A Metal-organic framework as highly efficient and reusable catalyst for the solvent-free 1,3-dipolar cycloaddition of organic azides to alkynes

Peng Li,Sridhar Regati, Huicai Huang, Hadi D. Arman, John C.-G. Zhao,* and Banglin Chen*

Department of Chemistry, University of Texas at San Antonio One UTSA Circle, San Antonio, Texas 78249-0698

SupplementaryInformation

Table of Contents

General Information	S-1
Experimental Procedures	S-1
Table S1: Crystal Data of Cu-MOF	S-2
Figure S1	S-3
Figure S2	S-4
Figure S3	
Compound Characterization Data	S-6
Additional References	S-6
NMR spectrum	S-7

General Information

Copper acetate hydrate $[Cu(OAc)_2 \cdot 2H_2O], 2, 4, 6-tri(4-pyridyl) - 1, 3, 5-triazine (Ptz), 2, 6-naphthalenendisulfonic acid disodium salt (2, 6-Napds), acetylenes, and organic azides were purchased from commercial sources and used as received. Thermogravimetric analysis (TGA) was performed on a Mettler Toledo TGA under N₂ flow and heated from room temperature to 600 °C (at 10 °C/min). X-ray photoelectron spectroscopy was carried out using a Thermo Scientific ESCALAB 250Xi photoelectron spectrometer. The X-ray source was Al Ka with 50 eV operating at 150 kV and 150W. The base pressure of the system was <math>2 \times 10^{-9}$ Torr.

Experimental Procedures

Synthesis of Cu-MOFs

Crystals of the Cu-MOF were synthesized under hydrothermal conditions: A mixture of $Cu(OAc)_2 \cdot 2H_2O$ (18mg, 0.10mmol), 2,6-Napds (16mg, 0.050 mmol), Ptz (31mg, 0.10mmol)and D.I. water (10 mL)was stirred at rt for 4 hand then transferred to a 30 mL Teflon-lined autoclave. The autoclaves were heated at 170 °C for 4 days under autogenous pressure, followed by slow cooling at a rate of 10°C/min to rt. Dark red block crystals were isolated after filtration and washed by D.I. water three times. Yield: 38 mg (76% based on Cu(OAc)_2 \cdot 2H_2O).

General Procedure for the Catalytic Reaction

To a mixture of the phenylacetylene (**1a**, 102 mg, 1.0 mmol) and benzylazide (**2a**, 133 mg, 1.0 mmol) in a sample vial was added the Cu-MOF catalyst (1.3 mg, 0.0025 mmol, 0.25 mol %). the mixture was stirred at 50 °C for the time given in the Tables (see text). After completion of the reaction, CH_2Cl_2 (2 mL) was added and the mixture was centrifuged to recover the catalyst. The organic layer was concentrated and thecrude product was purified by column chromatography. Before reuse, the recovered catalyst was washed with CH_2Cl_2 (5 mL) and activated by heating at 50 °C under vacuum for 2 h.

Table S1. Crystal data and structure refinement for Cu-MOF

Identification code	Cu-MOF	
Empirical formula	C23 H16 Cu N6 O4 S	
Formula weight	536.04	
Temperature	98(2) K	
Wavelength	0.71073 Å	
Crystal system, space group	Triclinic, P-1	
Unit cell dimensions	a = 8.886(2) Å alpha = $68.732(11)$ deg.	
	b = 10.307(3) Å beta = 70.997(18) deg.	
	c = 12.913(3) Ågamma = 85.639(18) deg.	
Volume	1040.9(5) Å ³	
Z, Calculated density	2, 1.710 mg/m^3	
Absorption coefficient	1.198 mm ⁻¹	
F(000)	546	
Crystal size	0.24 x 0.20 x 0.10 mm	
Theta range for data collection	2.12 to 27.50 deg.	
Limiting indices	-11<=h<=8, -13<=k<=13, -16<=l<=16	
Reflections collected / unique	7526 / 4727 [R(int) = 0.0206]	
Completeness to theta $= 27.50$	98.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.000 and 0.870	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4727 / 0 / 364	
Goodness-of-fit on F ²	0.996	
Final R indices [I>2sigma(I)]	R1 = 0.0361, wR2 = 0.0928	
R indices (all data)	R1 = 0.0375, wR2 = 0.0947	
Largest diff. peak and hole	0.956 and -0.493 e.A ⁻³	
CCDC No.	1013552	



Figure S1.PXRD of as-synthesized Cu-MOF and Cu-MOF after catalytic reactions



Figure S2. TGA curve of Cu-MOF.



Figure S3. XPS spectra of Cu-MOF.

Compound Characterization Data

Except for the product of Table 2, entry 8, all the other products are known compounds and have identical spectroscopic data as those reported.¹

1-Benzyl-4-[2-(trifluoromethyl)phenyl]-1H-1,2,3-triazole (Table 2, entry 8): White solid, mp:



77-78 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.99 (d, J = 7.7 Hz, 1H), 7.79 – 7.71 (m, 2H), 7.64 (t, J = 7.3 Hz, 1H), 7.49 (t, J = 7.5 Hz, 1H), 7.40 (d, J = 8.3 Hz, 3H), 7.31 (t, J = 8.2 Hz, 2H), 5.63 (s, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 144.7, 134.6, 132.0, 131.7, 129.5, 129.1, 128.8, 128.3, 127.9,

127.4, 127.2, 126.2, 125.9, 125.2, 123.0, 54.2. v_{max} (neat, cm⁻¹): 1609, 1578, 1552, 1489, 1459, 1434, 1360, 1344, 1312, 1284, 1225, 1206; HRMS (ESI): *m*/*z* calcd. for C₁₆H₁₃FN₃([M+H]⁺) 304.1056; found 304.1045.

Additional References

(a) Kamata, K.; Nakagawa, Y.Yamaguchi, K. Mizuno, N. J. Am. Chem. Soc. 2008, 130, 15304–15310. (b)Friscourt, F. Boons, G. J.Org.Lett.2010, 12, 4936–4939. (c)Ladouceur, Sebastien, Soliman, Ahmed M. Zysman-Colman, Eli.Synthesis2011, 3604-3611. (d) Beneteau, V. Olmos, A.Boningari, T. Sommer, J. Pale, P.TetrahedronLett.2010, 51, 3673-3677. (e) Alonso, F. Moglie, Y. Radivoy, G. Yus, M.TetrahedronLett. 2009, 50, 2358–2362. (f)Masuyama, Y. Yoshikawa, K. Suzuki, N. Hara, K. Fukuoka, A. TetrahedronLett.2011, 13, 52, 6916-6918. (g) Nakamura, T. Terashima, T. Ogata, K. Fukuzawa, S. Org.Lett.2011, 13, 620–623.





S-8











S-11



S-12



S-13









S-16



S-17









