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# The use of reduced copper metal-organic frameworks to facilitate CuAAC click chemistry

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A reduced copper metal-organic framework (rCu-MOF) containing Cu<sup>1</sup> ions was prepared by reducing raw MOFs (Cu-BTC). A series of polymer functionalizations and coupling reactions could subsequently be achieved *via* CuAAC click chemitry thus, demonstrating high activity, facile recyclablity and good structural stability of rCu-MOFs for catalytic applications.

Metal-organic frameworks (MOFs) are a class of crystalline materials consisting of metal ions or clusters coordinated to organic ligands.<sup>1, 2</sup> The large diversity in structures, pore sizes and adsorption affinities make MOFs of great interest for energy and environmental applications, such as hydrogen storage<sup>3-5</sup> and gas separation.<sup>6-8</sup> Recently, rapid progress in the development of heterogeneous catalysts has been achieved in the form of MOFs. This is attributed to their high surface area, well-defined coordination nano-space, diversity in metal and functional groups, as well as, the ability to retain crystallinity and regularity after catalytic reactions.<sup>9</sup> Generally, MOFs are engineered to offer three attributes for catalytic purposes: (i) metal ions or metal clusters,<sup>10</sup> (ii) functional struts<sup>11, 12</sup> and, (iii) encapsulated/loaded catalysts.<sup>13, 14</sup> In addition, MOFs also present potential to overcome the technical barrier in current commercially available heterogeneous catalysts, where the control of active site geometry cannot be achieved due to the reconstruction and redistribution of the metal atoms.<sup>15, 16</sup> This is in contrast to MOFs which exhibit stable structure and synthetically tuneable active site geometry.

MOFs containing mixed valence state ions (notably for Cu, Fe, Ce and V) are emerging microporous materials which have unique properties thus allowing them to have significant potential in various applications.<sup>17, 18</sup> For example, Daturi *et al.* demonstrated the co-existence of  $Cu^{II}/Cu^{I}$  in the Cu-MOF (HKUST-1).<sup>19</sup> Ye *et al.* 

reported a facile synthetic strategy for the fabrication of a mixed valence state Ce-MOF, which exhibited intrinsic oxidase-like activity.<sup>18</sup> Steiner and Zhang discovered that mixed-valence state Cu-MOF had dual pore size distribution and presented superior water stability compared to HKUST-1.<sup>20</sup> Chen and Shustova investigated the electronic properties and selective adsorbate binding of the mixed-valence state Cu-BTC and Cu-NIP.<sup>21</sup> These studies provide guidance for the application of MOFs for heterogeneous catalysis and gas purification.

The Cu<sup>1</sup>-catalyzed azide-alkyne cycloaddition (CuAAC)<sup>22-26</sup> is arguably the most powerful toolbox for polymer functionalization and coupling applications in modern polymer chemistry. Conventional catalysts, such as copper halide (CuX) compounds have suffered from their inefficient catalytic ability due to their low solubility (hence low surface area) and low stability under common reaction conditions (*i.e.* heating and exposure to oxygen). Due to this short coming, some improved liganded Cu<sup>1</sup> systems were studied and shown to significantly increase the solubility of Cu<sup>1</sup> in both organic and aqueous solvents. This led to enhanced catalytic abilities.<sup>27, 28</sup> However, in these systems, the dissolved Cu<sup>1</sup> ions may result in potential contamination, which in turn leads to complicated purification steps. We thus saw this is an opportunity to develop a new heterogeneous catalyst for CuAAC click chemistry by employing the reduced Cu-MOF containing Cu<sup>1</sup> ions.

Herein, we report a study on the catalytic properties of a reduced Cu-MOF (rCu-MOF). As far as we know, this is the first example of reduced MOF nanoparticles (containing Cu<sup>1</sup> ions) which can facilitate CuAAC click chemistry. The rCu-MOF was synthesized in the laboratory and well-characterized by XRD, SEM, XPS and TGA, *etc.* The catalytic ability of the rCu-MOFs was then demonstrated by a series of successfully polymer functionalizations and coupling reactions. This rCu-MOF catalyst also presents advantages such as, high hydrothermal stability and facile recyclability in comparison with conventional catalysts.

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<sup>&</sup>lt;sup>+</sup> Electronic Supplementary Information (ESI) available: [details of experiments and characterization on the precursors and MOF materials]. See

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**Scheme 1.** a) Schematic illustration for the preparation of reduced copper metal-organic framework (rCu-MOF): (i) coordination reaction between Cu<sup>2+</sup> and benzene 1,3,5-tricarboxylate (BTC) and (ii) reduction of the Cu-BTC in the presence of hydroquinone at 150 °C. b) Schematic representations for various polymer functionalizations and coupling reactions utilizing rCu-MOFs *via* CuAAC chemistry. c) Chemical structures of the synthesized precursors for the CuAAC reactions.

The rCu-MOF containing both Cu<sup>II</sup>/Cu<sup>I</sup> ions was prepared *via a* two-step process as shown in Scheme 1a. Firstly, the MOF Cu-BTC (HKUST-1) was synthesized according to a previously reported procedure.<sup>29</sup> The raw MOF was reduced in the presence of hydroquinone to give a dark colour crystal, rCu-MOF. This 'green' synthesis of MOFs employs non-hazardous reactants at relatively mild synthetic conditions, producing less waste than conventional procedures. A series of CuAAC reactions for polymer modification and coupling purposes were then investigated by utilizing the microporous rCu-MOF as the heterogeneous catalyst (Scheme 1b).

Digital images were taken to display the dispersion quality of the Cu-BTC and the rCu-MOF crystals in different solvents immediately after ultrasonication (Fig. 1a and b). Just after ultrasonication, the Cu-BTC shows poor dispersion in all the solvents, but the rCu-MOF shows relatively good dispersion in DMSO and methanol. We characterized the morphology of Cu-BTC and rCu-MOF by SEM measurements (Fig. 1c and 1d) which indicate successful formation of the MOF crystals. It should be noted that the rCu-MOF (Fig.1d) presented an irregular morphology compared to Cu-BTC (Fig. 1c). This may be attributed to partial structural damage during the reduction process. The strong aggregation tendency of both Cu-BTC and rCu-MOF is also suggested by the SEM images. The DLS results for Cu-BTC and rCu-MOF aqueous suspensions are inserted in Fig. 1c and 1d. The rCu-MOF exhibits a smaller average hydrodynamic diameter ( $D_{\rm H}$ ) of ca. 165 nm, while the raw Cu-BTC has a  $D_{\rm H}$  value of ca. 218 nm.

XPS was used to investigate the oxidation states of Cu in the Cu-BTC and the rCu-MOF crystals. Fig. 1e shows the peaks in the Cu  $2p_{3/2}$  region. In the top spectrum, the peak at 934.6 eV is attributed to Cu<sup>II</sup> in the Cu-BTC. In the case of rCu-MOF, the relative abundance of Cu<sup>II</sup> and Cu<sup>III</sup> can be obtained by a peak fitting procedure performed on the Cu  $2p_{3/2}$  signal (bottom spectrum). Calculation of the areas of the Cu<sup>II</sup> peak and the Cu<sup>III</sup> structure gives a ratio of 44% Cu<sup>II</sup> to 56% Cu<sup>III</sup> which is in agreement with previous



**Fig. 1** Digital images of a) Cu-BTC and b) rCu-MOF dispersions in 5 different solvents immediately after ultrasonication. (Left to right: DMSO, methanol, DI H<sub>2</sub>O, THF and CHCl<sub>3</sub>). c-d) SEM images of the synthesized Cu-BTC and the rCu-MOF crystals, respectively. The scale bars represent 2  $\mu$ m. Their respective DLS data are inserted. e) High resolution Cu 2p<sub>3/2</sub> XPS spectra for the Cu-BTC (top) and the rCu-MOF (bottom) crystals. f) Comparison of the XRD patterns for the synthesized Cu-BTC (top) and the rCu-MOF (bottom).

studies.<sup>20, 21</sup> This result demonstrates the co-existence of Cu<sup>1</sup> and Cu<sup>II</sup> in the rCu-MOF. The broad XPS spectra of the MOFs are shown in Fig. S1 (ESI<sup>+</sup>). The X-ray diffraction (XRD) pattern shows that the crystalline structure changed after MOF reduction (Fig. 1f). The porous feature of the rCu-MOF was confirmed by conducting a CO<sub>2</sub> adsorption experiment. Surprisingly, the rCu-MOF exhibits an enhanced CO<sub>2</sub> uptake ability (19.5 mmol/g) due to its enlarged surface area (> 3260 m<sup>2</sup>/g, BET) compared to the Cu-BTC, where the CO<sub>2</sub> uptake is of 6.3 mmol/g and the BET surface area is of 570 m<sup>2</sup>/g. TGA measurements revealed that rCu-MOF contains 36 wt. % of Cu (Fig.S2, ESI<sup>+</sup>).

We subsequently investigated the possibility of applying the rCu-MOF in the Cu<sup>1</sup>-catalyzed azide-alkyne cycloaddition (CuAAC) chemistry. Firstly, 'click' reactions for polymer modification were achieved. An azide functionlized poly(ethylene glycol) (PEG-N<sub>3</sub>, P1) was used to conjugate with propargyl 1-pyrene butyrate (C1) and propargyl alcohol (C2) in the presence of rCu-MOF to afford  $\omega$ -pyrene and  $\omega$ -OH terminated PEGs. MALDI-ToF MS of the resulting products revealed a single monomodal series and a clear shift to higher molecular weights, indicating a quantitative yield of the coupling products (Fig. 2a-c). This was also demonstrated by the observation of proton signals from the characteristic triazole rings by <sup>1</sup>H NMR analysis (Fig. S3a-b,ESI<sup>+</sup>). As 'click' chemistry is known as a powerful

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**Fig. 2** a-c) MALDI-TOF MS of azide functionalized PEG (P1), the resultant  $\omega$ -OH and  $\omega$ -pyrene terminated PEGs. d) Schematic illustration of the preparation of PMMA-*b*-PMMA *pseudo*-block copolymer *via* CuAAC reaction using rCu-MOFs. e) GPC evolution of the resultant PMMA-*b*-PMMA copolymer.

synthetic strategy for the preparation of block copolymers, we investigated a 'click' coupling reaction between high molecular weight poly(methyl methacrylate)-azide (P2,  $M_n = 5.2$  kDa,  $M_w/M_n = 1.11$ ) and the alkyne-functionalized poly(methyl methacrylate) (P3,  $M_n = 12.0$  kDa,  $M_w/M_n = 1.27$ ) under similar conditions (Fig. 2d). The GPC trace (blue colour) of the resulting *pseudo*-block copolymer (PMMA-*b*-PMMA, Fig. 2e) shows a clear shift to the higher molecular weight region with a small amount of tailing observed. This revealed a high yield of the coupling product. The successful coupling reaction was also shown by the <sup>1</sup>H NMR analysis (Fig. S3c, ESI<sup>+</sup>). These combined results demonstrate the catalytic ability of the rCu-MOF for CuAAC click chemistry.

To further explore the catalytic performance of the rCu-MOF, a CuAAC reaction between the propargal alcohol (C2) and the 3azidopropyl anthrancene-9-carboxylate (C3) was used as a probe reaction (Fig. 3a) so that the characteristic proton signals display acceptable peak resolution. Briefly, the reaction mixture (in  $CD_3OD$ ) was degassed by bubbling  $N_2$  for 20 min and subsequently sampled in a NMR tube. After the addition of ca. 1.2 mg rCu-MOF, the NMR tube was placed in a 60 °C oil bath. In situ <sup>1</sup>H NMR spectra was then recorded at various time intervals to track the concentrations of each species (Fig. 3b). Characteristic proton signals assigned to (i) the alkyne group b and methylene group a of C2, (ii) the methylene group j of C3 and, (iii) the methylene groups a' and j' next to the triazole ring could be easily identified in the enlarged <sup>1</sup>H NMR spectra (Fig. 3c-d). This demonstrates the successful CuAAC click chemistry.

The evolution of these proton signals also revealed the reaction speed of the CuAAC system. As shown in Fig. 3e, the integral ratios of the peaks j and j' were used to plot the conversion of C3 over reaction time. It should be noted that the conversion calculated from the other reference peak (*i.e.* from a) is identical to the value



Fig. 3 <sup>1</sup>H NMR spectroscopy was used to trace the reaction mixture composition throughout the course of the CuAAC reaction in the presence of rCu-MOF. a) Schematic representations for the CuAAC coupling reaction between C2 and C3. b). Full <sup>1</sup>H NMR spectra obtained at various time intervals. c) Evolution of the single proton derived from the alkyne group b and the protons derived from the methylene group j. d) Evolution of the protons derived from the methylene group a. e) Conversion vs. time plots of rCu-MOF for 3 cycles compared to CuBr for control experiment. The calculated the following conversion by Eq. was , where  $A_j$  and  $A_{j'}$  are the integral areas of -)  $\times 100\%$ Conv.(%) = (1 - $A_i + A_i$ 

peaks j and j', respectively.

Table 1. Summary of the catalytic performance.

Entries	Catalyst <sup>a</sup>	120 min TON <sup>b</sup>	TOF <sup>ª</sup> (min <sup>-1</sup> ) <sup>b</sup>
Cycle-1	rCu-MOF	19.4	19.2
Cycle-2	rCu-MOF	19.0	18.7
Cycle-3	rCu-MOF	18.8	17.9
C-1	Cu-BTC	-	-
C-2	CuBr	7.6	6.6

<sup> $^{\circ}</sup>The rCu-MOF (1.2 mg), Cu-BTC (1.0 mg) and CuBr (1.0 mg) were fed as catalysts. <sup><math>^{b}</sup>TON and TOF are calculated based on the total number of Cu<sup>1</sup> ions. The mass of Cu<sup>1</sup> ions in rCu-MOF was calculated through the TGA (36 wt.% of Cu<sup>1</sup> and Cu<sup>11</sup>) and XPS (44% of Cu<sup>1</sup>) analysis.</sup>$ </sup>

using the aforementioned method. The proton signal assigned to the triazole ring b' is not suitable for calculation as it is overlapped by the proton signals of aromatic ring. Generally, the CuAAC system in the presence of rCu-MOF presents a high reaction speed with *ca*. 90 % conversion of the C3 and C2 within 2 hours. In the case of the control experiment using CuBr as catalyst, only *ca*. 80 % conversion was observed within same time frame.

Furthermore, like other heterogeneous catalysts, rCu-MOF catalysts allow for easier post-reaction separation, less contamination and facile recyclability when compared to homogeneous catalysts. To examine the recyclability of the rCu-MOF catalyst, CuAAC reactions of C2 and C3 was further repeated twice (Fig. 3e) in the presence of rCu-MOF recovered from the

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previous reaction. After 2 hours of heating, the repeat reactions were successfully carried out as revealed by <sup>1</sup>H NMR analysis (Table S1, ESI<sup>+</sup>). This indicates the high structural stability of the rCu-MOF. Zhang et al. also observed this ideal when heating rCu-MOF under  $\rm O_2$  at 200  $^{\rm o}C$  which resulted in only a slight oxidation of  $\rm Cu^{I}$  to  $\rm Cu^{II.^{20}}$ We further characterized the filtrated reaction mixture by ICP-OES to detect any leached Cu ions. Notably, no trace of copper could be detected (sensitivity ~10 ppb). Through the calculation of turnover number (TON) and turnover frequency (TOF), we further identified the difference between rCu-MOF and CuBr in catalytic activity (Table 1). Firstly, we can find that the 2 hour TON value dropped ca. 2 % after each cycle. In addition, from TOF for each cycle, we can see that the Cu<sup>1</sup> ions activity dropped *ca*. 3 and 5 % for Cycle 2 and Cycle 3, respectively. This small amount of decay activity from Cycle-1 to Cycle-3 is likely attributed to both material loss and oxidation of  ${\rm Cu}^{\rm I}$  to  ${\rm Cu}^{\rm II}.^{30}$  Despite the small reduction (<5 %), the overall activity of the rCu-MOF is still outstanding. In contrast, raw Cu-BTC (C-1, containing Cu<sup>II</sup> ions only) could not exhibit any catalytic ability for the CuAAC reaction under the same conditions. Additionally, the conventional CuBr catalyst presents a much lower activity with the TON and TOF values of 7.6 and 6.6, respectively (C-2 in Table 1). All of these results demonstrate excellent catalytic activity as well as facile recyclability of the rCu-MOFs.

For comparison, a homogeneous liganded Cu<sup>I</sup> system for CuAAC reaction of C2 and C3 was performed. An improved catalytic activity of the Cu<sup>I</sup>/PMDETA was observed, whereby the conversion achieves ~ 99% within 40 minutes and the calculated TOF is of 27 (Table S2, ESI<sup>+</sup>). Although the rCu-MOFs system (TOF is of 19) is less active than the solution system, it brings a huge advantage of no requirement for purification steps.

#### Conclusions

In summary, a reduced copper metal-organic framework (rCu-MOF) has been prepared and fully-characterized. Using these rCu-MOFs a series of 'Click' reactions were successfully conducted with quantitative yield. When compared to the conventional copper halide catalyst, higher activity and facile recyclability of the rCu-MOF catalyst was observed. These properties combined with its ease of synthesis, lack of heavy metal contamination and high structural stability make the rCu-MOFs attractive catalytic materials for industrial applications. This study opens new avenues for rCu-MOFs in the field of polymer chemistry.

### Notes and references

- S. R. Batten, N. R. Champness, X.-M. Chen, J. Garcia-Martinez, S. Kitagawa, L. Ohrstrom, M. O'Keeffe, M. P. Suh and J. Reedijk, *Cryst. Eng. Comm.*, 2012, **14**, 3001-3004.
- H.-C. J. Zhou and S. Kitagawa, Chem. Soc. Rev., 2014, 43, 5415-5418.
- J. L. C. Rowsell and O. M. Yaghi, Angew. Chem. Int. Ed., 2005, 44, 4670-4679.

- L. J. Murray, M. Dinca and J. R. Long, *Chem. Soc. Rev.*, 2009, **38**, 1294-1314.
- J. Goldsmith, A. G. Wong-Foy, M. J. Cafarella and D. J. Siegel, *Chem. Mater.*, 2013, **25**, 3373-3382.
- R. J. Kuppler, D. J. Timmons, Q.-R. Fanga, J.-R. Li, T. A. Makal, M. D. Young, D. Yuan, D. Zhao, W. Zhuang and H.-C. Zhou, *Coord. Chem. Rev.*, 2009, **253**, 3042-3066.
- J.-R. Li, R. J. Kuppler and H.-C. Zhou, *Chem. Soc. Rev.*, 2009, **38**, 1477-1504.
- M. Matsumoto and T. Kitaoka, *Adv. Mater.*, 2016, **28**, 1765-1769. J. Liu, L. Chen, H. Cui, J. Zhang, L. Zhang and C.-Y. Su, *Chem. Soc. Rev.*, 2014, **43**, 6011-6061.
- I. Luz, F. X. L. i. Xamena and A. Corma, *J. Catal.*, 2012, **285**, 285-291.
- 11. S. S.-Y. Chui, S. M.-F. Lo, J. P. H. Charmant, A. G. Orpen and I. D. Williams, *Science*, 1999, **283**, 1148-1150.
- 12. S. Horike, M. Dincă, K. Tamaki and J. R. Long, *J. Am. Chem. Soc.*, 2008, **130**, 5854-5855.
- L. Chen, Y. Yang and D. Jiang, J. Am. Chem. Soc., 2010, 132, 9138-9143.
  - K. Xie, Q. Fu, Y. He, J. Kim, S. J. Goh, E. Nam, G. G. Qiao and P. A. Webley, *Chem. Commun.*, 2015, **51**, 15566-15569.
  - F. Tao, M. E. Grass, Y. Zhang, D. R. Butcher, J. R. Renzas, Z. Liu, J. Y. Chung, B. S. Mun, M. Salmeron and G. A. Somorjai, *Science*, 2008, **322**, 932-934.
- F. Tao, M. E. Grass, Y. Zhang, D. R. Butcher, F. Aksoy, S. Aloni, V. Altoe, S. Alayoglu, J. R. Renzas, C.-K. Tsung, Z. Zhu, Z. Liu, M. Salmeron and G. A. Somorjai, *J. Am. Chem. Soc.*, 2010, **132**, 8697-8703.
- G. Férey, F. Millange, M. Morcrette, C. Serre, M.-L. Doublet, J.-M. Grenèche and J.-M. Tarascon, *Angew. Chem. Int. Ed.*, 2007, 46, 3259-3263.
  - Y. Xiong, S. Chen, F. Ye, L. Su, C. Zhang, S. Shen and S. Zhao, *Chem. Commun.*, 2015, **51**, 4635-4638.
  - J. Szanyi, M. Daturi, G. Clet, D. R. Baerc and C. H. F. Peden, *Phys. Chem. Chem. Phys.*, 2012, **14**, 4383-4390.
- 20. A. Ahmed, C. M. Robertson, A. Steiner, T. Whittles, A. Ho, V. Dhanak and H. Zhang, *RSC Adv.*, 2016, **6**, 8902-8905.
- A. S. Duke, E. A. Dolgopolova, R. P. Galhenage, S. C. Ammal, A. Heyden, M. D. Smith, D. A. Chen and N. B. Shustova, *J. Phys. Chem. C*, 2015, **119**, 27457-27466.
- H. C. Kolb, M. G. Finn and K. B. Sharpless, Angew. Chem. Int. Ed., 2001, 40, 2004-2021.
- 23. M. Meldal and C. W. Tornøe, *Chem. Rev.*, 2008, **108**, 2952-3015.
- 24. V. K. Tiwari, B. B. Mishra, K. B. Mishra, N. Mishra, A. S. Singh and X. Chen, *Chem. Rev.*, 2016, **116**, 3086-3240.
- C. Wang, D. Ikhlef, S. Kahlal, J.-Y. Saillard and D. Astruc, Coord. Chem. Rev., 2016, 316, 1-20.
  - D. Ikhlef, C. Wang, S. Kahlal, B. Maouche, D. Astruc and J.-Y. Saillard, *Comp. Theor. Chem.*, 2015, **1073**, 131-138.
  - C. Deraedt, N. Pinaud and D. Astruc, J. Am. Chem. Soc., 2014, **136**, 12092-12098.
  - C. Wang, D. Wang, S. Yu, T. Cornilleau, J. Ruiz, L. Salmon and D. Astruc, ACS Catal., 2016, **6**, 5424-5431.
- R. Ameloot, E. Gobechiya, H. Uji-i, J. A. Martens, J. Hofkens, L. Alaerts, B. F. Sels and D. E. D. Vos, *Adv. Mater.*, 2010, 22, 2685-2688.
  - J. A. Bennett, I. P. Mikheenko, K. Deplanche, I. J. Shannon, J. Wood and L. E. Macaskie, *Appl Catal B Environ.*, 2013, **140–141**, 700-707.

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