A mesoporous metal-organic framework used to sustainably release copper(II) into reducing aqueous media to promote the CuAAC click reaction

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Table S1. “Recyclability” of Cu@MOF1 and Cu@MOF3 materials

Fig. S1 – Simulated and experimental PXRD patterns
Fig. S2 – Adsorption-desorption isotherms of MOF1 and MOF3 and the corresponding pore size distributions
Fig. S3 – 'H-NMR spectrum of NaOD-digested MOF2
Fig. S4 – FT-IR spectrum of MOF2 and MOF3
Fig. S5 – UPLC chromatogram with the MS spectra of NaOH-digested MOF2
Fig. S6 – 'H-NMR spectrum of NaOD-digested MOF3
Fig. S7 – UPLC chromatogram with the MS spectra of NaOH-digested MOF3

1H- and 13C-NMR data of compounds 4 – 7, 8 – 10

1H- and 13C-NMR spectra of compounds 4 – 7, 8 – 10
Figure S1. A. PXRD patterns simulated (1.54056 Å) from the crystal data of Cr-MIL-101, and recorded for a sample of MOF 1 (Cr-MIL-101-NH₂) and MOF 3 (Cr-MIL-101-TBTA). B. PXRD patterns recorded for a sample of CuSO₄·5H₂O, MOF1, MOF1/CuSO₄ and Cu@MOF1.
Figure S2. N\textsubscript{2} adsorption-desorption experiments and calculated pore size distribution of Cr-MIL-101-NH\textsubscript{2} (MOF1, red) and MOF3 (blue). N\textsubscript{2} adsorption desorption isotherms were performed on a Micromeritics ASAP 2020 apparatus and measured at liquid N\textsubscript{2} temperature (77 K).

A known amount of sample (about 50 mg) was loaded into the sample cell and degassed under vacuum (10^{-5} Torr) at 150 °C for 11 h. The BET specific surface areas (1620 m\textsuperscript{2}/g for MOF1 calculated in the P/P° range 0.0617-0.2016 and 730 m\textsuperscript{2}/g for MOF3 calculated in the P/P° range 0.0641-0.2015) and pore size distribution were calculated from the desorption isotherms.

- Calculated total pore volume (MOF1: 1.22 cm\textsuperscript{3}/g, MOF3: 0.79 cm\textsuperscript{3}/g).
- Calculated micropore volume and micropore surface area (MOF1: 0.560 cm\textsuperscript{3}/g and 737 m\textsuperscript{2}/g, respectively, MOF3: 0.252 cm\textsuperscript{3}/g and 262 m\textsuperscript{2}/g, respectively).
Figure S3. 7.0-8.4 ppm-range $^1$H-NMR spectrum (300 MHz, NaOD/D$_2$O or d$_6$-DMSO) of the digested MOF 2. For $^1$H-NMR measurements, a MOF sample ($\approx$ 10 mg) was suspended in D$_2$O (1 mL), and a solution of 40 wt% NaOD in D$_2$O (2 µL) was added. The solution was allowed to stand for 16 hours at room temperature, filtered on alumina (aluminum oxide 90 active neutral from Merck) to remove chromium salts, and then analyzed by NMR. It should be noted the presence of $\approx$ 20 % of remaining BDC-NH$_2$ (signals denoted “x”), and of BDC (signal denoted “o”) probably due to a deamination reaction.
Figure S4. FT-IR spectra of MOF 2 and MOF 3 (as synthesized and after one reaction run) displaying azido bands at 2122 cm⁻¹.
Figure S5. UPLC chromatogram (inset plot) of the digested products in approx. 0.02 M NaOH of MOF 2 (retention time: 1.616 min) with the mass spectrum acquired in ESI negative mode corresponding to 2-azidoterephthalic acid (C₈H₅N₃O₄, MW=207.143).
Figure S6. 7.1-8.1 ppm-range $^1$H-NMR spectrum (300 MHz, NaOD/D$_2$O) of the digested MOF 3. For $^1$H-NMR measurements, a MOF sample (≈ 10 mg) was suspended in D$_2$O (1 mL), and a solution of 40 wt% NaOD in D$_2$O (2 µL) was added. The solution was allowed to stand for 16 hours at room temperature, filtered on alumina and analyzed by NMR. Signals denoted “#” in the spectrum refer to BDC$_2^2$-NH$_2$, “x” to BDC$_2^2$-N$_3$, “o” to BDC$_2^3$-TBTA, and signal denoted “$\$” refers to BDC$_2^2$. 
Figure S7. Mass spectra acquired in ESI negative mode of 2-azidoterephthalic acid (BDC-N$_3$, C$_8$H$_5$N$_3$O$_4$, MW 207.143) and of 2-[4-[[bis[(1-benzyltriazol-4-yl)methyl]amino]methyl] triazol-1-yl]terephthalic acid (BDC-TBTA, C$_{31}$H$_{28}$N$_{10}$O$_4$, MW 604.62) with the UPLC chromatogram (254 nm detection) of the digested products in ≃ 0.02 M NaOH of MOF 3; Retention times: 1.591 min for BDC-N$_3$ and 2.845 min for BDC-TBTA; Ratio: BDC-N$_3$/BDC-TBTA 82/18.
Table S1a. “Recyclability” of Cu@MOF1 and Cu@MOF3 materials in the CuAAC reaction between benzyl azide and 3-phenyl-1-propyne at room temperature in methanol/water 95/5. Reaction conditions: 3-phenyl-1-propyne (0.86 mmol, 1 equiv), benzyl azide (1.03 mmol, 1.2 equiv), sodium ascorbate (10 mg, 6 mol%), MOF (10 mg), methanol/water 95/5 (1 mL). After each run of 24 h, the solid material was centrifuged, washed with ethyl acetate, dried under vacuum, and then used directly in the next run.

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<th>Cu@MOF1</th>
<th>Cu@MOF3</th>
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*aHistograms of these data are represented in Fig.4.
**1H- and 13C-NMR data and spectra of compounds 4 – 7, 8 – 10**

**1H-NMR** spectra were recorded on a Bruker Avance 300 spectrometer at 300 MHz using CDCl₃ as solvent. The residual proton signal of the deuterated solvent was used as an internal reference (CDCl₃ δ = 7.26 ppm).

**J-MOD 13C- NMR** spectra were recorded on a spectrometer on a Bruker Avance 300 spectrometer at 75 MHz. The carbon signal of the deuterated solvent was used as an internal reference (CDCl₃ δ = 77.0 ppm).

NMR data for **1,4-dibenzyl-1H-1,2,3-triazole (1)**, **4-benzyl-1-dodecyl-1H-1,2,3-triazole (2)**, **1-benzyl-4-phenyl-1H-1,2,3-triazole (3)** and **1-benzyl-4-hexyl-1H-1,2,3-triazole (9)** are consistent with data already published [ref. S1-S2]

**1-Dodecyl-4-phenyl-1H-1,2,3-triazole (4) [ref. S3]**

Purified by flash chromatography: gradient petroleum ether/ethyl acetate 95/5 to 20/80 in 15 min.
Yield: 94%

1H NMR (300 MHz, CDCl₃) δ 7.83 (d, J = 7.3 Hz, 2H); 7.74 (s, 1H); 7.42 (t, J = 7.3 Hz, 2H); 7.32 (t, J = 7.3 Hz, 1H); 4.38 (t, J = 7.2 Hz, 2H); 1.93 (m, 2H); 1.29 (m, 18H); 0.87 (t, J = 7.0 Hz, 3H); 13C NMR (75 MHz, CDCl₃) δ 147.7; 130.7; 128.8; 128.0; 125.6; 119.3; 50.4; 31.9; 30.3; 29.6; 29.5; 29.34; 29.28; 29.0; 26.5; 22.6; 14.1; LRMS (DCI-NH₃, M+H) Found: 314.2.

**1-Benzyl-4-(3-methylphenyl)-1H-1,2,3-triazole (5)**

Purified by flash chromatography: gradient petroleum ether/ethyl acetate 95/5 to 20/80 in 15 min.
Yield: 98%

1H NMR (300 MHz, CDCl₃) δ 7.66 (br s, 2H); 7.56 (d, J = 7.5 Hz, 1H); 7.25-7.38 (m, 6H); 7.12 (d, J = 7.5 Hz, 1H); 5.54 (s, 2H); 2.37 (s, 3H); 13C NMR (75 MHz, CDCl₃) δ 148.2; 138.4; 134.6; 130.3; 129.0; 128.8; 128.6; 127.9; 126.3; 122.7; 119.5; 54.1; 21.3; HRMS (DCI-CH₄, M+H) Calculated for C₁₆H₁₆N₃: 250.1344. Found: 340.1341.

**9-(1-Benzyl-1H-1,2,3-triazol-4-yl)-9H-fluoren-9-ol (6)**

Purified by flash chromatography: gradient petroleum ether/ethyl acetate 80/20 to 20/80 in 15 min.
Yield: 93%

1H NMR (300 MHz, CDCl₃) δ 7.62 (m, 2H); 7.58 (m, 2H); 7.36 (td, J = 7.5 Hz, 1.3 Hz, 2H); 7.24-7.33 (m, 5H); 7.17-7.20 (m, 2H); 7.14 (s, 1H); 5.39 (s, 2H); 3.83 (s, 1H); 13C NMR (75 MHz, CDCl₃) δ 150.7; 147.8; 139.5; 134.3; 129.3; 128.9; 128.6; 128.2; 127.9; 124.8; 120.4; 120.1; 78.5; 54.0; HRMS (DCI-CH₄, M+H) Calculated for C₂₂H₁₈N₃O: 340.1450. Found: 340.1445.
9-(1-Dodecyl-1H-1,2,3-triazol-4-yl)-9H-fluoren-9-ol (7)

Purified by flash chromatography: gradient petroleum ether/ethyl acetate 80/20 to 20/80 in 15 min. Yield: 97%

1H NMR (300 MHz, CDCl$_3$) $\delta$ 7.62 (t, $J = 8.3$ Hz, 4H); 7.37 (td, $J = 7.3$ Hz, 1.2 Hz, 2H); 7.28 (td, $J = 7.4$ Hz, 1.1 Hz, 2H); 7.13 (s, 1H); 4.20 (t, $J = 7.3$ Hz, 2H); 3.88 (s, 1H); 1.79 (m, 2H); 1.25 (m, 18 H); 0.88 (t, $J = 7.0$ Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 150.3; 148.0; 139.5; 129.3; 128.2; 124.8; 120.1; 78.5; 50.3; 31.8; 30.1; 29.5; 29.4; 29.3; 28.9; 26.4; 22.6; 14.1; HRMS (DCI-CH$_4$, M+H) Calculated for C$_{27}$H$_{36}$N$_3$O: 418.2858. Found: 418.2668.

1-Benzyl-4-butyl-1H-1,2,3-triazole (8) [ref. 3]

Purified by flash chromatography: gradient petroleum ether/ethyl acetate 95/5 to 20/80 in 15 min. Yield: 98%

1H NMR (300 MHz, CDCl$_3$) $\delta$ 7.22-7.38 (m, 5H); 7.18 (s, 1H); 5.47 (s, 2H); 2.67 (t, $J = 7.5$ Hz, 2H); 1.61 (m, 2H); 1.34 (m, 2H); 0.89 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 134.9; 128.9; 128.5; 127.8; 53.9; 31.4; 25.3; 22.2; 13.7; LRMS (DCI-NH$_3$, M+H) Found: 216.1.

1-Dodecyl-4-hexyl-1H-1,2,3-triazole (10)

Purified by flash chromatography: gradient petroleum ether/ethyl acetate 95/5 to 20/80 in 15 min. Yield: 96%

1H NMR (300 MHz, CDCl$_3$) $\delta$ 4.26 (t, $J = 7.2$ Hz, 2H); 2.66 (t, $J = 7.5$ Hz, 2H); 1.84 (m, 2H); 1.62 (m, 2H); 1.21 (m, 27H); 0.84 (t, $J = 6.8$ Hz, 6H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 148.3; 120.3; 50.1; 31.8; 31.5; 30.3; 29.5; 29.4; 29.3; 29.2; 28.9; 28.8; 26.4; 25.6; 22.6; 22.5; 14.0;13.9; HRMS (DCI-CH$_4$, M+H) Calculated for C$_{20}$H$_{40}$N$_3$: 322.3222. Found: 322.3225.

References


Compound 4
Compound 5
Compound 7
Compound 8
Compound 10