Supplementary Information

Linker-Dependent Nitric Oxide Storage and Release Behavior in Cu-Based Metal–Organic Frameworks

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Experimental Details

Reagents

All chemicals were purchased from commercial suppliers and used without further purification unless otherwise stated.

- $Cu(NO_3)_2 \cdot 3H_2O$ (≥99%, Sigma-Aldrich)
- Glutaric acid (≥99%, Sigma-Aldrich)
- 1,2-bis(4-pyridyl)ethylene (≥98%, TCI)
- 4,4′-azopyridine (≥98%, Alfa Aesar)
- N,N-dimethylformamide (DMF, anhydrous, ≥99.8%, Merck)

Table S1. Crystalline data for Cu-MOF 1 and Cu-MOF 2.

	Cu-MOF **1**		Cu-MOF **2**	
Chemical formula	$C_{22}H_{22}Cu_2N_2O_8$		$C_{20}H_{20}Cu_2N_4O_{10}$	
Formula weight	569.49 g/mol		603.48 g/mol	
Temperature	296(2) K		100(2) K	
Wavelength	0.71073 Å		0.71073 Å	
Space group	C 2/c		C 2/c	
a	25.027(14) Å		24.697(11) Å	
b	13.234(8) Å		13.156(5) Å	
c	8.547(5) Å		8.534(3) Å	
α	90°		90°	
β	91.708(5)°		93.86(3)°	
γ	90°		90°	
Volume	2829.(3) $Å^3$		2766.5(18) $Å^3$	
Density (calc.)	1.337 g/cm^3		1.449 g/cm^3	
Reflections collected	19188		45135	
Independent reflections	3654 [R(int) = 0.0866]		3514 [R(int) = 0.0635]	
Goodness-of-fit on F2	0.932		1.079	
Final R indices	2514 data; I>2σ(I)	R_1 = 0.0422, wR_2 = 0.0857	2664 data; I>2σ(I)	R_1 = 0.0549, wR_2 = 0.1536
	all data	R_1 = 0.0697, wR_2 = 0.0933	all data	R_1 = 0.0783, wR_2 = 0.1720
Largest diff. peak and hole	0.456 and -0.572 $eÅ^{-3}$		1.668 and -0.588 $eÅ^{-3}$	

Nitric Oxide Loading and Releasing Studies

For the dehydration process, 10 mg of Cu-MOF 1 or 2 was dehydrated in a vacuum at 150 °C for 24 h, and stored sealed. The activated Cu-MOF was placed in a 40 mL vial, and the vial was placed in a Parr bottle (200 mL) that was connected to an in-house NO reactor. The reactor was flushed with Ar gas (99.99%) thrice for 10 min each to remove oxygen before charging NO. The reaction bottle was then charged under 10 atm of NO using ultrapure grade (99.5%) NO gas provided by Dong-A Specialty Gases (Seoul, Korea), which was purified over KOH pellets to remove trace NO degradation products. The bottle was then sealed for 72 h at 25 C. Prior to removing the NO-charged Cu-MOFs, unreacted NO was purged from the chamber with Ar thrice. The NO⊂Cu-MOFs were stored in a sealed container at –20 °C until further use.

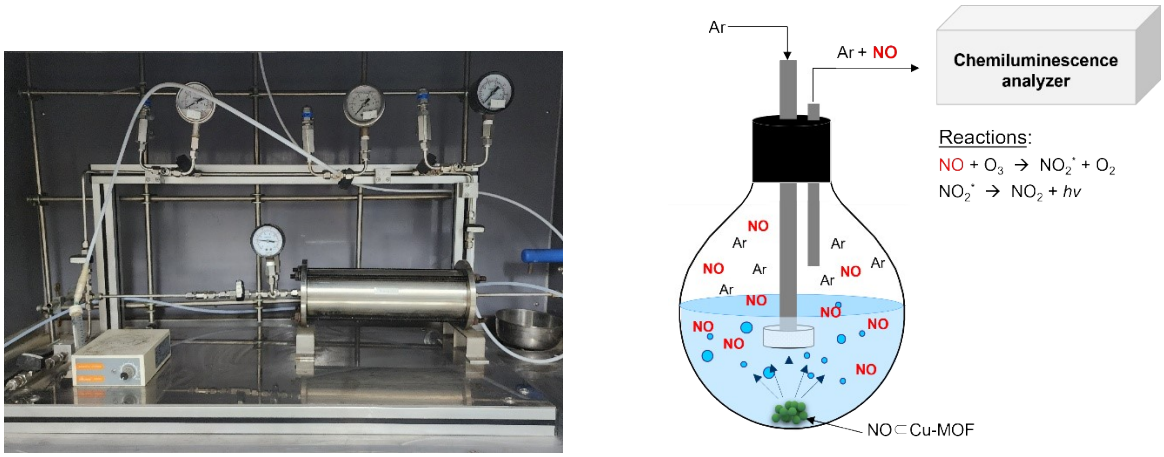

Figure S1. In-house NO reactor for NO loading and Apparatus for NO release measurement.

The NO release profiles of NO⊂Cu-MOFs were monitored in deoxygenated phosphate-buffered saline (PBS; 0.01 M, pH 7.4) at 37 °C using a Sievers 280i chemiluminescence NO analyzer (Boulder, CO, USA). NO released from 5 mg of NO⊂Cu-MOF in 50 mL of PBS (0.01 M, pH 7.4 at 37 °C) was transported to the analyzer by a stream of Ar gas (70 mL·min^{-1}) passed

through the reaction cell. The instrument was calibrated with air passed through a zero filter (0 ppm NO) and a 45 ppm NO gas standard (balanced with N_2; Dong-Woo Gas Tech, Siheung, Korea). The total amount of NO released, t[NO]; maximum flux of NO release, $[NO]_m$; half-life of NO release, $t_{1/2}$; time necessary to reach $[NO]_m$, t_m; and duration time of NO release for sustained fluxes of NO ≥1.0 ppb $\cdot mg^{-1}$, t_d, were determined for the evaluation of NO⊂Cu-MOFs.