Postsynthetic Diazeniumdiolate Formation and NO Release from a MOF

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ELECTRONIC SUPPLEMENTARY INFORMATION

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Experimental Section


Modification of MOFs. A 24 mL (6 dram, VWR Catalog #66011-143) vial containing approximately 55-60 mg of the MOF (IRMOF-3, UMCM-1-NH$_2$, IRMOF-1, and UMCM-1) and ~14 mL of degassed (N$_2$ purged) CHCl$_3$ was placed in a Parr bomb and the bomb was purged with N$_2$ for approximately 1 h. Afterwards, the bomb was charged with 100 psi of NO for 24 h. After NO exposure, it was observed that the CHCl$_3$ solution was turquoise and bubbles evolved from the crystals. The CHCl$_3$ solution was decanted and the crystals were washed with CHCl$_3$ (4×12 mL) before soaking in 12 mL of CHCl$_3$ for 3 d, with fresh CHCl$_3$ added every 24 h.

Modification of NH$_2$-BDC ligand with NO. 2-Amino-1,4-benzenedicarboxylic acid (0.5 mmol, NH$_2$-BDC) was placed in a tall, thin 24 mL vial and dissolved in 12 mL of degassed (N$_2$ purged) MeOH. The vial was placed in a Parr bomb and the bomb was purged with N$_2$ for approximately 1 h. Afterwards, the bomb was charged with 100 psi of NO for 24 h. After NO exposure, an orange precipitate had formed on the side of the vial. The orange solid was isolated by filtration through a medium porous Buchner funnel, washed copiously with MeOH, and vacuum dried at room temperature.

Solid State UV-Vis analysis. Approximately 15-20 mg of modified/NO exposed MOF (typically soaked in CHCl$_3$) was air dried for ~15 min before UV-Vis analysis. The samples were then gently crushed and placed on the sample holder and flattened with a spatula. Solid-state spectra were collected using a StellarNet EPP2000C spectrometer with a diffuse reflectance probe.

FT-IR analysis. Approximately 5-10 mg of modified/NO exposed MOF (typically soaked in CHCl$_3$) was air dried for ~15 min before FT-IR analysis. FT-IR spectra were collected using a Bruker ALPHA-P FT-IR spectrometer with diamond ATR.
D8 Advance diffractometer at 40 kV and 40 mA with Cu Kα \((\lambda = 1.5418 \text{ Å})\). The experimental backgrounds were corrected and data was smoothed using the Jade 5.0 software package. MOF samples were air dried for \(\sim 15\) min prior to data collection. IRMOF-3 and IRMOF-3-NONO (15 mg soaked in DMF) was measured with a scan speed of 10 sec/step, a step size of 0.02° in \(2\theta\), and a \(2\theta\) range of 3-40°. UMCM-1-NH₂ and UMCM-1-NONO (soaked in CHCl₃) was measured with a scan speed of 5 sec/step, a step size of 0.02° in \(2\theta\), and a \(2\theta\) range of 2-35°.

**Thermal Analysis.** Approximately 10-20 mg of modified MOF was used for TGA measurements. The samples were dried on a vacuum line for 24 h at room temperature. Samples were analyzed under a stream of N₂ using a TA Instrument Q600 SDT running from room temperature to 600 °C with a scan rate of 5 °C/min.

**BET Surface Area Analysis.** Approximately 40-60 mg of modified MOF (previously soaked in CHCl₃) was evacuated on a vacuum line for 24 h at room temperature. The sample was then transferred to a preweighed sample tube and degassed at 25 °C on a Micromeritics ASAP 2020 Adsorption Analyzer for a minimum of 12 h or until the outgas rate was <5 mmHg. The sample tube was re-weighed to obtain a consistent mass for the degassed modified MOF. BET surface area (m²/g) measurements were collected at 77 K by N₂ on a Micromeritics ASAP 2020 Adsorption Analyzer using a volumetric technique at the pressure range of \(P/P₀ = 0.015-0.15\).

**Single-Crystal X-ray Diffraction.** Single crystals of the modified MOF in CHCl₃ were mounted on nylon loops with Paratone oil and placed under a nitrogen cold stream (100 K for IRMOF-3-NONO and 200 K for UMCM-1-NONO). Data were collected on Bruker Apex diffractometers using Mo Kα radiation (\(\lambda = 0.71073 \text{ Å}\)) controlled using the APEX 2.0 software package. Cell determinations were performed on all modified MOFs using the APEX software package.

**NO release studies.** 20.0 mL of 0.01 M phosphate buffer solution (pH 7.4) was transferred to a vial. \(\sim 10\) mg of sample (dried under vacuum overnight at room temperature) was accurately weighed out and transferred to the phosphate buffer solution and sonicated for 15 min. A 200 µL aliquot of the digested sample was diluted to a final volume of 2.5 mL with phosphate buffer solution. A 50 µL aliquot of the diluted sample was transferred to the well of a 96-well microliter plate. Each well was treated with the components of the Griess reagent system as per the manufacturer instructions (Promega). The amount of nitrite was determined spectrophotometrically with a BioTek ELx808-plate reader monitoring the absorbance at 540 nm.
Figure S1. Diffuse reflectance solid-state UV/Vis spectra of A) NONO-BDC (—) and NH$_2$-BDC (−−), B) UMCM-1-NONO (—) and UMCM-1-NH$_2$ (−−), C) IRMOF-1+NO (—) and IRMOF-1 (−−), and D) UMCM-1+NO (—) and UMCM-1 (−−).
Figure S2. FT-IR spectra of A) UMCM-1-NH$_2$ (---) and UMCM-1-NONO (--), B) NH$_2$-BDC (---) and NONO-BDC (--), C) IRMOF-1 (---) and IRMOF-1+NO (--), and D) UMCM-1 (---) and UMCM-1+NO (--).
Figure S3. Crystals of IRMOF-3 (top) and UMCM-1-NH₂ (bottom) after modification with NO.
Figure S4. PXRD analysis of A) IRMOF-3 (---) and IRMOF-3-NONO (−−−) and B) UMCM-1-NH₂ (----) and UMCM-1-NONO (-----).

Figure S5. TGA Analysis of A) IRMOF-3, B) IRMOF-3-NONO, C) UMCM-1-NH₂, and D) UMCM-1-NONO.
Figure S6. Derivative plots of the TGA analysis of A) IRMOF-3-NONO (––) and IRMOF-3 (– –) and B) UMCM-1-NONO (––) and UMCM-1-NH₂ (– –). The boxed area indicates the area of weight loss due to the NONOate functionality.

Figure S7. N₂ adsorption isotherm of A) IRMOF-3-NONO and B) UMCM-1-NONO.

Figure S8. Release of NO from IRMOF-3-NONO after the initial release (left) and 10 days later (right).