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COMMUNICATION

Adsorption of Tetranitromethane in Zeolitic Imidazolate Frameworks Yields Energetic Materials

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Porous frameworks consisting of functionalized imidazolate ligands and zinc nodes are employed as hosts for the oxidant tetranitromethane to produce energetic composite materials. This new class of energetic materials are achieved through the facile strategy of oxidant adsorption wherein fuel and oxidant are intimately mixed yielding a material that responds violently to thermal and impact stimuli.

Metal–organic frameworks (MOFs) are a class of coordination polymers prepared by metal-mediated self-assembly of multitopic organic ligands, wherein metal-ligand bonds lead to 2-D or 3-D crystalline networks.[1] The porosity and structural stability of many MOFs permits a host of applications including gas storage, separations, and catalysis.[2-11] Recently, several research groups have demonstrated the potential for MOFs to perform as explosives.[12-14] Explosives are a class of high-energy materials typically containing fuel and oxidizer that respond rapidly to stimuli by releasing large amounts of energy and gases. While metal-organic species have been used for many years as primary explosives (e.g., lead styphnate and mercury fulminate),[15] one of the major goals for the energetics field is to develop more eco-friendly materials (containing no toxic metals) that exhibit performance comparable to widely used energetic materials. Many MOFs are constructed from non-toxic metals, and numerous reported energetic MOFs exhibit good thermal stability and promising performance.[16-24]

In contrast to many non-energetic MOFs, energetic MOFs generally lack permanent porosity. The only viable route to increasing their oxygen content is therefore covalent modification of the ligand, and this often impacts the structure, making the purposeful design of energetic MOFs challenging. Recently, we demonstrated the utility of porous MOFs loaded with oxidizing guests as explosives.[25] A non-energetic, fuel-rich framework, MOF-5, was loaded with the energetic oxidizers tetranitromethane (TNM) and hexanitroethane (HNE). The fuel and oxidizer composites, MOF-5-TNM and MOF-5-HNE, were highly energetic and exhibited high sensitivity to impact, leading the materials to be classified as primary explosives. In contrast to secondary explosives, primary explosives are more sensitive to stimuli and while this material property is desirable in some military and commercial devices such as blasting caps, detonators, and primers,[26,27] the most used energetic materials are relatively insensitive secondary explosives. In this study, a new class of energetic MOFs is produced by applying the oxidant adsorption method to porous materials containing functionalized imidazolate ligands. Specifically, zeolitic imidazolate frameworks (ZIFs) were employed in the adsorption of TNM to develop an understanding of how host structure can influence impact sensitivity and thermal stability.

MOFs are often synthesized with carboxylate-containing ligands wherein the carboxylate carbon is already oxidized and therefore the oxygen provided by this substituent does not add substantially to the overall heat released upon detonation. The development of frameworks based on linkers with high atomic percentages of nitrogen is of particular interest relative to carboxylate-based frameworks because, in addition to their energetic nature, nitrogen-rich ligands tend to exhibit good thermal stability. However, these new high-nitrogen MOFs lack sufficient oxygen content to fully convert all of the fuel atoms into gaseous products (CO_2, H_2O, etc.), which means that some fuel is wasted during decomposition.

ZIFs are MOFs consisting of imidazolate linkers that bridge tetrahedral metal ions to form topologies similar to zeolites. ZIF-8,[28] $[Zn(mim)_2]$[29] (mim = 2-methylimidazolate; Figure 1), was chosen for initial studies because its properties are well known and it is commercially available as Basolite Z1200. Other ZIFs have very recently been reported to act as hypergolic fuels.[30] ZIF-8 is an oxygen-free framework comprised of 2-methylimidazolate ligands bridging Zn^{2+} ions to form a

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x crystalline solid with sodalite (**sod**) topology. It has a surface area in excess of 1500 m^2/g and contains large, spherical pores with a diameter of 11.6 Å. The pores are connected by narrow (3.4 Å) windows, which allow guests to enter the framework.[28] Analysis of the solvent accessible volume of the guest-free crystal structures of ZIF-8 yielded a pore volume of 50%, which is the volume that is accessible to oxidant guests. We predict that the combination of ZIF-8 (fuel) and TNM (oxidant) mixed on the molecular scale will result in an energetic composite that outperforms both individual components.

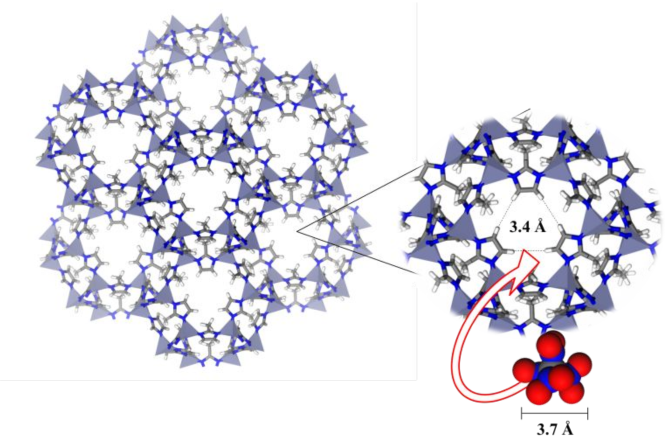

Fig. 1 Crystal structure of ZIF-8 shown with pore aperture measurements to illustrate the size relative to tetranitromethane.

Oxidant adsorption in ZIF-8 was conducted by soaking crystals in neat TNM in a capped glass vial at 50 °C. Samples were withdrawn from the vial after a period of time and rinsed with cold pentane. The structural integrity of these crystals after oxidant adsorption was confirmed by powder X-ray diffraction (PXRD). The ZIF-8-TNM composites were evaluated by TGA after 2, 4, and 6 hour incubation times in TNM; uptake did not increase substantially after 4 hours. The relatively slow uptake of TNM in ZIF-8 is likely due to the large molecular diameter of TNM (3.7 Å) compared to the pore aperture of ZIF-8 (3.4 Å), as shown in Figure 1. In TGA experiments, the composite exhibits an initial mass loss around 60 °C, which can be attributed to the escape of TNM guests from the pores of ZIF-8. In order to quantify the total amount of TNM captured in the pores of ZIF-8, TGA data was collected on a sample of ZIF-8-TNM held isothermally at 150 °C for 3 hours. This experiment revealed that 15.8 wt% of the ZIF-8-TNM composite is TNM. The complete removal of TNM by this heating regime was confirmed by infrared spectroscopy (IR) analysis wherein the signal of TNM disappears after isothermal heating of the ZIF-8-TNM composite. Note: the total TNM loading is somewhat underestimated by this method due to some guest loss under ambient conditions.

Initial differential scanning calorimetry (DSC) measurements were collected at 50 °C/min ramp rate on ZIF-8-TNM crystals and two broad exothermic peaks were observed. The first exothermic event corresponds to composite decomposition, followed by decomposition of the TNM that escaped from the ZIF as the temperature increased. To prevent the escape of TNM from the ZIF prior to ignition, some excess TNM was added to the DSC sample (in a sealed, high-pressure sample pan). The resulting DSC thermal curve displays a single exothermic transition occurring at 175 °C due to decomposition of ZIF-8-TNM. When using a 1:1.1 mass ratio of ZIF-8-TNM to excess TNM, the ΔH_{DSC} for this exothermic event is 5.63 kJ/g (Figure 2), which is more than four times the heat release from neat TNM.

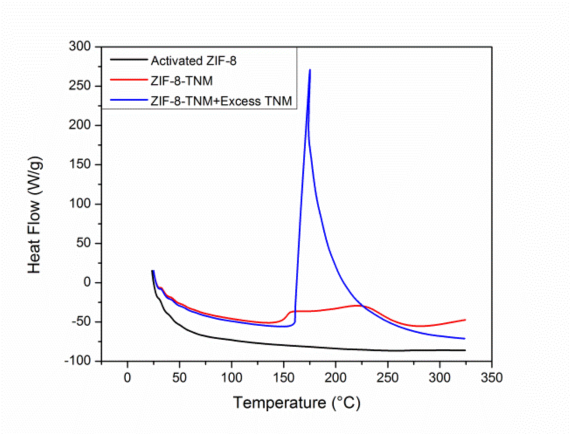

Fig. 2 DSC traces of activated ZIF-8 (black), ZIF-8-TNM composite (red), and ZIF-8-TNM composite with excess TNM (blue) collected on a common scale (exothermic is up).

In explosive materials, oxygen balance describes the amount of oxygen present relative to the amount required to completely convert all fuel atoms (carbon, hydrogen, and metals) into CO_2, H_2O, and metal oxide (nitrogen is assumed to be converted to N_2). The ideal oxygen balance for an explosive is 0%, which means that the material has sufficient oxygen for no fuel to be wasted. Pristine ZIF-8 is non-explosive, as it contains no oxygen and has an oxygen balance of -155%. Upon maximum loading with TNM, the oxygen balance of the composite improves to -122%. Although an improvement in the oxygen balance of ZIF-8-TNM as compared to ZIF-8 was achieved, more neutral oxygen balances are characteristic of high-performing explosives (*vide infra*). A solution to this problem would be oxidant adsorption into a ZIF with a more neutral oxygen balance of the unloaded framework and higher porosity for increased loading of TNM. ZIF-70 meets these requirements.

ZIF-70 is a mixed linker[31-34] material comprised of zinc ions coordinated to both 2-nitroimidazole and imidazole, and has a reported surface area of greater than 1700 m^2/g. This structure has a gmelinite (**gme**) topology and features wide channels with a diameter of 15.9 Å and large pore windows (13.1 Å). In ZIF-70 the nitro substituent is significant because it provides oxidizing power for the fuel-rich framework, as opposed to the oxygen-free ZIF-8. The resulting oxygen balance of pristine ZIF-70 (-92%) is inherently more neutral than ZIF-8. Analysis of the crystal structure of guest-free ZIF-70 yielded a solvent-accessible volume of 54%. Given these features, we predict that ZIF-70-

TNM will possess a more neutral oxygen balance than ZIF-8-TNM.

To determine maximum achievable oxidant adsorption in ZIF-70, the material was first placed in neat TNM for loading. Unexpectedly, this method resulted in a loss of long range order of the bulk material as evidenced by the PXRD pattern, which showed a loss of peaks due to ZIF-70 and the emergence of two new, broad peaks. As a more mild alternative approach, TNM was adsorbed into porous ZIF-70 crystals by vapor diffusion at room temperature. Adsorption of TNM into ZIF-70 was monitored and quantified by TGA after 30 minutes, 1, 2, and 3 hours. The ZIF-70-TNM composite reached maximum adsorption after 3 hours, wherein 46.7 wt% of the composite was TNM, as determined by mass lost in the initial step of the TGA (Figure 3). ZIF-70 has a larger pore volume than ZIF-8 therefore it is capable of storing more oxidant guests within the framework and the larger pore apertures lead to more complete oxidant permeation. The loading of TNM into ZIF-70 up to 46.7 wt.% corresponds to a composite material density of 1.50 g/cm^3.

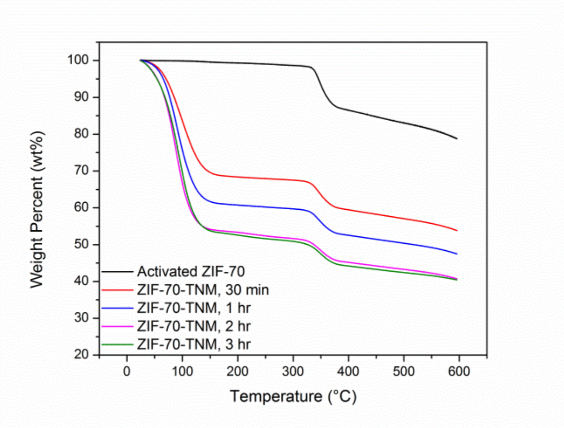

Fig. 3 Thermogravimetric analysis of ZIF-70-TNM after 30 min, 1 hour, 2 hours and 3 hours of oxidant loading by vapor diffusion at room temperature. ZIF-70-TNM reaches maximum loading of 46.7 wt% TNM.

Thermal analysis of the ZIF-70-TNM composite by DSC reveals two broad exothermic events (see ESI). This behavior is similar to the ZIF-8-TNM composite. Again, to prevent premature escape of the TNM from the composite, additional neat TNM was placed into the DSC pan with ZIF-70-TNM. Upon heating the material exhibits a single exothermic transition at 158 °C with 6.00 kJ/g of energy released, when the ratio of ZIF-70-TNM to excess TNM is 1:1. For reference, a DSC measurement of pristine ZIF-70 displays an exothermic event at 371 °C which corresponds to 1.40 kJ/g of energy released; this exothermic decomposition is presumably due to the reaction of the oxygen of the nitro groups with the fuel atoms of the ZIF. Collectively these results demonstrate that not only is the energy release improved by incorporation of nitrated linkers, but also the nitro group can lead to more thermally sensitive composite materials as well. The saturation of ZIF-70 with TNM at 46.7 wt% corresponds to an oxygen balance of -26.5% for the composite, which is significantly more neutral than the industry standard TNT (-73.9%) and approaching HMX (-21.6%).

Table 1 Thermal and physical properties of TNM, non-energetic frameworks, energetic composites, and reference secondary energetic materials.

	Oxygen balance (%)	**Density (g/cm^3)**	**DSC Decomp. (°C)**	**ΔH_{DSC} (kJ/g)**
TNM	48.9	1.62	219	0.859
ZIF-8	-155	0.925	>500	-
ZIF-8-TNM	-122	1.10	175	5.63
ZIF-70	-92.7	0.802	371	1.40
ZIF-70-TNM	-26.5	1.50	158	6.00
Monoclinic TNT[35]	-74.0	1.65	298	1.70
PETN[36]	-10.0	1.85	207	-
δ-HMX[37]	-21.6	1.76	279	-

In energetic materials, high energy content and low sensitivity are often desirable, but these two properties generally conflict with each other because high energy materials tend to be more sensitive to stimuli.[38] Sensitivity tests are used to evaluate the safe handling requirements for energetic materials and to determine their probability of initiation under a given set of conditions. Small scale impact sensitivity tests were performed to determine the drop height required to attain a 50% probability of a positive response (dH_{50}). These measurements help to determine the conditions under which ZIF-8-TNM and ZIF-70-TNM may be safely handled and to demonstrate how the adsorption of oxidant guests influence the impact sensitivity of ZIF-8 and ZIF-70. The dH_{50} values of ZIF-8-TNM and ZIF-70-TNM were determined using the Bruceton up-down technique[39] wherein a 5 lb. weight is allowed to freefall from pre-measured distances onto a non-hermetic DSC pan containing the test material. On this particular apparatus,[40] TNM exhibits a dH_{50} of 34 cm, whereas ZIF-8-TNM and ZIF-70-TNM exhibit dH_{50} values of 36 cm and 17 cm, respectively (see Figure 4). Based on the impact sensitivity of PETN (dH_{50} = 21 cm) determined with our in-house apparatus, ZIF-8-TNM and ZIF-70-TNM demonstrate impact sensitivity near the borderline of primary and secondary explosives, and ZIF-70-TNM could possibly serve as a replacement primary explosive.

The development of new energetic materials is ultimately motivated by the drive for improved performance at a given cost and sensitivity; prediction of energetic performance including detonation velocity and detonation pressure is most typically carried out through computation. There are established methods for the prediction of energetic performance including the Kamlet-Jacobs (K-J) equations[41] and modern thermochemical software typified by Cheetah.[42] However, each method has restrictions. For example, the K-J equations were developed in 1968 for high-energy density compounds containing only carbon, hydrogen, nitrogen and oxygen and these equations are difficult to apply to modern explosives that contain metal ions. On the other hand, Cheetah thermochemical code can predict the performance of metal containing explosives, but only if the heat of formation (ΔH_f) and the density of the material have been determined. The overall composite densities of ZIF-8-TNM and ZIF-70-TNM were calculated based on the weight percent of the absorbed oxidant observed by the mass loss prior to ZIF decomposition in TGA, as well as the density of the framework. The energetic performance parameters for ZIF-8-TNM were predicted using Cheetah with known heats of formation of the framework[43] and oxidant (TNM).[44] ZIF-8-TNM has a predicted detonation velocity (V_d) of 3.01 km/s and a detonation pressure (P) of 2.69 GPa.

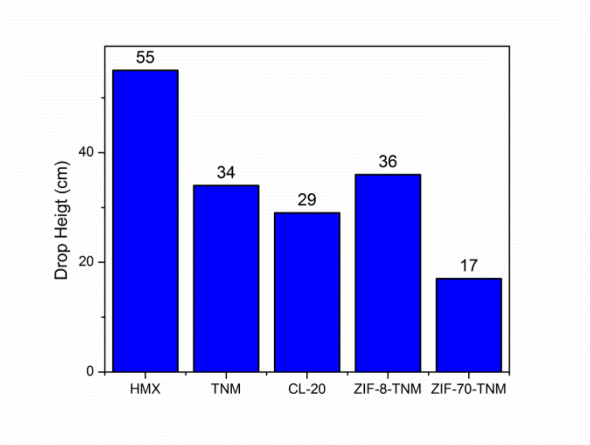

Fig. 4 The dH_{50} values of known explosive materials with the explosive ZIF composites.

Unlike ZIF-8, the standard molar enthalpy of formation ($\Delta H_f°$) of ZIF-70 was previously unknown. We determined this value by measuring the molar enthalpy of combustion ($\Delta H_{m,comb}°$) of ZIF-70 by oxygen bomb calorimetry, coupled with Hess's law and the known enthalpies of formation of products ZnO(s), CO_2(g) and H_2O(l). Given this data, the $\Delta H_f°$ of ZIF-70 was calculated to be +76.0 kJ/mol (see ESI). Next, the detonation performance of ZIF-70-TNM, including detonation velocity and detonation pressure, was evaluated using Cheetah theoretical calculations. ZIF-70-TNM exhibits a detonation velocity of 6.11 km/s and a detonation pressure of 14.2 GPa. ZIF-70-TNM displays detonation performance greater than ZIF-8-TNM, and greater than that of a typical primary explosive. This finding validates the critical role of pore volume and linker chemistry in determining performance for MOF-oxidant hybrids.

The development of eco-friendly energetic materials that strike a balance between good performance and sensitivity is currently one of the main goals of the energetics field. Here we report a straightforward and facile strategy to produce energetic composite materials by leveraging pre-existing MOFs (ZIF-8 and ZIF-70) as fuel and TNM as the oxidizing guest. The ZIF-8-TNM composite exhibits an improved oxygen balance compared to the pristine oxygen-free ZIF-8 structure; however, the relatively low uptake of oxidant guests leads to modest performance as an explosive. The large pores of ZIF-70 and the presence of 2-nitroimidazole ligands led to a significantly improved oxygen balance (-27.2%) and improved detonation performance. Moving forward, the oxidant adsorption strategy could be applied to other robust metal organic frameworks. Additionally, the adsorption of solid explosive guests would be the next viable step in the development of energetic MOF composites to overcome the escape of volatile oxidant from pores of the frameworks.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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Absorption of tetranitromethane in the zeolitic imidazolate frameworks ZIF-8 and ZIF-70 is a facile route to borderline primary/secondary explosives that contain no toxic heavy metals.