

Supplementary Information

Rendering Non-Energetic Microporous Coordination Polymers Explosive

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Table of Contents

1. Experimental Procedures
2. Powder X-ray Diffraction (PXRD) of MOF-5, MOF-5-TNM, and MOF-5-HNE
3. Nitrogen sorption isotherms and consistency criteria for applying the BET method to the N₂ sorption isotherms of MOF-5
4. Differential Scanning Calorimetry
5. Vapor Pressure Experiments
6. Solid Decomposition Product Analysis: thermal initiation
7. Solid Decomposition Product Analysis: initiation by impact
8. Cheetah Calculations
9. References

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1. Experimental Procedures

Caution: Although no unplanned detonations were encountered during this work, TNM, HNE, MOF-5-TNM and MOF-5-HNE are all dangerous explosives. Proper safety practices and equipment was used to prevent an explosion due to friction, heat, static shock, or impact. Be aware that the potential for severe injury exists if these materials are handled improperly.

Synthesis of MOF-5. MOF-5 was synthesized by a method previously reported in the literature.¹

Activation. Samples were activated by exposure to a dynamic vacuum (10^{-2} Torr) for 24 hours.

Synthesis of Hexanitroethane (HNE). HNE was synthesized by a method previously reported in the literature.²

MOF-5-TNM. For the adsorption of TNM, 10.0 mg of MOF-5 was weighed into a 4 mL vial in an N₂ filled glovebox. Outside of the glovebox, TNM (0.20 mL) was added to a 20 mL scintillation vial, capped, and allowed to come to equilibrium with the atmosphere in the vial. The 4 mL vial containing the MOF-5 was removed from the glovebox, opened to air, inserted into the 20 mL vial containing TNM, and capped. TNM was allowed to vaporize, come to equilibrium with the chamber, and adsorb into MOF-5 for variable amounts of time. To stop the adsorption, the 4 mL vial (containing MOF-5-TNM) was removed from the chamber and capped.

MOF-5-HNE. For the adsorption of HNE, 10.0 mg of MOF-5 was weighed into a 4 mL vial in a N₂ filled glovebox. The sample was then removed from the glovebox and

transferred to a small aluminium boat. This boat was inserted into a Schlenk tube containing 25.0 mg of HNE. The Schlenk tube was connected to a vacuum line and carefully evacuated to 50 mTorr, then closed. HNE was allowed to sublime in the chamber and adsorb into MOF-5 for variable amounts of time. The adsorption was stopped by releasing the vacuum in the chamber, the product (MOF-5-HNE) was collected in a 4 mL vial, and capped.

Powder X-ray diffraction. Powder X-ray diffraction (PXRD) patterns were collected using a Rigaku R-axis Spider diffractometer with an image plate detector and graphite monochromated Cu-K α radiation (1.5406 Å). The patterns were collected with the tube operating at 40 kV and 44 mA. Images were collected in transmission mode with χ set at 45°, ϕ rotating at 10°/min, and ω oscillating between 5° and 50° to minimize the effects of preferred orientation. Integration of the resulting images was performed in the AreaMax (2.0) software package with a step size of 0.1 in 2θ .

Gas sorption measurements. Sorption experiments were carried out using a NOVA *e*-series 4200 surface area analyser (Quantachrome Instruments, Boynton Beach, Florida, USA). N₂ (99.999%) was purchased from Cryogenic Gases and used as received. For N₂ measurements, a glass sample cell was charged with ~20 mg sample and analysed at 77 K. Sorption isotherms were collected in the NOVAwin software.

Thermogravimetric Analysis. A TA Instruments Q50 TGA was used to obtain thermogravimetric data in which the analyte was heated from ~25 °C to 600 °C at a rate of 10 °C/min and analysed in a platinum pan under flowing nitrogen.

Vapor pressure measurements. Vapor pressure experiments (shown in Figure S4 and S5) were performed as previously described.³ Here, the TGA was heated to 30 °C for

MOF-5-TNM and 45 °C for MOF-5-HNE and held for 10 hours. In this case, the degree by which the vapor pressure was suppressed was calculated by dividing the slope of the weight loss of the pure oxidant by the slope of weight loss of the MCP-oxidant mixture.

Differential Scanning Calorimetry. Thermograms of each sample were recorded on a TA Instruments Q10 DSC. All experiments were run using a TzeroTM DSC High Pressure Capsule Kit and studied under a nitrogen purge with a heating rate of 20 °C/min, covering the temperature range of ~100 °C to ~300 °C. Calibration of the instrument was performed using an indium standard. Thermograms were analysed using TA Universal Analysis 2000, V 4.5A.

Raman Spectroscopy. Raman spectra were obtained using a Renishaw inVia Raman microscope equipped with a CCD detector, 785 nm laser, 1200 lines/mm grating, and 65 µm slit was used for collecting data. Spectra were collected using a static scan mode and analysed using the Wire 4.2 software package. Calibration of the instrument was performed using a silicon standard for all experiments.

2. Powder X-Ray Diffraction (PXRD) of MOF-5, MOF-5-TNM (30 min, 1 hour, 3 hours, and 24 hours), and MOF-5-HNE (5 minutes, 10 minutes, 15 minutes, 30 minutes, 1 hour)

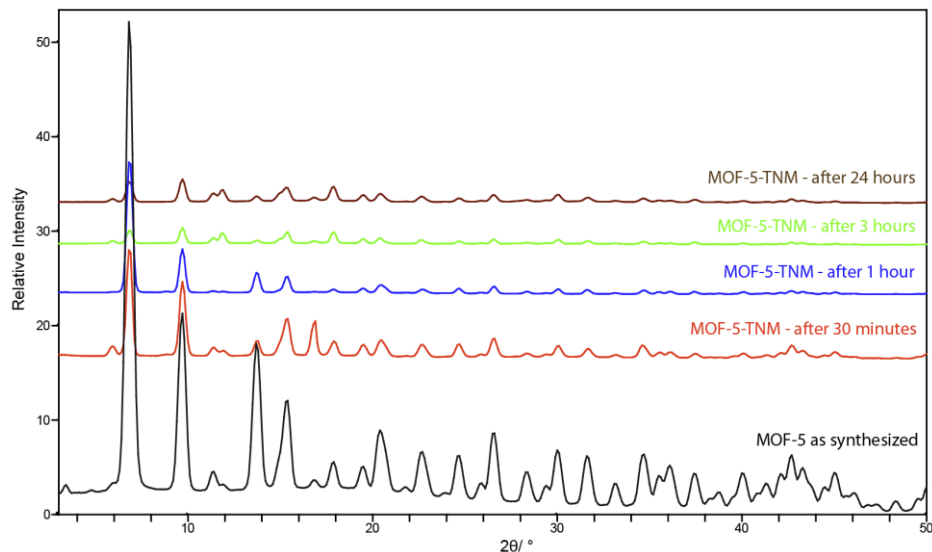


Figure S1. Powder X-Ray diffraction patterns collected to monitor the structural integrity of MOF-5 as a function of TNM loading – As synthesized MOF-5 (black), MOF-5-TNM after 30 minutes (red), MOF-5-TNM after 1 hour (blue), MOF-5-TNM after 3 hours (green), and MOF-5-TNM after 24 hours (brown).

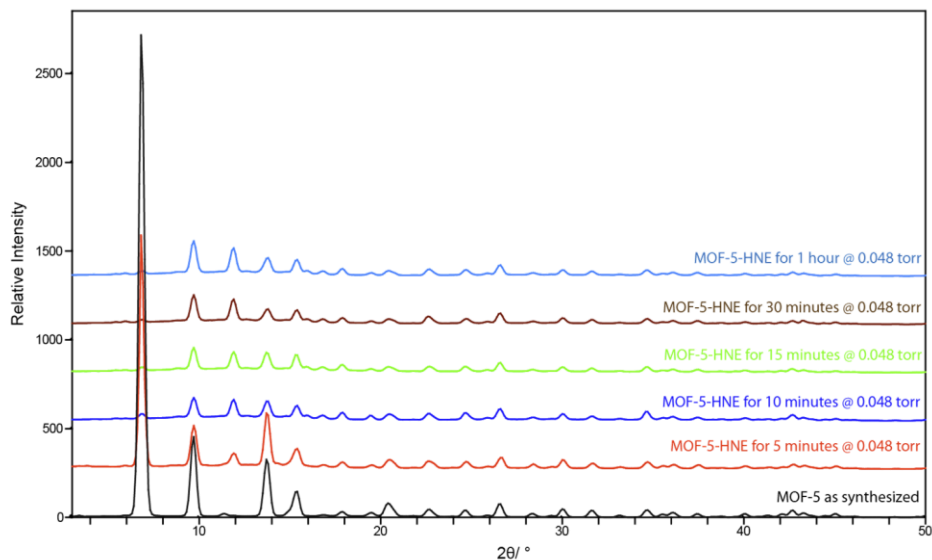


Figure S2. Powder X-Ray diffraction patterns collected to monitor the structural integrity of MOF-5 as a function of HNE loading at 0.048 torr – As synthesized MOF-5 (black), MOF-5-HNE after 5 minutes (red), MOF-5-HNE after 10 minutes (blue), MOF-5-HNE

after 15 minutes (green), MOF-5-HNE after 30 minutes (brown), and MOF-5-HNE after 1 hour (light blue).

3. Nitrogen sorption isotherm and consistency criteria for applying the BET method to the N₂ sorption isotherms of MOF-5⁴

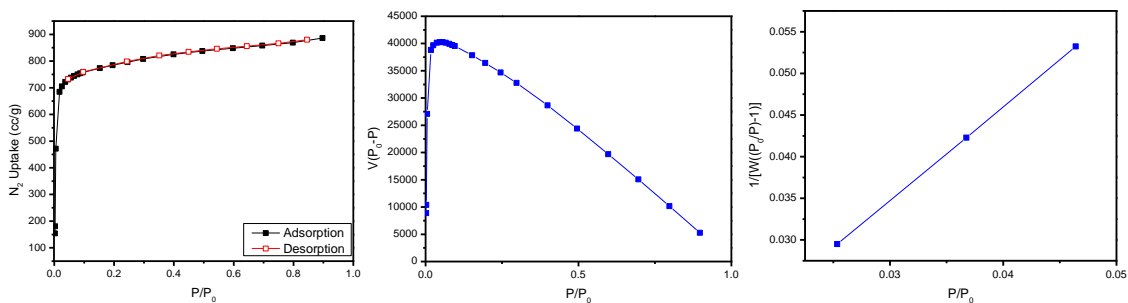


Figure S3. (left) Nitrogen sorption isotherm collected on MOF-5, (middle) Consistency criterion plot for determining the P/P₀ range for BET analysis, and (right) BET plot used to calculate the surface area of MOF-5 (3087 m²g⁻¹)

4. Differential Scanning Calorimetry (DSC)

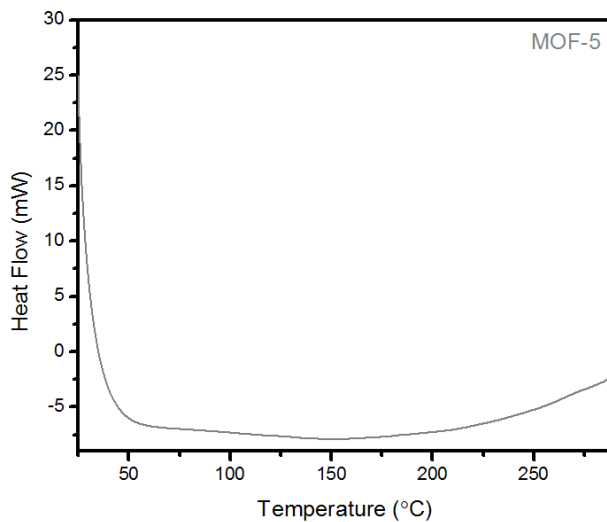


Figure S4. DSC of thermogram of MOF-5 at 20 °C min⁻¹ in the high-pressure pans

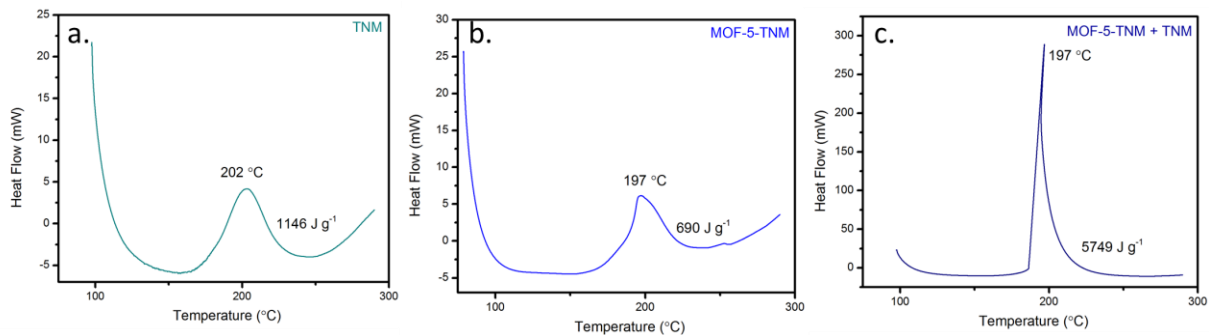


Figure S5. DSC of thermograms of TNM (0.754 mg), MOF-5-TNM (1.01 mg), and MOF-5-TNM (0.650 mg) with excess TNM (0.786 mg) at 20 °C min⁻¹ in the high-pressure pans

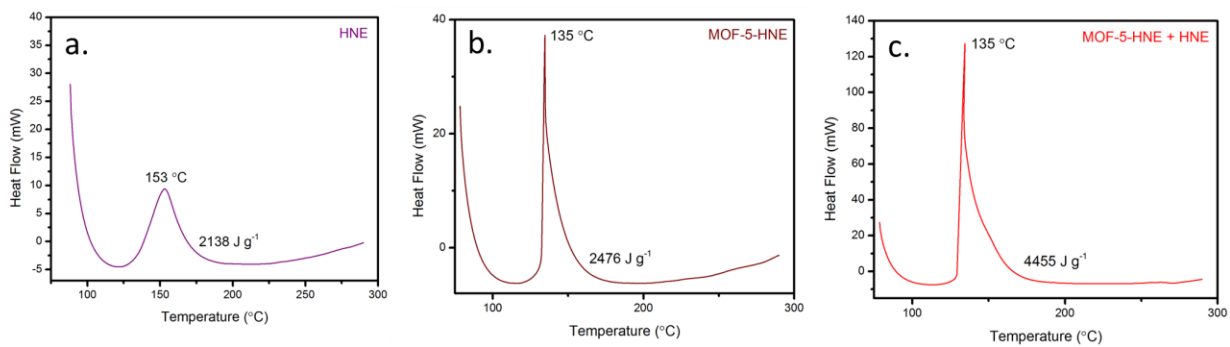


Figure S6. DSC of thermograms of HNE (0.460 mg), MOF-5-HNE (0.460 mg), and MOF-5-HNE (0.426 mg) with excess HNE (0.514 mg) at 20 °C min⁻¹ in the high-pressure pans

5. Vapor Pressure Measurements

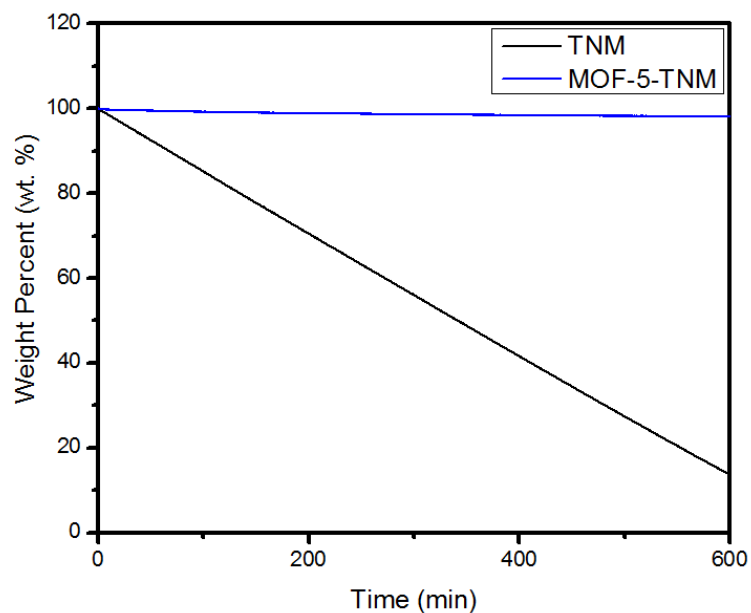


Figure S7. Plot of the weight percent loss as a function of time for TNM (black) and MOF-5-TNM (blue).

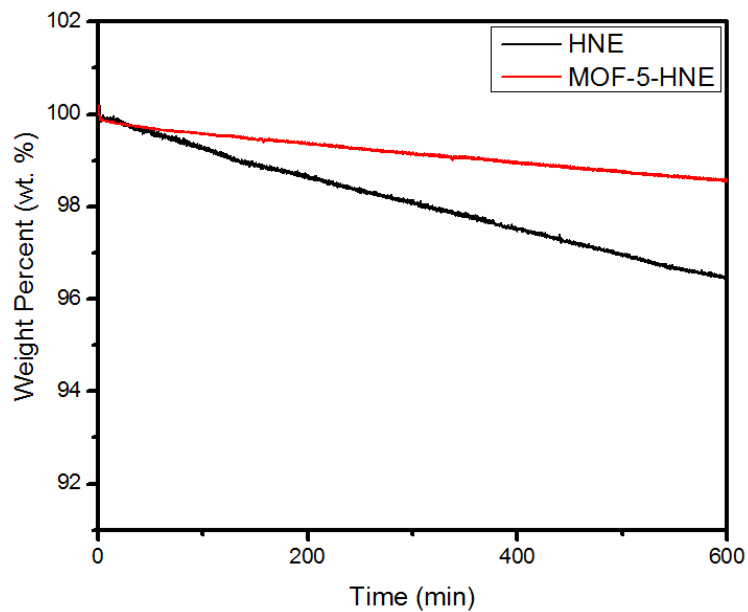


Figure S8. Plot of the weight percent loss as a function of time for HNE (black) and MOF-5-HNE (red).

6. Solid Decomposition Product Analysis: thermal initiation

MOF-5-TNM

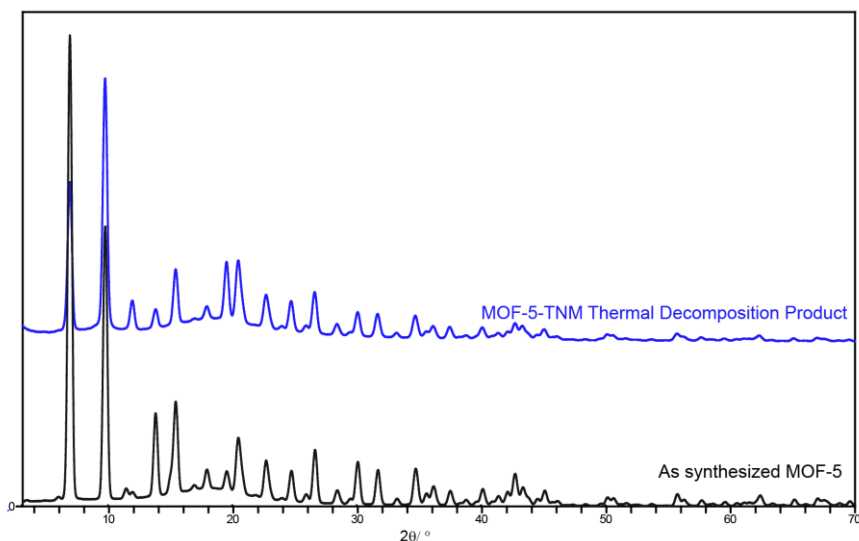


Figure S9. PXRD of as synthesized MOF-5 (black) and the thermal decomposition product of MOF-5-TNM (blue) showing a retention of the crystal structure after thermal initiation

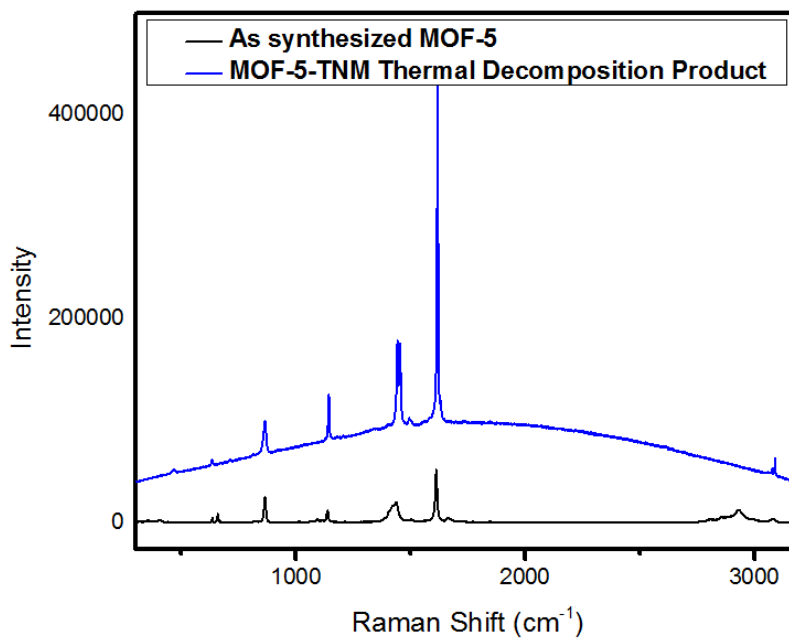


Figure S10. Raman Spectra of as synthesized MOF-5 (black) and the thermal decomposition product of MOF-5-TNM (blue)

MOF-5-HNE

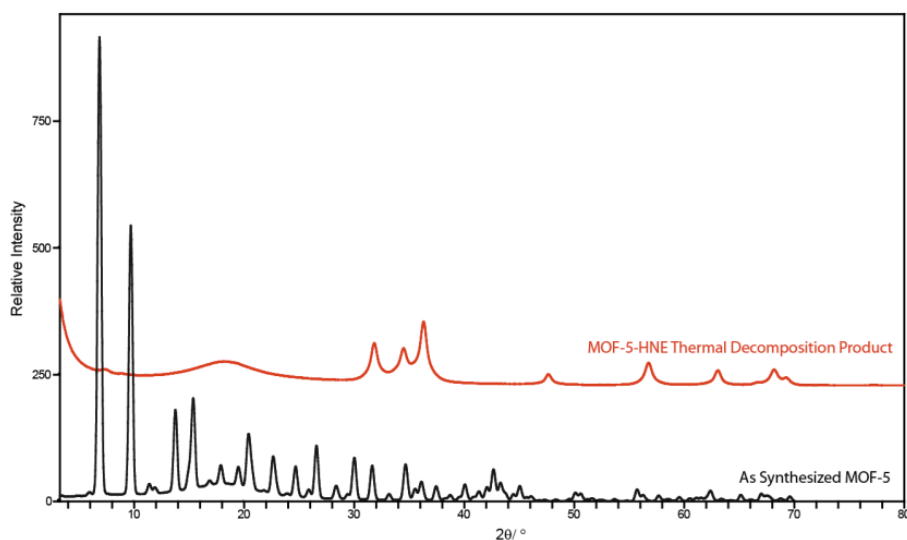


Figure S11. PXRD of as synthesized MOF-5 (black) and the thermal decomposition product of MOF-5-HNE (red) showing the conversion of MOF-5-HNE to a mixture of carbon and zinc oxide

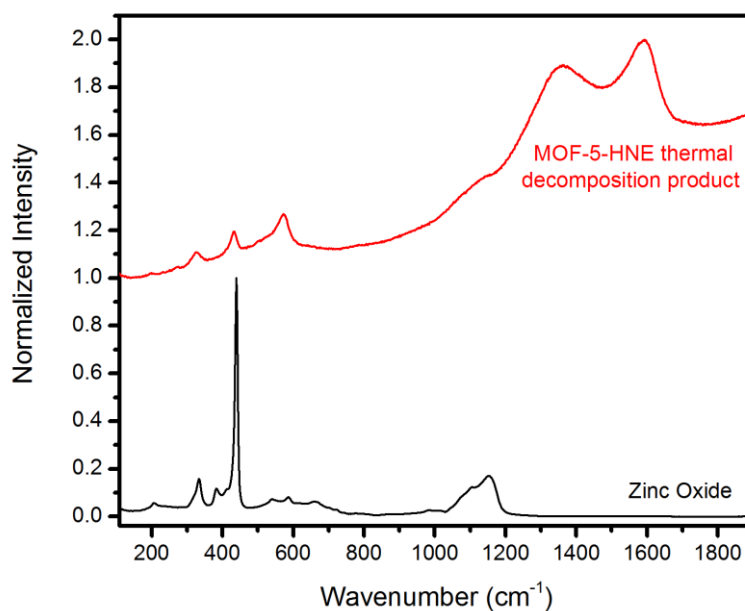


Figure S12. Raman spectra of zinc oxide (black) and the thermal decomposition product of MOF-5-HNE (red) showing the conversion of MOF-5-HNE to a mixture of carbon and zinc oxide

7. Solid Decomposition Product Analysis: initiation by impact

MOF-5-TNM

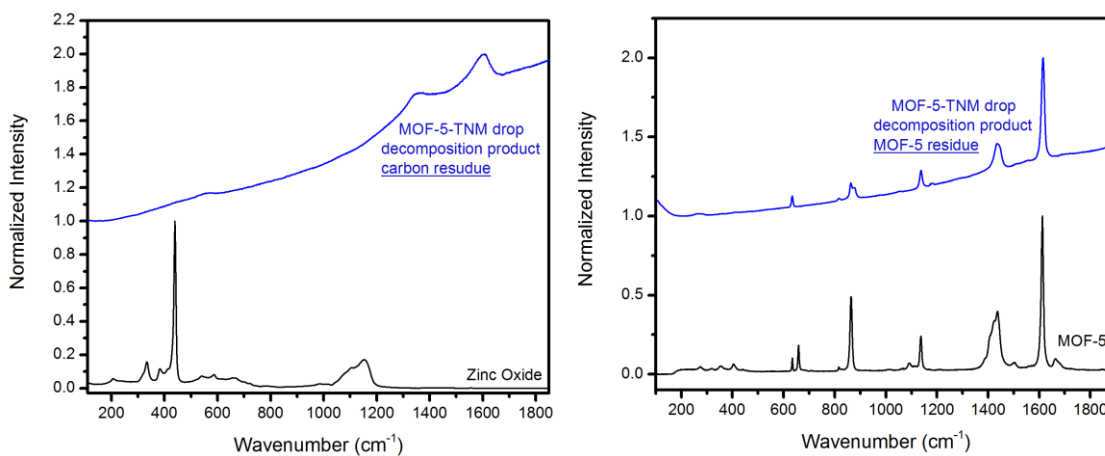


Figure S13. Raman Spectra of the impact decomposition products for MOF-5-TNM: (left) MOF-5-TNM decomposition product (carbon residue, blue) and Zinc oxide (black) for comparison and (right) MOF-5-TNM decomposition product (MOF-5 residue, blue) and MOF-5 for reference (black).

MOF-5-HNE

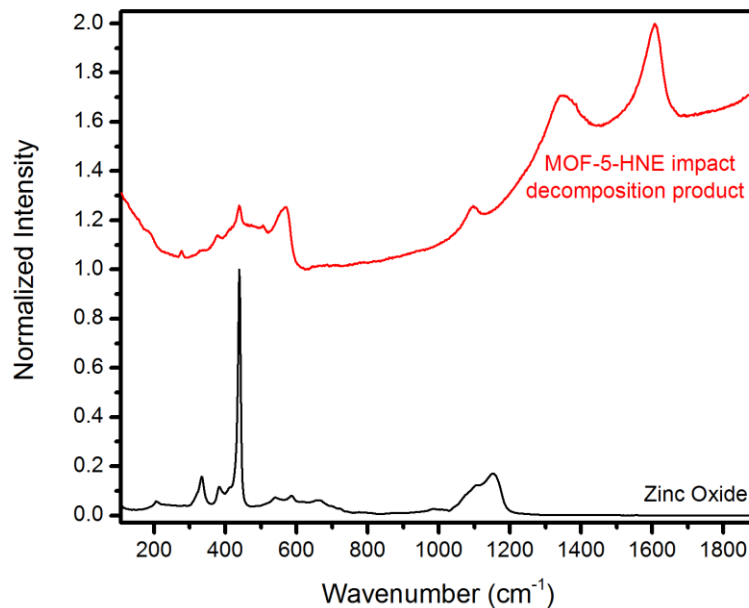


Figure S14. Raman spectra of zinc oxide (black) and the decomposition product of MOF-5-HNE (red) after impact showing the conversion of MOF-5-HNE to a mixture of carbon and zinc oxide

8. Cheetah Calculations

The values that were important for evaluating the performance of the oxidants (TNM/HNE), MOF-5, and the composite materials were density, molecular formula, and heat of formation.⁵ These values were plugged into Cheetah 7.0 and used to determine the oxygen balance and detonation velocity. The relative ratios of the oxidants to MOF-5 were evaluated using TGA and used to determine the molecular weight and empirical formula of the composite materials. The heat of formation of the oxidants were available through Cheetah and the MOF-5 heat of formation was taken from the literature.⁵ The total heat of formation for the composite was estimated as shown below:

$$\Delta H_{f-composite} = \Delta H_{f-oxidant} + \Delta H_{f-MOF} \left(\frac{MW \text{ contribution of MOF from composite}}{MW \text{ of pure MOF}} \right)$$

The density of the composites was determined using the following calculation:

$$Density (g \text{ cm}^{-3}) = density \text{ of MOF} + [density \text{ of MOF} \times ratio \text{ of oxidant to MOF}]$$

9. References

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