyzing a borylation yielding 34% of the

final borylated biphenyl product. Lalonde et al.[55] introduced the use of deprotonated metal imidazolates, exposing NHC sites as catalysts to convert an α,β-unsaturated ketone to the corresponding benzyl ether in the presence of benzyl alcohol in a yield significantly higher than by use of the corresponding homogenous NHC catalyst.

We here report the use of mechanochemically active metal-organic framework as a catalyst to induce click chemistry (CuAAC) (see **Scheme 1**) by mechanochemical activation. For the preparation of the NHC we used a bifunctional linker, 4-aminobenzoic acid (Scheme 1, (**1**)). In the second step, the NHC ligand is further used to synthesize a MOF, ideally forming a Cu(I) bis(NHC) in the pore ((Scheme 1, (**2**)) according to the procedure described by Burgun et al.[56] It has been demonstrated that in such bis-NHC-containing catalysts a labile bond from the initially inactive Cu(I) center is broken, generating an active Cu(I) mono(NHC) which subsequently is capable to catalyze a click reaction.[36,37,39–41] Subsequently, we here investigate whether such Cu-NHC complexes located inside the MOF's can be mechanochemically activated, as their higher rigidity compared to linear polymers or polymeric networks should lead to a quite efficient activation by ultrasound or upon embedding into polymer.

2. Results and Discussions

The wide number of NHC ligands in the field of organometallic catalysis has made it possible to use NHC precursors for the synthesis and design of NHC-containing MOFs.[54] For this purpose, 1,3-bis(4-carboxyphenyl)imidazolium chloride (**1**) was synthesized from 4-aminobenzoic acid in a two-step process as described in the literature[57] and was characterized by NMR-spectroscopy (¹H and ¹³C), IR and ESI-TOF (for details, see Supporting Information). The MOF (**2**) containing the Cu(I) bis(NHC) ligand catalytic site was synthesized by a
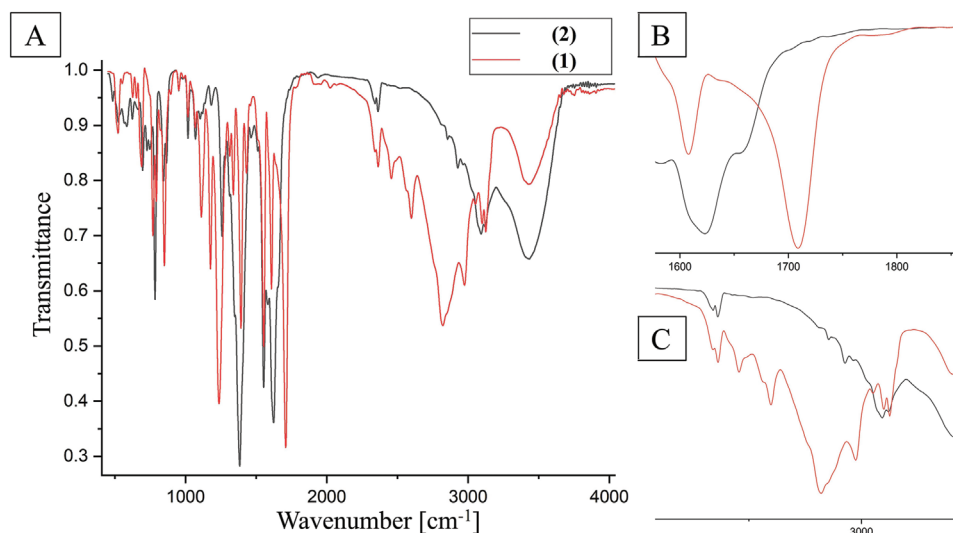
Figure 1. A) IR spectra of (1) and (2) with the relevant regions enlarged to show the differences in peaks of the carboxylic acid group of (1) B) at 1710 cm^{-1} belonging to the C=O stretching and C) in the 2400–3075 cm^{-1} region belonging to the O–H stretching bands.

solvothermal method starting from (**1**), along with one equivalent of $Zn(NO_3)_2 \cdot 6H_2O$ and half an equivalent of $[Cu(CH_3CN)_4]PF_6$, dissolved in dry DMF and stirred at 120 °C for 10 days.[56] The synthesis of this Cu(I) bis(NHC) complex follows the free-carbene route, induced by deprotonation of (**1**) in the presence of a base such as dimethylamine, formed by the in situ decomposition of DMF.[56] MOF (**2**) was synthesized inside a closed vial, finally formed by directly precipitating from the solvent DMF and further purifying by washing with solvents such as DMF and methanol. The obtained grey powder was then dried in air, and further under vacuum.

A comparison of the IR spectra of the precursor (**1**) and the MOF (**2**) (see **Figure 1**) shows two differences, indicative of the successful formation of the MOF (**2**). The strong and broad peak in the 2400–3075 cm^{-1} region (see Figure 1C) and the strong peak at 1710 cm^{-1} (see Figure 1B) belong to the O–H stretching and the C=O stretching-bands of the carboxylic acid. These two peaks disappear in the MOF (**2**), indicating the successful coordination of Zn^{2+} with both of the –OH and the C=O of the precursor (**1**). The broad peak at 3424 cm^{-1} shows the presence of water molecules in (**2**).

The thermogravimetric analysis (TGA) of (**2**) (see **Figure 2**) shows a mass decrease of up to 20% at 320 °C until the MOF (**2**) shows a reasonable thermal stability after which it suffers a further mass loss of ≈40% till 500 °C. This proves that a primordial thermal destruction prior to the desired mechanochemical activation can be excluded, as also exemplified later during the sonochemical experiments.

To quantify the amount of copper (Cu) and zinc (Zn) in the MOF, flame atomic absorption spectroscopy (FAAS) was conducted (for calibration see Figure S4, Supporting Information). The calibration for Cu and Zn reported a correlation coefficient for both analyses, R^2, as 0.9977 and 0.9946 respectively, while the relative standard deviation, % RSD, was 1.1% and 1.6% respectively. On measurement of the MOF (**2**), the mass percentage of Cu was determined to be 4.66% while the percentage of Zn was 8.97%. The corresponding atomic ratio of
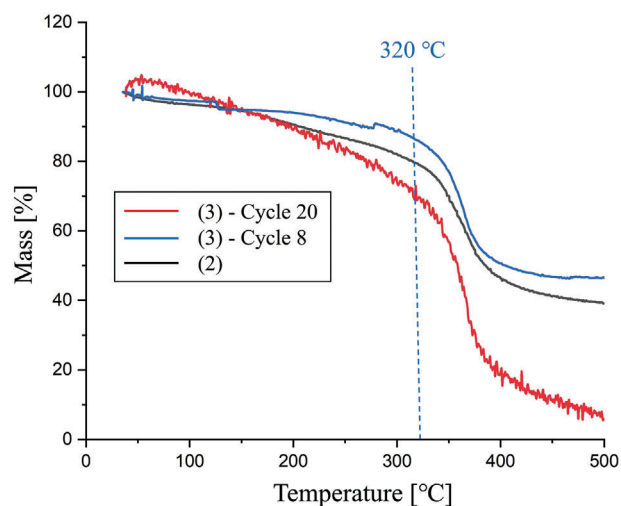

Figure 2. A comparison of the thermogravimetric analysis (TGA) conducted of the MOF pre (2) and post (3) sonication.

Cu and Zn was 0.52:1 = Cu:Zn which is close to the expected atomic ratio of 0.53:1 in the literature for an analogous MOF ($[Zn_4O\{Cu(\mathbf{L})_2\}_2]$,[56] as schematically shown in Scheme 1.

On conducting powder X-ray diffraction (PXRD), it was found that the crystallinity of the sample was low. This could be due to the removal of solvent by drying, as literature[58,59] has described the collapsing of a MOF crystal structure, causing a "crystal-to-amorphous" transformation on the removal of guest molecules (solvent molecules that are present within a MOF structure), leading to our final MOF (**2**) as an amorphous material (see Figure S6, Supporting Information).

Based on these results we do have generated a MOF bearing the incorporated Cu(I) bis(NHC) units, now useful for a subsequent mechanochemical activation, able to be subsequently monitored by a coupled CuAAC reaction of the then formed Cu(I)
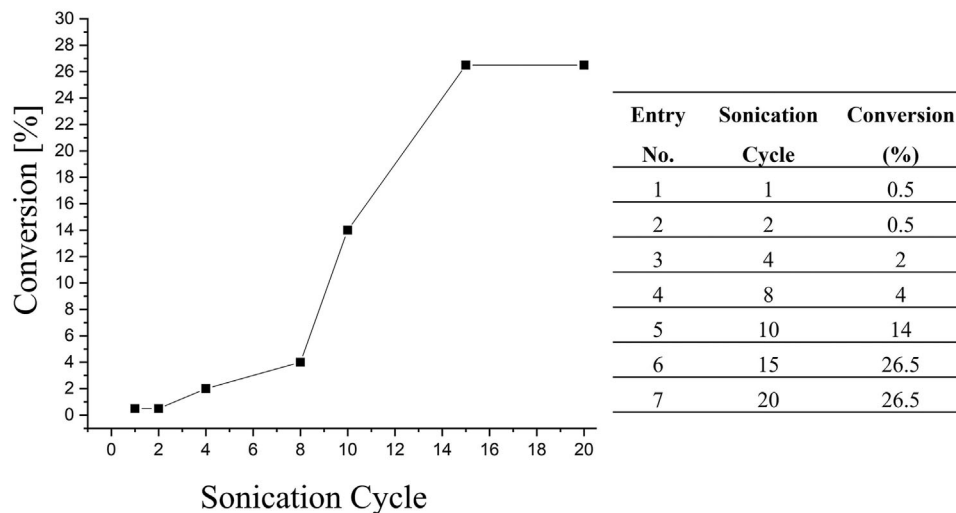
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Entry No.	Sonication Cycle	Conversion (%)
1	1	0.5
2	2	0.5
3	4	2
4	8	4
5	10	14
6	15	26.5
7	20	26.5

Figure 3. The increase of the % conversion of 1-benzyl-4-phenyl-1*H*-1,2,3-triazole formed from a 1:1 mixture of benzylazide and phenylacetylene via CuAAC over 20 cycles of mechanochemical activation by ultrasonication of (2). Each cycle was conducted under the following conditions: 5 s Pulse, 10 s Pause for 30 min (actual sonication time = 90 min) at amplitude of 30% and a subsequent resting time of 45 min. Monitoring of the coupled catalytic CuAAC was done via ^{1}H NMR spectroscopy.

mono(NHC) complexes, which are known to be catalytically active.

To activate the MOF mechanochemically, we have used sonochemistry by ultrasound, as friction or agitation in a liquid to produce tensile forces is normally difficult but can be overcome by the use of sonication. When sonicating liquids, the sound waves that propagate into the liquid result in alternating high-pressure (compression) and low-pressure (rarefaction) cycles and results in transmission of mechanical energy which could lead to bond breakage in molecules in solution.[60] Previously, the principle of using sonication resulting in rupturing bonds within the layers of a MOF has been demonstrated by the synthesis of 2D metalorganic networks (MONs) from MOFs using the "top-down" approach, resulting in more active sites being exposed and an improvement of catalytic activity.[61,62] Depending on the size of the solid particle (such as a MOF) in a liquid–solid heterogenic system, application of ultrasound produces different effects. At a frequency of 20 kHz, the size of the cavitating bubbles is around 100–150 μm. If the solid particle size is at least twice the size of the bubble, the bubble collapses asymmetrically resulting in a microjet formation resulting in jets of high-speed liquids directed at the surface of the solid particles. The shock waves associated with these microjets can cause significant damage to the surfaces of the solid particles, resulting in new surfaces being formed and exposed.[63,64] It can be hypothesized that a catalytic activity can only be gained due to newly formed surfaces of the cracked MOF by ultrasonication. However, the actual mechanism being followed is under investigation in our laboratories to prove the presented hypothesis and will be discussed further in detail in our future publications. To measure the mechanochemical activity of the synthesized (2), we therefore performed ultrasonication experiments to induce sonochemical destruction of the MOF and in turn a copper(I)-catalyzed azide alkyne cycloaddition (CuAAC) reaction of the then catalytically active Cu(I)-complex after mechanochemical removal of one of the NHC ligands. We have used the click reaction between the benzylazide and phenylacetylene as a model reaction to probe the activity of the MOF (2) in view of its catalyst activity. The use of ultrasound or mechanical stress is expected to activate a latent Cu(I) bis(NHC) complexes as described previously.[36–41] On application of an external force, one of the two NHC ligands shielding and attached to the Cu(I) should be cleaved, rupturing the mechanochemically labile bond present between the NHC-carbon and the Cu(I) allows the first step, a coordination of the alkyne-ligand with the available Cu(I) to form copper acetylide[38] to form the 1,2,3-triazole product. All adducts and the product, 1-benzyl-4-phenyl-1*H*-1,2,3-triazole, can be monitored by ^{1}H NMR spectroscopy before, during and after sonication. As seen in **Figure 3**, upon multiple cycles of sonication at a 30% amplitude for a reaction mixture of benzylazide and phenylacetylene in a 1:1 ratio in THF:MeOH 9.67:0.33 and the added MOF (2) (10 wt%, which equals to 2 mol% of Cu), an increasing conversion of the products formed by the CuAAC was observed, with the highest conversion of 26.5% obtained after 20 sonochemical cycles. In **Figure 4**, ^{1}H NMR spectra of the ultrasound experiments after different sonication cycles are shown. The peak at 4.34 ppm (marked by the red box), belonging to the –CH$_2$– of the benzylazide, was used as the reference and the percent conversion were calculated by utilizing the ratio of the integral of the reactant and the product peaks. As a control experiment, we conducted the same reaction in the presence and absence of MOF (2). In the presence of the MOF (2), Cycle 0 (see Figure 4i) shows the reaction at the beginning without any sonication, while at Cycle 8 (see Figure 4ii), up to 4% conversion were achieved. On continuation over a period of 20 cycles of ultrasound (see Figure 4iii), the proton signal from benzylazide shows a decline, while peaks associated with the product (5.58 ppm (green box) and 8.11 ppm (blue box)) obtained due to the CuAAC shows an increase, with the final percent conversion calculated as 26.5% (see Figure 4). On comparing with previously conducted experiments with other Cu(I) bis(NHC) based catalysts, it can be seen that the achieved conversion of 26.5% after 20 cycles of sonication was previously accomplished with 10 cycles of sonication while
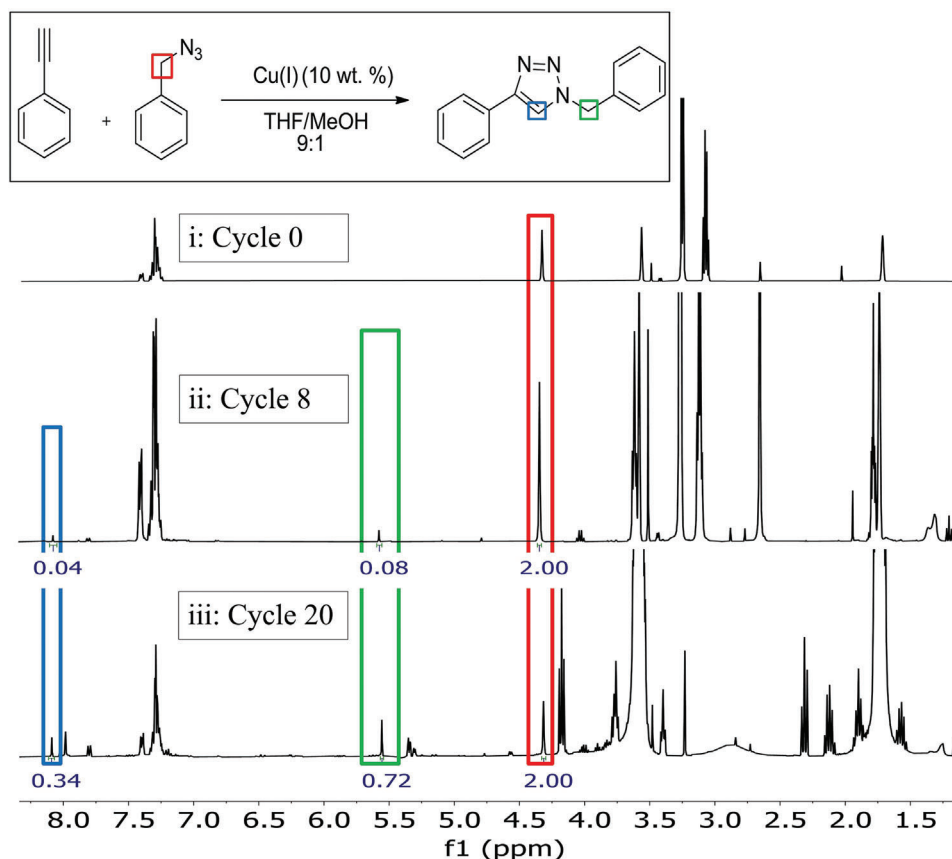
Figure 4. Mechanochemical activation of the MOF (2) by ultrasound and monitoring of the coupled catalytic CuAAC showing selected NMR spectra at i) Cycle 0, ii) Cycle 8, and iii) Cycle 20 of the ultrasonication experiments conducted in the presence MOF (2) to induce CuAAC of benzylazide and phenylacetylene. For the product 1-benzyl-4-phenyl-1H-1,2,3-triazole the NMR-resonances are as follows: ^{1}H NMR (400 MHz, THF-d$_8$, δ): 8.11 (s, 1H), 5.58 (s, 2H).

using polymer-based biscarbene catalysts, with polyisobutylene (28% conversion) with a molecular weight of 17, 200 g mol^{-1} as well as with polystyrene (23% conversion) with a molecular weight of 6800 g mol^{-1}.[36] A bis(NHC) catalyst with a elastin-like peptide chain {[Cu(C$_{10}$COOH–(VPGVG)$_4$–NHC)$_2$]Br} was able to achieve a conversion of 5.6% after 17 cycles of sonication.[37] The here observed conversions are thus in line with previous observations.

A set of three control experiments without ultrasonication with the benzylazide-phenylacetylene model system were also conducted. The first two controls consisted of experimentation to check any catalytic activity in the presence of MOF (2) at room-temperature (RT) and at 60 °C (see Figure S7, Supporting Information) while the third was without the presence of the MOF (2) at 60 °C. The control experiment at 60 °C with no added MOF (2) showed no conversion. In the presence of the MOF (2), a conversion of less than 2% was observed after 50 h (equivalent to time taken to perform 20 cycles of ultrasonication) at RT while at 60 °C, a conversion of up to 10% after 50 h (equivalent to time taken to perform 20 cycles of ultrasonication) was observed.

To ensure that the conversion obtained during ultrasonication at room-temperature in the presence of (2) is clearly via mechanochemical activation and not by thermal processes, a sonication thermal control was monitored over multiple cycles of sonication experiments to check eventual temperature changes (see Figure S8, Supporting Information). A single sonication cycle runs for 90 min so cooling was conducted via two different approaches, first named as *1ce cool*, i.e., cooled at the very beginning, and the second names as *2ce cool*, i.e., cooled on once at the beginning and once after 45 min at an average room temperature (RT) of 22 °C. The ultrasonication experiment conducted with MOF (2) used the *2ce cooling* system. The average temperature with *1ce cooling* was measured to be 26 °C while in *2ce cooling* it was 18.5 °C. It shows that the temperatures reached a maximum of 26 °C, and the conversion reaction achieved through sonication is therefore based entirely on mechanochemical activation and was not thermally induced.

However, we were interested about the fate of the MOF before and after sonication, as we hypothesized that sonication led to an at least partial destruction of the MOF, indicated also by its catalytic activity. Thus, scanning electron microscopy (SEM), atomic force microscopy (AFM) and PXRD measurements before and after sonication were conducted to probe the structure of the MOF (see Supporting Informatoin for more details). In both the sets of microscopy images (see Figure S5, Supporting Information), it can be seen that the native MOF (2) has larger structures that are broken into smaller, more disordered particles after 20 cycles of sonication in the sonicated MOF (3). In PXRD,

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multiple new peaks were seen at higher 2theta (2θ) values (see Figure S6, Supporting Information) in the sonicated MOF (**3**) which are not visible in the case of the MOF that underwent thermal control at 60 °C. This indicates that the structure of the MOF did undergo an at least partial destruction leading to the new peaks. This, along with the additional signals appearing in the ^{1}H NMR spectrum at 5.35, 7.78, and 7.98 ppm (see Figure 4) can be interpreted to not only the decomposition of the MOF structure but also to the decomposition of the NHC ligand itself. Furthermore, the TGA conducted for the sonicated MOF (**3**) at Cycle 8 (corresponding to 4% conversion achieved) and Cycle 20 (corresponding to 26.5% conversion achieved) shows a mass loss of 15% and 30% till 320 °C respectively. The TGA curves at 500 °C show ≈45% and ≈6% of mass still left at Cycle 8 and Cycle 20 of sonication respectively. In previous years working with different Cu(I) bis(NHC)s, it was observed that on ultrasonication, the latent biscarbene complex is activated to form the Cu(I) mono(NHC), but further many cycles of sonication resulted in a destructive pathway leading to the decomposition of the NHC as well.[36,65] This can be seen also in our sample with the achieved conversion of 4% at Cycle 8 of sonication, where the mass change at 500 °C is more or less similar to the native MOF (**2**), and thus it could be assumed that the structure of the MOF is still at least partially retained while acting as a catalyst for the "click" reaction. The increase of conversion % was continuous till Cycle 15 (an increase of the conversion from 4% to 26.5%) after which the conversion to form the click product has stopped, which could correspond to the destruction of MOF structure. Consequently, this leads to a limitation in the achievable percent conversion and could further explain the plateauing curve of conversion beyond Cycle 15 as seen in Figure 3 and would also indicate that the powder collected after sonication predominantly consisted of organic material, most likely the decomposed ligand.

3. Conclusion

Mechanochemical activation of a metal organic framework (MOF) synthesized with organic linkers based on imidazolium was achieved. The MOF (**2**), prepared with 1,3-bis(4-carboxyphenyl)imidazolium chloride (**1**) as linker, showed good thermal stability up to 320 °C. The conducted FAAS measurement of the MOF determined the Cu and Zn percentage to be 4.66% and 8.97% respectively with the atomic ratio 0.52:1 = Cu:Zn, similar to the expected atomic ratio of 0.53:1 for an analogous MOF ([Zn$_4$O{Cu(L)$_2$}$_2$]. 10 wt% of the Cu containing MOF (**2**) added as catalyst to a CuAAC resulted in a 26.5% conversion of phenylacetylene and benzylazide in a 1:1 ratio in THF:MeOH 9.67:0.33 to 1-benzyl-4-phenyl-1H-1,2,3-triazole by "click" chemistry (CuAAC), as confirmed by ^{1}H NMR, on mechanochemical activation by ultrasonication over a period of 20 sonication cycles. We hypothesize that ultrasonication led to an at least partial destruction of the MOF structure to obtain Cu(I), indicated by SEM, AFM, and PXRD of the post-sonicated MOF, as well as by the appearance of additional signals in the corresponding ^{1}H NMR spectrum. The partial destruction of the MOF (**2**) was additionally confirmed by comparing the TGA of the MOF before and after sonication. Overall, this work here demonstrates that the MOF can be mechanochemically activated, relying on an established Cu(I) bis(NHC) complex, known to

also activate in polymers and polymer networks. The MOF here shows quite similar, if not higher activities, which prospects an interesting feature for embedding MOFs into polymer networks for a subsequent mechanochemical detection of friction and wear using those compounds as filler materials inside, e.g., polyurethanes or epoxy-based materials.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the Supporting Information of this article.

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