Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supplementary Information

Adsorption of Tetranitromethane in Zeolitic Imidazolate Frameworks Yields Energetic Materials

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1. Experimental procedures

Caution: Although no unplanned detonations were encountered during this work, ZIF-8-TNM and ZIF-70-TNM are dangerous energetic materials. Proper safety practices and equipment were 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 ZIF-8. ZIF-8 was synthesized and activated using methods previously reported in literature[1] and stored in a nitrogen glovebox. The surface area of the material was confirmed by N_2 adsorption (Figure S3).

Synthesis of ZIF-70. ZIF-70 was synthesized and activated using methods previously reported in literature[2] and stored in a nitrogen glovebox. The surface area of the material was confirmed by N_2 adsorption (Figure S4). A sample of ZIF-70 was dissolved in DCl/D_2O and a ^{1}H NMR spectrum was obtained; integration of the spectrum indicated a 2.05:1 ratio of imidazole to 2-nitroimidazole in our ZIF-70.

ZIF-8-TNM. To absorb TNM, 10.0 mg of ZIF-8 was weighed into a 4 mL vial in an N_2 filled glove box. The sample was then removed from the glove box and 0.2 mL of TNM was added directly to the vial containing ZIF-8 crystals at room temperature. The 4 mL vial containing ZIF-8 and TNM was placed on a heat block set at 50 °C. TNM was allowed to absorb into ZIF-8. To stop the adsorption, the 4 mL vial containing ZIF-8-TNM was removed from the heat block, the crystals were vacuum filtered and rinsed with cold pentane.

ZIF-70-TNM. To absorb TNM, 10.0 mg of ZIF-70 was weighed into a 4 mL vial in an N_2 filled glove box. Separately, 0.2 mL of TNM was added to a 20 mL glass vial outside the glovebox. The 4 mL vial containing ZIF-70 was removed from the glovebox, uncapped, and then inserted into the 20 mL glass vial containing ZIF-70 and the 20 mL vial then capped. TNM was allowed to vaporize, come to equilibrium and absorb into ZIF-70. To stop the adsorption, the 4 mL vial containing ZIF-70-TNM was removed from the system and capped.

Powder X-Ray diffraction. Powder patterns of ZIF-8, ZIF-70, ZIF-8-TNM and ZIF-70-TNM were collected with a Panalytical Empyrean using Cu-Kα radiation (λ = 1.54187 Å) and operating at 45 kV and 40 mA. The instrument is equipped with a Bragg-Brentano HD X-ray optic and an X'Celerator Scientific detector operating in continuous 1D scanning mode. Samples were prepared by pressing them onto a glass slide fitted into a sample holder to minimize height error. The patterns were collected by scanning 2θ from 5° to 50° with a 0.02° step size and a step speed of 0.125 seconds. The data were processed using Jade 8 XRD Pattern Processing, Identification & Quantification analysis software (Materials Data, Inc.). The powder patterns were compared to respective simulated powder patterns from single crystal XRD structures available from the Cambridge Crystallographic Data Centre and were found to be in good agreement with the predicted patterns.

Gas sorption measurements. Sorption experiments were carried out using a NOVA - series 4200 surface area analyzer (Quantachrome Instruments, Boynton Beach, Florida, USA). N_2

(99.999%) was purchased from Cryogenic Gases and used as received. For N_2 measurements, a glass sample cell was charged with ~50 to 100 mg of sample and analyzed 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 analyzed in a platinum pan under flowing nitrogen.

Differential scanning calorimetry. Thermograms of each sample were recorded on a TA Instruments Q10 DSC. All experiments were run using a Tzero^{TM} DSC High Pressure Capsule Kit and studied under a nitrogen purge with a heating rate of 50 °C/min, covering the temperature range of ~25 °C to 350 °C. This heating rates is fast enough that full equilibration of the sample temperature will not be achieved and thus comparisons of relative decomposition temperatures are most appropriate. Calibration of the instrument was performed using an indium standard. Thermograms were analyzed using TA Universal Analysis 2000, V 4.5A. All samples were hermetically sealed in high pressure capsules for DSC measurements, and were weighed prior to and after heating to ensure that no mass escaped the pan during analysis.

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 used for collecting data. Spectra were collected using static scan mode and analyzed using the Wire 4.2 software package. Calibration of the instrument was performed using a silicon standard for all experiments.

Oxygen bomb calorimetry. The enthalpy of formation of ZIF-70 was determined with a constant volume Parr 6200 isoperibol calorimeter fitted with a 1109X high strength semi-micro oxygen combustion vessel. This vessel is suitable for testing energetic materials and is optimized for the measurement of small energy releases. Distilled water was used to fill the bucket and nichrome wire was used to ignite each sample, approximately 10 cm per test. Samples were pressed into pellets and combusted in an oxygen atmosphere at a pressure of 29 bar. ZIF-8 (which has a known enthalpy of formation) was used to determine the calorimeter constant. For each pellet pressed, approximately 100 mg of as-synthesized ZIF-70 was ground into a powder in an N_2 filled glovebox. The samples were removed from the glovebox and pressed using a Parr pellet press to form a pellet. The reported data are the average of 3 single measurements.

2. Powder X-Ray Analysis (PXRD) of ZIF-8, ZIF-8-TNM, ZIF-70, and ZIF-70-TNM

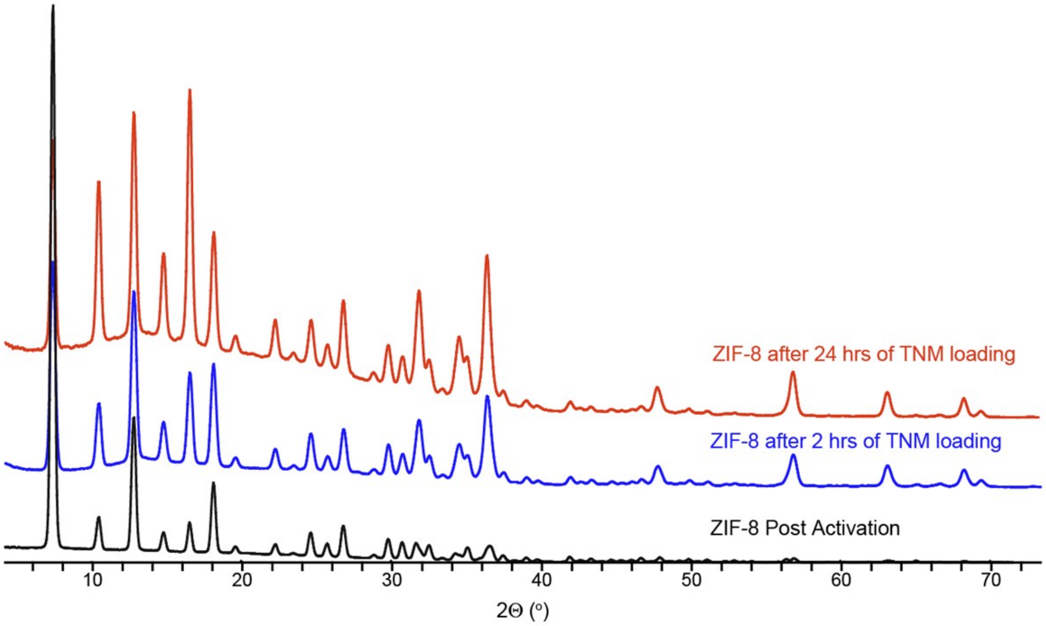

Figure S1. Powder X-Ray diffraction patterns collected to monitor the structural integrity of ZIF-8 during TNM loading at elevated temperatures: as synthesized ZIF-8 (black), ZIF-8-TNM after 2 hours (blue), ZIF-8-TNM after 24 hours (red).

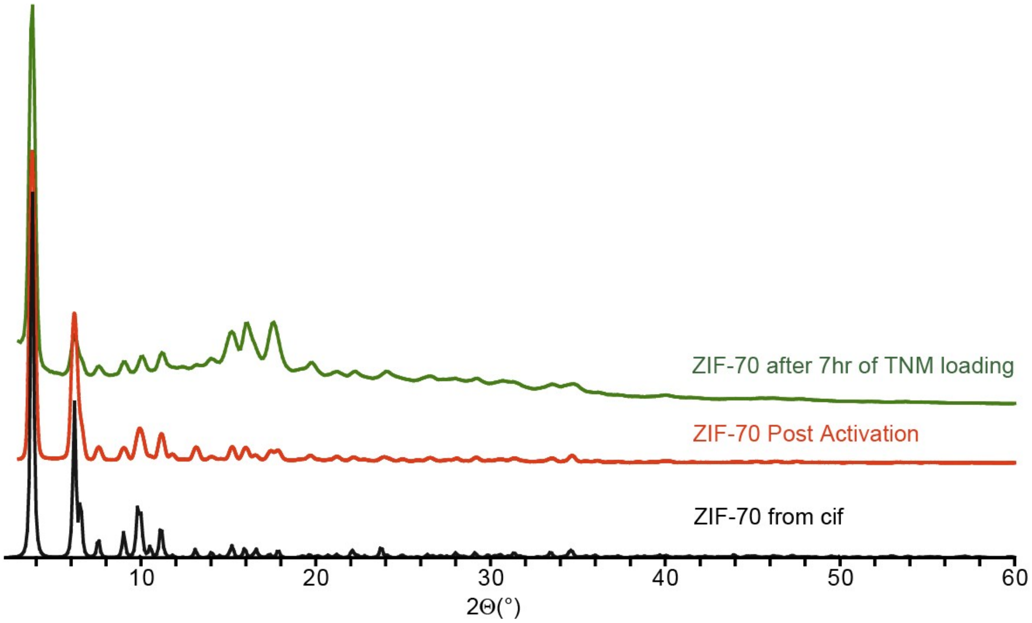

Figure S2. Powder X-Ray diffraction patterns collected to monitor the structural integrity of ZIF-70 during TNM vapor loading at room temperature: simulated ZIF-70 pattern (black), as synthesized ZIF-70-TNM (red), ZIF-70-TNM after 7 hours (green).

3. N_2 sorption isotherms and criteria for applying the BET method to N_2 sorption isotherms of ZIF-8 and ZIF-70

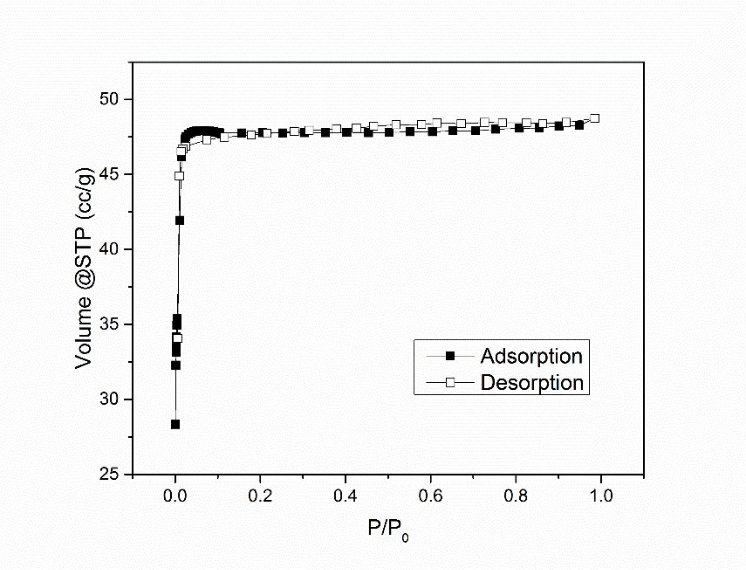

Figure S3. Evacuated ZIF-8 displays Type 1 isothermal behavior and has an apparent surface area of 1388 m^2/g (BET model).

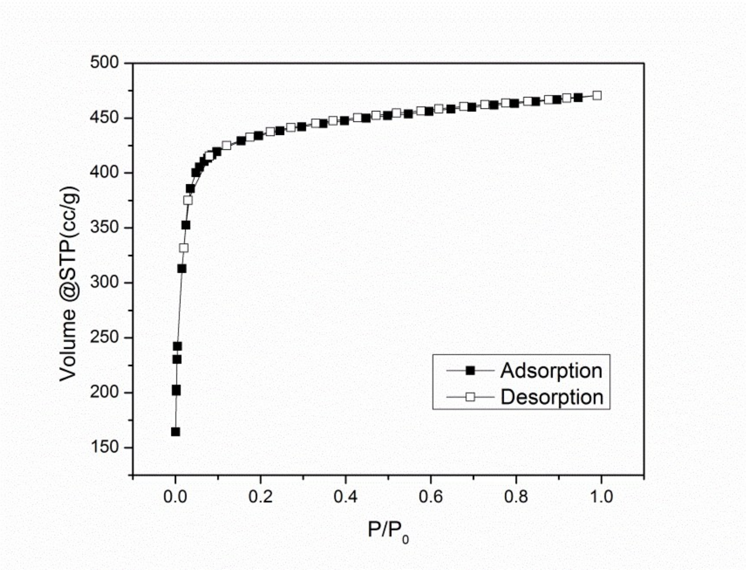

Figure S4. Evacuated ZIF-70 displays Type 1 isotherm behavior and has an apparent surface area of 1776 m^2/g (BET model).

4. Differential scanning calorimetry of TNM, ZIF-8, ZIF-8-TNM, ZIF-70 andZIF-70-TNM

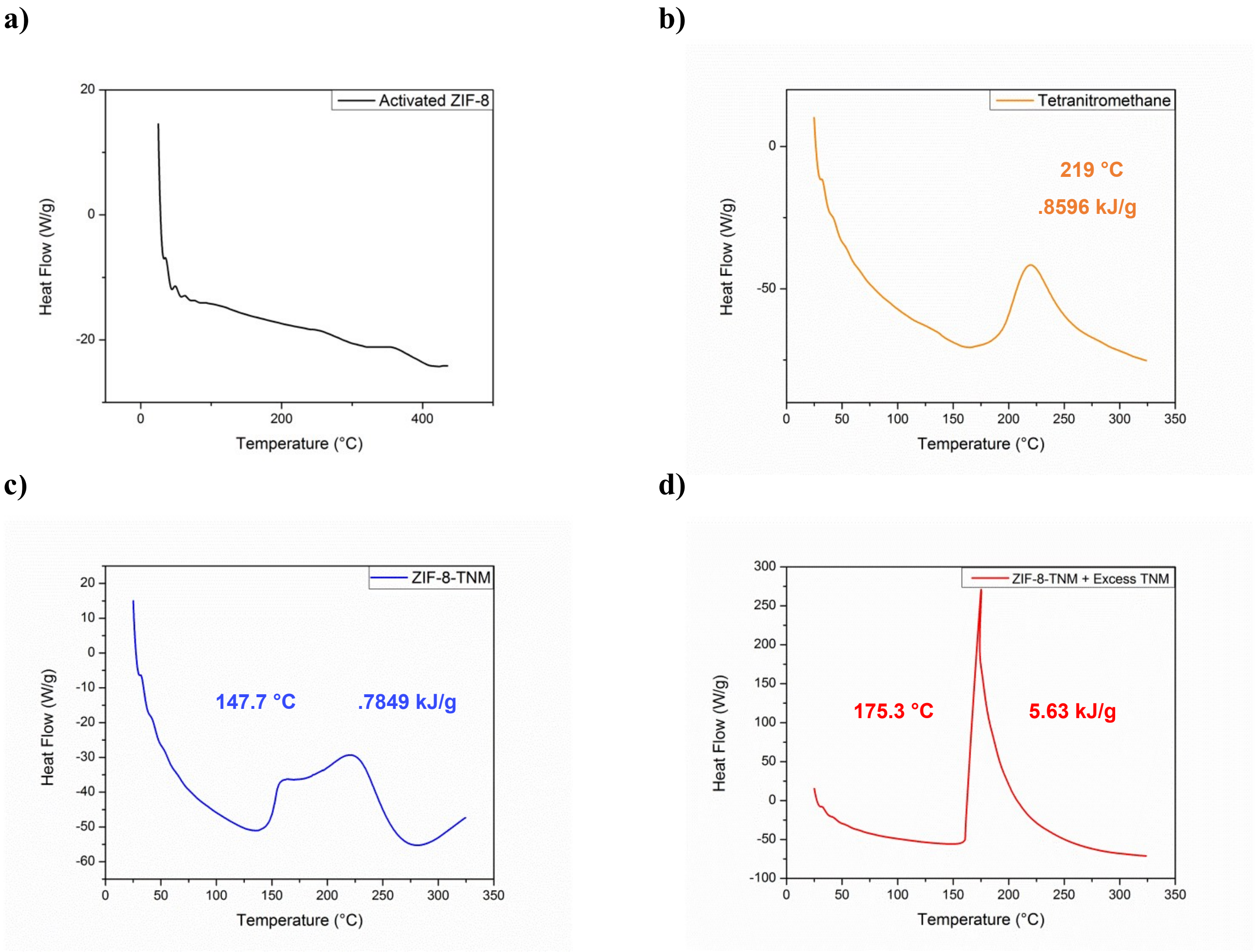

Figure S5. DSC thermograms of activated ZIF-8 collected at 50 °C min^{-1} shows no phase changes occurring up to 450 °C, TNM (1.94 mg), ZIF-8-TNM composite (2.88 mg), and ZIF-8-TNM composite (0.802 mg) + excess TNM (0.941) collected at 50 °C min^{-1} in high pressure pans to contain prevent the release of product gases.

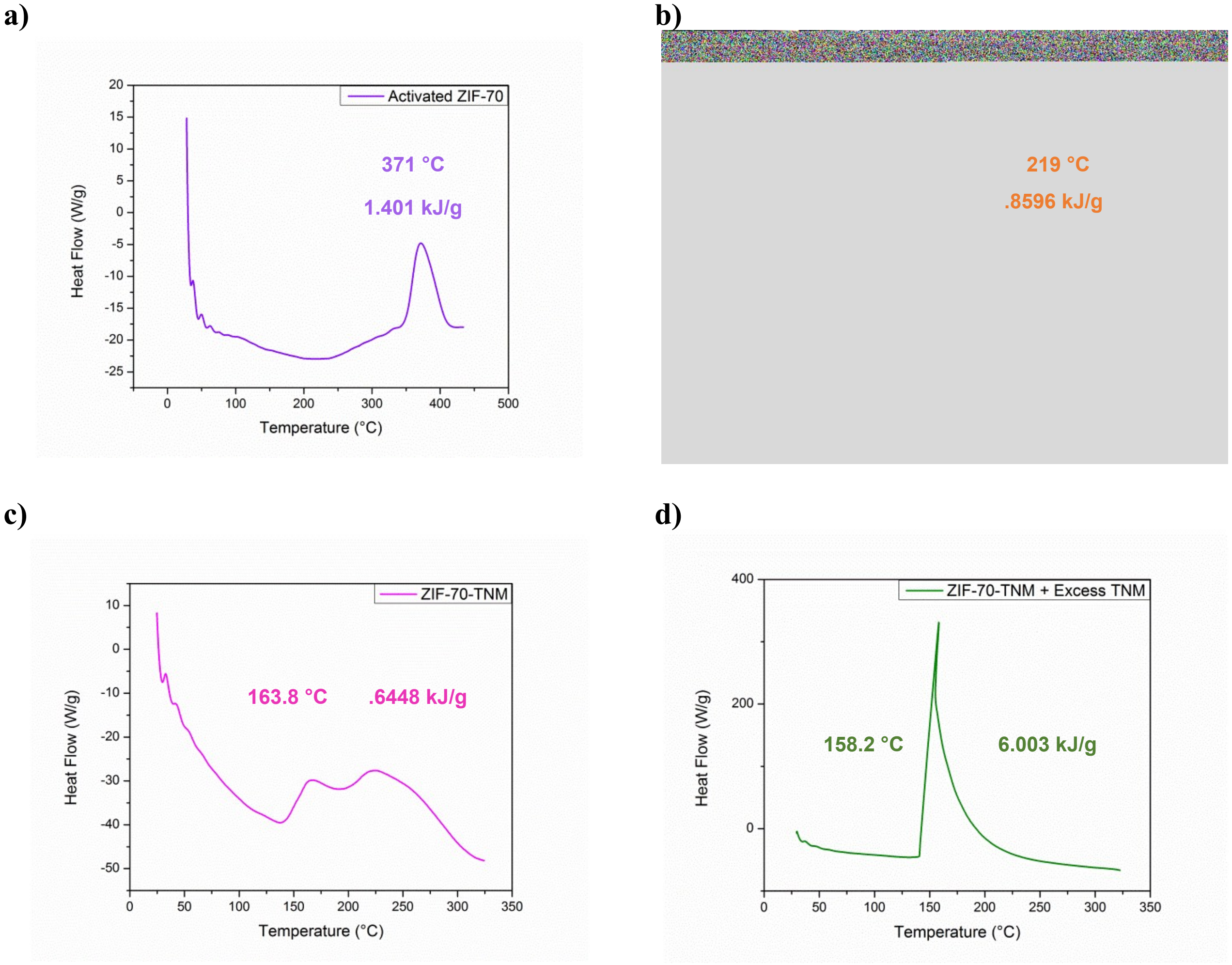

Figure S6. DSC thermogram of ZIF-70 collected at 50 °C min^{-1}in an aluminum hermetic pan displays an exothermic event at 371 °C with energy release that equals 1401 J/g. TNM (1.94 mg), ZIF-70-TNM (1.37 mg), and ZIF-70-TNM (0.814 mg) + excess TNM (0.812 mg) were collected at 50 °C min^{-1} in high pressure pans to contain prevent the release of product gases.

5. Thermogravimetric analysis of ZIF-8 and -70, ZIF-8-TNM, ZIF-70-TNM

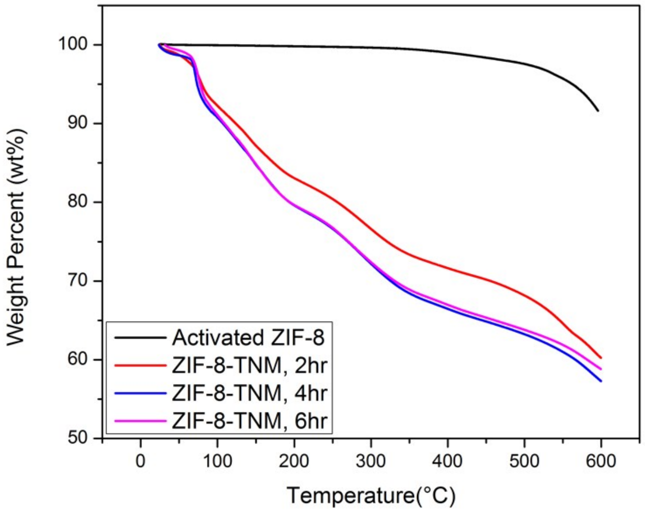

Figure S7. TGA traces of evacuated ZIF-8 and ZIF-8-TNM composites formed with three different loading times. ZIF-8-TNM reaches saturation after 4 hours of loading. Mass loss is a convolution of guest loss and framework decomposition.

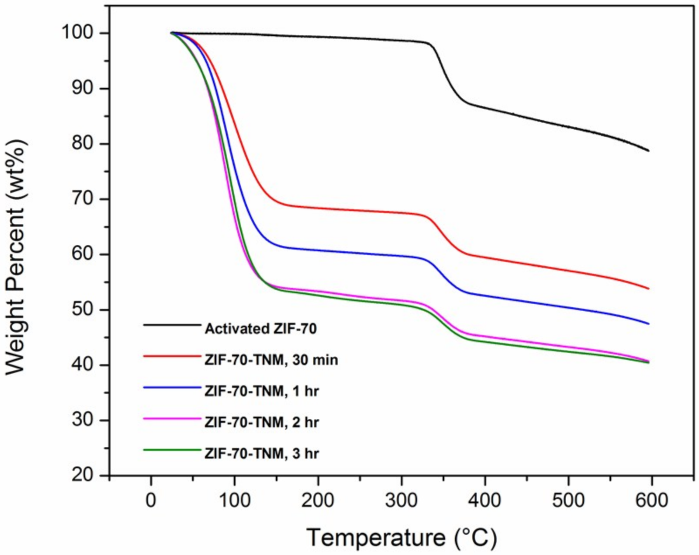

Figure S8. TGA traces of evacuated ZIF-70 and ZIF-70-TNM composites formed with four different loading times. ZIF-8-TNM reaches saturation after 3 hours of loading, at which point the composite is 46.7 wt% TNM.

6. Calculation of ΔH°_f of ZIF-70

Calorimeter calibration with ZIF-8

To determine the heat of formation of our ZIF-70, we first determined a calorimeter constant for our oxygen bomb calorimeter by the combustion of the chemically similar ZIF-8, which has a reported ΔH°_f of -81.5 kJ/mol.[5] The balanced equation for the combustion of ZIF-8 is given by:

$$Zn(C_4H_5N_2)_2\,(s) + 11\,O_2\,(g) \longrightarrow ZnO\,(s) + 8\,CO_2\,(g) + 5\,H_2O\,(l) + 2\,N_2\,(g)$$

With the ΔH°_f of ZnO (*s*), CO_2 (*g*), and H_2O (*l*),[6] ΔH°_{rxn} for ZIF-8 combustion can be calculated:

$$\Delta H^\circ_{rxn} = -350.5 + 8(-393.5) + 5(-285.8) - (-81.5) = -4846 \text{ kJ/mol}$$

Because the bomb calorimeter is a constant-volume system, it measures the internal energy change ΔU°_{rxn} (rather than enthalpy change, ΔH°_{rxn}) of a reaction, and a small correction can be made based on the change in number of moles of gas from reactants to products.[7]

$$\Delta U^\circ_{rxn} = \Delta H^\circ_{rxn} - \Delta n_g RT$$
$$\Delta U^\circ_{rxn} = -4846 \text{ kJ/mol} - (-1)(8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(298.15 \text{ K})(0.001 \text{ kJ/J}) = -4843.5 \text{ kJ/mol}$$

Three samples of ZIF-8 (commercial BASF Basolite Z1200, stored in a nitrogen-filled glovebox until use) were pressed into pellets for combustion in the calorimeter. Some corrections to the measured heat release must be made. First, there is an estimated 8.5 J of electrical resistive heating of the nichrome wire each time the calorimeter is fired. Next, some of the nichrome wire combusts in the bomb, releasing 6.3 J/mg of wire burned. The mass of the wire was measured before firing and then again after the experiment to determine the mass of wire burned. It is also possible to titrate the nitric acid produced during the combustion and account for that extra heat release,[8,9] but we found that the zinc oxide-hydroxide residue left after combustion of both ZIF-8 and ZIF-70 was already basic, so no nitric acid correction was performed. One example calculation is shown for an experiment in which a 96.205 mg pellet of ZIF-8 was combusted, the temperature rise of the calorimeter was 1.6022 °C, and 9.1 mg of nichrome wire was burned:

$(4{,}843{,}500 \text{ J}\cdot\text{mol}^{-1})(0.096205 \text{ g}/227.58 \text{ g}\cdot\text{mol}^{-1}) = 2047.5$ J released by combustion of ZIF-8

$2047.5 \text{ J} + 8.5 \text{ J} + (6.3 \text{ J}\cdot\text{mg}^{-1})(9.1 \text{ mg}) = 2113.33$ J total heat produced in calorimeter

$2113.33 \text{ J}/1.6022\ ^\circ\text{C} = 1319.01 \text{ J}\cdot{}^\circ\text{C}^{-1}$ calorimeter constant

Two other runs yielded values of 1311.84 and 1319.51 $\text{J}\cdot{}^\circ\text{C}^{-1}$.

The average value of the three gives a **calorimeter constant of 1316.8 $\text{J}\cdot{}^\circ\text{C}^{-1}$.**

Determination of the heat of combustion and ΔH°_f of ZIF-70

Before determining the heat of combustion of ZIF-70, its composition must be determined, as the ratio of imidazole to 2-nitroimidazole can vary among preparations. As noted in the synthetic section above, NMR revealed a ratio of 2.05:1 imidazole to 2-nitroimidazole in our sample. That indicates an empirical formula of $Zn(C_3H_3N_2)_{1.344}(C_3H_3N_3O_2)_{0.656}$, or $ZnC_6H_{5.344}N_{4.656}O_{1.312}$, for our ZIF-70. The combustion reaction of our ZIF-70 is given by the equation:

$$ZnC_6H_{5.344}N_{4.656}O_{1.312}\,(s) + 7.18\,O_2\,(g) \longrightarrow ZnO\,(s) + 6\,CO_2\,(g) + 2.672\,H_2O\,(l) + 2.328\,N_2\,(g)$$

Three samples of ZIF-70 were pressed into pellets and burned in the calorimeter. An example calculation is given for one pellet of mass 92.437 mg, where the temperature rise was 1.1437 °C and 10.3 mg of nichrome wire was consumed:

$(1.1437\ ^\circ C)(1316.8\ J\cdot{}^\circ C^{-1}) - 8.5\ J - (6.3\ J\cdot mg^{-1})(10.3\ mg) = 1432.6$ J heat released due to combustion of ZIF-70

$-1.4326\ kJ/(0.092437\ g/229.04\ g\cdot mol^{-1}) = -3549.77\ kJ\cdot mol^{-1}$ ($\Delta U^\circ_{combustion}$ of ZIF-70)

Now convert to enthalpy of combustion

$$\Delta H^\circ_{rxn} = \Delta U^\circ_{rxn} + \Delta n_g RT$$

$\Delta H^\circ_{combustion} = -3549.77\ kJ\cdot mol^{-1} + (1.148)(8.314\ J\cdot mol^{-1}\cdot K^{-1})(298.15\ K)(0.001\ kJ/J) =$
$-3546.9\ kJ\cdot mol^{-1}$

The two other samples yielded values of $-3532.9\ kJ\cdot mol^{-1}$ and $-3573.8\ kJ\cdot mol^{-1}$.

The average **ZIF-70 $\Delta H^\circ_{combustion} = -3551.2\ kJ\cdot mol^{-1}$**.

Using the balanced equation for ZIF-70 combustion given above, along with the enthalpies of formation of ZnO (*s*), CO_2 (*g*), and H_2O (*l*) used above,

$-3551.2\ kJ\cdot mol^{-1} = -350.5 + 6(-393.5) + 2.672(-285.8) - \Delta H_f^\circ$ (ZIF-70)

ΔH_f° (ZIF-70) = + 76.0 kJ·mol^{-1}

7. References:

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