Title: Metal-organic frameworks induce hypergolic ignition of bulk metals

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Abstract

We demonstrate the unprecedented ability to induce hypergolic behavior, *i.e.* rapid and spontaneous ignition upon contact with an oxidizer, in non-hypergolic metal fuels by blending them with hypergolic metal-organic frameworks (HMOFs). Using magnesium, aluminum or zinc metal as the fuel, we demonstrate materials with ignition delays (IDs) below 50 ms, and calculated specific impulse (I_{sp}) in the 220-250 s range. These parameters are comparable to those of toxic and carcinogenic hydrazine-based hypergols conventionally used in aerospace technologies, suggesting a route to develop cleaner, safer propulsion systems.

Main text

Hypergolic materials, exhibiting rapid and spontaneous ignition upon contact with an oxidizer, are critical compo-nents of aerospace propulsion systems, used in applications including the maneuvering of satellites and other spacecraft (e.g. International Space Station), attitude correction and reusable spacecraft.[1-7] For over 60 years, the most common class of hypergolic fuels have been small molecule hydrazine derivatives, monomethylhydrazine (MMH) and unsymmetrical dimethylhydrazine (UDMH), which are both extremely toxic and carcinogenic.[8-10] The considerable safety and environmental risks associated with such hydrazine-based hypergolic fuels are a major hindrance to the development of aerospace technologies,[11-14] and have led to an urgent search for new, safer and more environmentally-friendly hypergolic fuels, including ionic liquids, coordination complexes, and borane-based liquid and solid-state systems.[15-23]

We have recently demonstrated how hypergolic behavior can be introduced by design to metal-organic framework (MOF) materials, through the incorporation of unsaturated vinyl ($CH=CH_2$) or acetylene ($C\equiv CH$) groups into imidazolate linkers of zeolitic imidazolate frameworks (ZIFs) based on zinc, cobalt or cadmium.[24] Measurement of hypergolic properties using standard ignition drop tests with white or red fuming nitric acid (WFNA, RFNA, respectively) as oxidizers revealed rapid ignition that was readily modulated by choice of components of these hypergolic MOFs (HMOFs). In particular, HMOFs based on Zn^{2+} and Co^{2+} exhibited ultrafast ignition,[24] with the time between contact of the MOF and liquid oxidizer (ignition delay, ID) well below 50 ms, a value often required for functional hypergolic materials (Figure 1a-c).[24,25] While such short ID values and high energy outputs in terms of energy density (E_v) and specific energy (E_g), highlight the potential of using MOFs as replacements for hydrazine-based hyper-gols,[26] the adoption of these materials on a large scale might be limited by material cost. As an alternative to using HMOFs as fuels alone, we have now explored their use as hypergolic additives that could embed hypergolic behavior into otherwise highly energy rich but non-hypergolic solids.
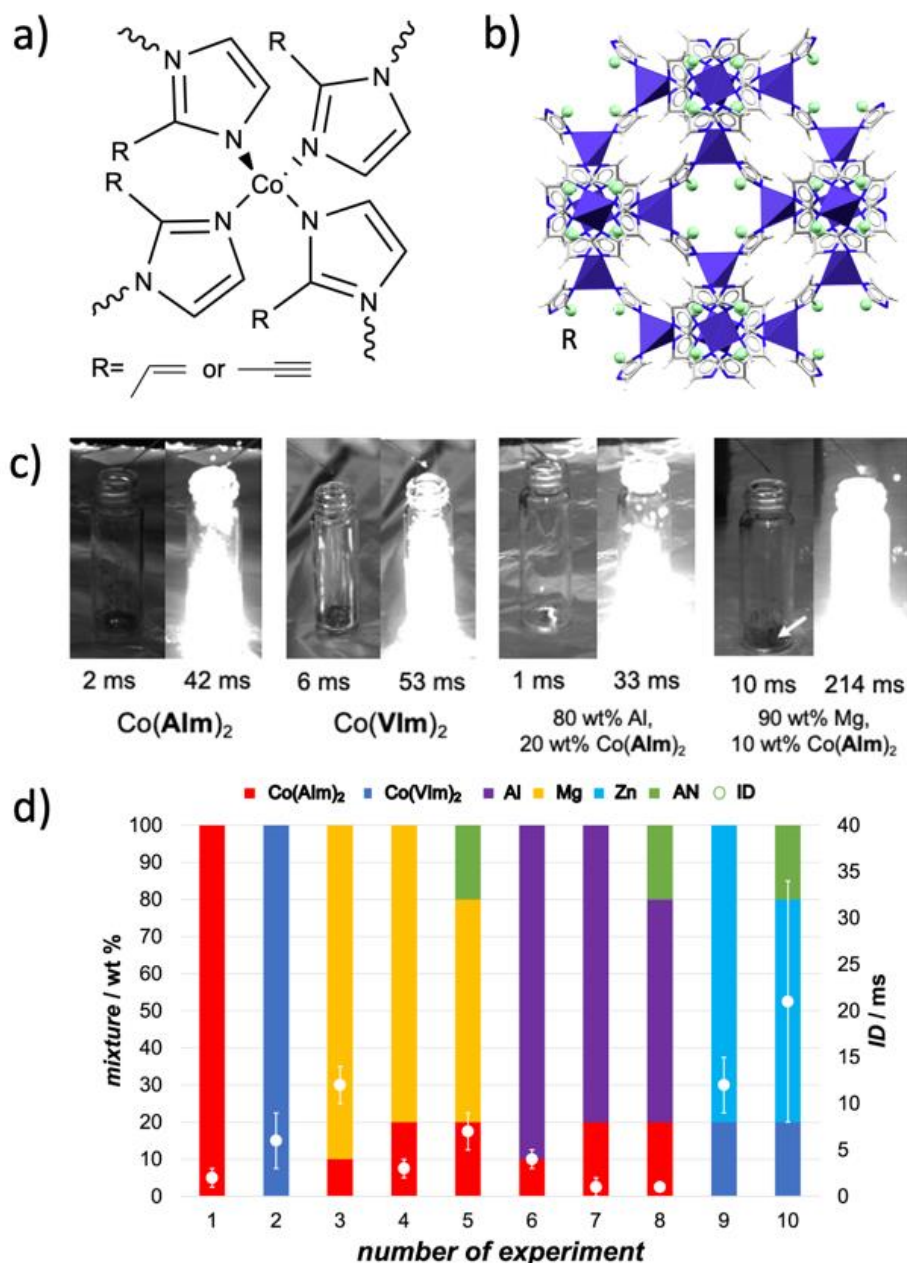
Figure 1. Overview of the Co(II)-based HMOFs and their use as triggers of hypergolic ignition in non-hypergolic metal powders: a) schematic and b) fragment of crystal structure. c) Selected images illustrating hypergolicity in droplet ignition tests, showing samples (left) at the time of first ignition (ID) and (right) at a randomly selected time during combustion. d) Illustration of ID values for selected mixtures of Co(**AIm**)$_2$ or Co(**VIm**)$_2$ with Mg, Al, Zn and/or AN. Each ID is shown as an average of three consecutive measurements.

Here, we describe the ability of HMOFs to induce hypergolic behavior in non-hypergolic metals commonly used as rocket fuels.[27,28] Specifically, we show how blending cobalt-based hypergolic ZIFs, in amounts from 2% to 25% by weight, enables rapid ignition of otherwise non-hypergolic magnesium and aluminum powders. The activity of HMOFs as triggers of hypergolic activity appears to extend beyond conventional metal fuels, as shown by hypergolic ignition of zinc

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powder. The mixtures of HMOFs with Mg, Al, or Zn exhibit low ID values, the ability to incorporate known solid fuel oxidizers ammonium perchlorate (AP) and nitrate (AN), and calculated high specific impulse (I_{sp}) matching that of hydrazine hypergols, suggesting a new application of MOFs as hypergolicity-inducing additives for known solid rocket fuels.

We first explored the ability of the sodalite-topology (SOD) framework composed of Co^{2+} nodes, and imidazolate ligand containing the C≡CH group in 2-position (**AIm**⁻) as a linker, to ignite non-hypergolic raw metal substrates. The framework Co(**AIm**)$_2$ was the best performing hypergolic MOF in our previous report.[24] The ignition properties, including ID, as well as height and duration of flame were evaluated using standard droplet ignition tests, in which a 10 µL volume of the WFNA oxidizer is dropped onto ca. 10 mg of a solid sample from a height of 4 cm. The WFNA addition was done using a 100 µL Hamilton syringe, and the ignition and combustion processes were monitored using a Redlake MotionPro Y4 camera at 1,000 frames per second (fps). We verified the behavior of pure solid Co(**AIm**)$_2$, showing ultrafast ignition with an ID of 2(1) ms, consistent with our prior work.[24] Particle size (d) for all herein used materials were explored using scanning electron microscopy (SEM, Table 1), and MOFs have also been characterized by nitrogen sorption measurements which revealed Brunauer-Emmet-Teller (BET) surface areas consistent with earlier reports (see SI).[24]

Table 1. Relevant characteristics of herein used materials: density (ρ, in g cm⁻³), temperature of melting or decomposition (T, in °C), relative molecular weight (M_r) and particle size (d, in µm).

Material	ρ / g cm⁻³	T / °C	M_r	d / µm
Co(**AIm**)$_2$	0.985	-	247.57	0.1
Co(**VIm**)$_2$	0.944	-	251.60	0.1
Mg	1.738	650	24.31	36
Al	2.700	660	26.59	5
Zn	7.140	420	65.38	10
AN	1.720	170	80.04	85
AP	1.950	200	117.49	2

Next, we explored the behavior of a mixture of commercial magnesium metal powder (Oakwood Chemical, lot no. 099285L02F) with Co(**AIm**)$_2$. In this case, as for all other described in this work, we found that the mixtures should be prepared either by manual grinding, resonant acoustic mixing (RAM) or speed mixing, while ball milling led to the loss of hypergolic behavior. While PXRD patterns of the materials showed little or no difference before or after ball milling, visual inspection indicated milling led to the formation of larger aggregates and flakes which might be deleterious to hypergolic behavior.

Magnesium metal on its own is not known to be a hypergol, and should not exhibit hypergolic ignition with WFNA. This was verified by WFNA drop tests which did not lead to ignition, but instead produced grayish suspensions. In contrast, a WFNA drop test on a mixture of magnesium metal with 10% Co(**AIm**)$_2$ by weight revealed rapid ignition, with ID of 12(2) ms (Figure 1c,d; ID values and observations on the combustion process are provided in Table S1 in the SI). Consequently, blending with small amount of Co(**AIm**)$_2$ converted normally non-hypergolic Mg metal into a powder material exhibiting ultrashort ID.

Even shorter IDs were observed for blends with otherwise also non-hypergolic aluminum metal (Goodfellow Cambridge Ltd, lot no. LS528898). Addition of 10% or 20% by weight of

Co(**AIm**)$_2$ led to extremely short ID delays of 4(1) ms and 1(1) ms, respectively, the latter exhibiting flames of over 5 cm in height lasting longer than 250 ms (see SI). Rapid ignition was also retained upon introducing AN oxidizer, with the mixture of 20% Co(**AIm**)$_2$, 60% Al powder and 20% AN by weight producing an ID of 1(0) ms (see SI).

These observations present Co(**AIm**)$_2$ as an effective hypergolic additive for metal fuels. Its use, however, might be limited by the overall low-yielding synthesis of the parent ligand HAIm.[24] Consequently, we explored the use of Co(**VIm**)$_2$, which was previously observed to exhibit longer IDs, but is based on the more readily accessible H**VIm** ligand. Addition of either 10% or 20% by weight of Co(**VIm**)$_2$ to magnesium powder enabled ignition with IDs of 48(11) ms and 42(17) ms, respectively (Figure 2a, also SI). Importantly, hypergolic ignition was observable even at lower MOF contents of 2% and 5% by weight, producing white flames of height exceeding 5 cm, and IDs of 62(9) ms and 56(9) ms, respectively (Figure 2a). Although these ID values are slightly above the recommended 50 ms for hypergolic ignition, they are highly significant because they demonstrate magnesium hypergolicity at very low content of a synthetically readily accessible hypergolic MOF. Conversely, increasing Co(**VIm**)$_2$ content to 25% by weight led to ultrafast ignition, with ID of 15(5) ms (Figure 2a). The Co(**VIm**)$_2$ HMOF was also effective in conferring hypergolicity to metallic aluminum powder. Although no hypergolicity was observed for mixtures containing 2% or 5% by weight of Co(**VIm**)$_2$, at 10% by weight loading the mixtures ignited with an ultrashort ID of 14(2) ms, which was further reduced to 7(1) ms for a MOF loading of 20% (Figure 2b, also SI).

We also explored the effect of oxygen-releasing additives that are commonly used in solid rocket fuels containing aluminum, such as ammonium nitrate (AN) and ammonium perchlorate (AP) (Figure 3, also SI). Notably, AP is highly popular as a solid fuel oxidant, but also represents an environmental hazard due to HCl release during its combustion.[29,30] The use of AN mitigates this hazard but at the cost of reduced performance and increased hygroscopicity.[31] Hypergolic behavior in mixtures of metals with Co(**VIm**)$_2$ was retained upon introduction of AN or AP in amounts comparable to the MOF. In particular, a mixture of 20% Co(**VIm**)$_2$, 60% Al metal and 20% AN by weight exhibited an ultrashort ID of 6(2) ms. An analogous mixture with AP exhibited a longer, but still ultrashort, ID of 28(11) ms.

The ability to induce hypergolic ignition is not limited to highly reactive magnesium and aluminum metals. This was demonstrated by the behavior of mixtures of metallic zinc and Co(**VIm**)$_2$ either alone, or in the presence of AN. Notably, a mixture of 80% zinc and 20% Co(**VIm**)$_2$ by weight exhibited rapid ignition with and ID of 12(3) ms, while a mixture of Zn (60% by weight), Co(**VIm**)$_2$ (20% by weight), and AN (20% by weight) underwent ignition with an ID of 21(13) ms accompanied by orange flames of >5 cm height (Figure 1d, also see SI).
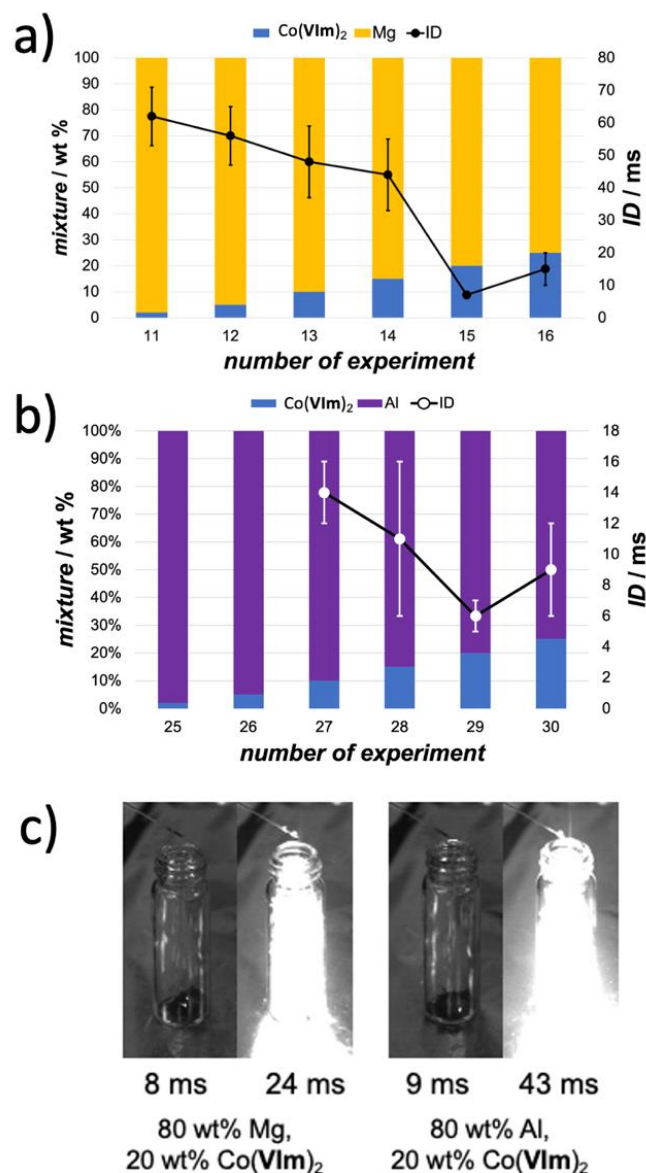
Figure 2. Overview of measured ID values for mixtures of Co($\mathbf{VIm}$)$_2$ with: a) magnesium powder and b) aluminum powder. Images of selected drop test experiments for mixtures of Co($\mathbf{VIm}$)$_2$ (20% by weight) with either Mg or Al metal. In each case, the left image is a of the sample at the time of first ignition (ID) and the right one is of the sample taken at a time that best illustrates the height and intensity of the flame.

The partially liquified residues obtained after combustion of different mixtures of magnesium or aluminum with Co($\mathbf{VIm}$)$_2$ were analyzed by PXRD and X-ray photoelectron spectroscopy (XPS). For mixtures with magnesium, PXRD analysis revealed only very weak X-ray reflections of the metal, indicating a high degree of combustion. Analysis by XPS of the residue after hypergolic drop test on a mixture of 80% Mg and 20% Co($\mathbf{VIm}$)$_2$ revealed that approximately 56% of magnesium was in the form of Mg(0), which can most likely be explained by the presence of unreacted Mg powder that was physically pushed out of the ignition area during the drop test. For

mixtures with aluminum, the X-ray reflections of the metal were still clearly visible in the residue after combustion, but with intensities ca. 10 times lower with respect to a comparable size sample before combustion (see SI). These analyses, however, should be taken with caution due to highly inhomogeneous nature of the samples after drop tests.
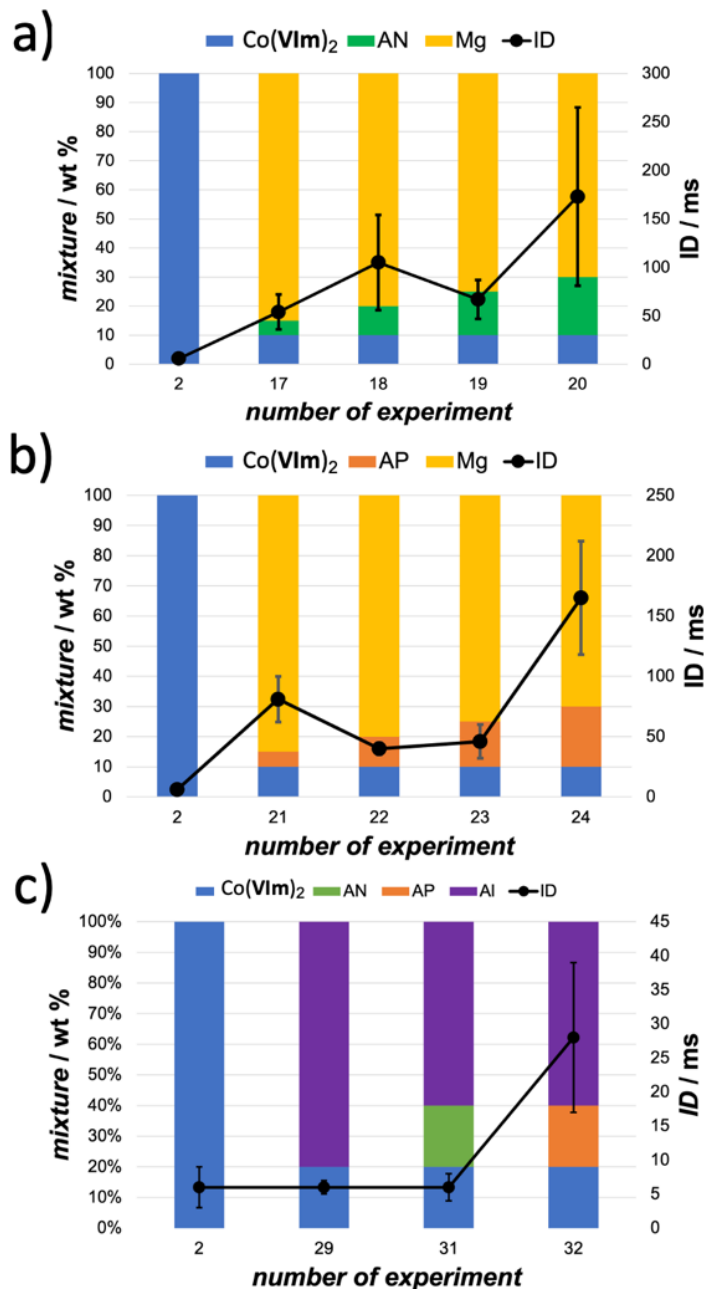

Figure 3. Overview of measured ID values for mixtures of Co(**VIm**)$_2$ with magnesium metal powder in the presence of: a) AN and b) AP. Selected IDs for mixtures of Co(**VIm**)$_2$ with aluminum alone, as well as in the presence of AN or AP.

In order to further verify the suitability of herein explored ZIFs as triggers of hypergolic activity for aluminum powder, we conducted a theoretical performance study by calculating the specific impulse (I_{sp}),[32] *i.e.* the ability of the fuel to generate thrust in rockets, using the NASA Chemical Equilibrium with Applications (CEA) package.[33] The calculated I_{sp} values were compared for all neat materials (Co(**AIm**)$_2$, Co(**VIm**)$_2$, Mg, Al, AN and AP) and for their selected mixtures that were evaluated in drop ignition tests. The I_{sp} values were calculated under equilibrium conditions, with a combustion pressure equal to 1000 psi and WFNA used as the oxidizer, under simulated conditions where the exhausted gas expands to atmospheric pressure. The O/F ratios are calculated based on the mass of the liquid oxidizer and the total mass of the fuel powder, including AN or AP additives, when applicable. For comparison, the combination of liquid oxygen (LOX) and liquid hydrogen (LH2) currently holds the highest I_{sp} among the common rocket fuel mixtures, at 386 s.[34] The hydrazine-based hypergols exhibit I_{sp} values around 230-260 s.[35]
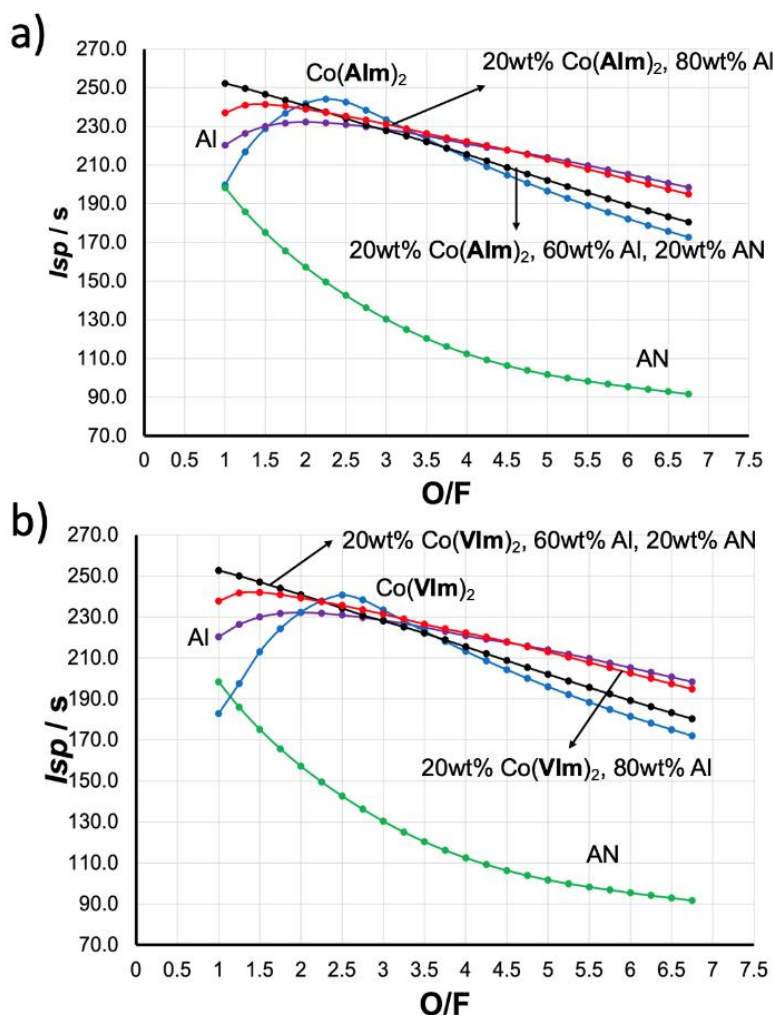

Figure 4. Overview of selected I_{sp} values calculated as a function of the O/F ratio for mixtures of: a) Co(**AIm**)$_2$ and b) Co(**VIm**)$_2$ with aluminum metal powder alone, as well as in the presence of AN or AP as oxidizers. Corresponding data for magnesium metal powder is provided in the SI.

The calculations revealed that Co(**AIm**)$_2$ provides a peak I_{sp} value of 244 s at the O/F ratio of 2.25, which is higher than pure Al powder (I_{sp} of 231 s at the O/F ratio of 1.75). This value is very close to that of hydrazine-based hypergols. Moreover, a mixture of 20% by weight of Co(**AIm**)$_2$ in aluminum powder is calculated to exhibit a comparable peak I_{sp} value of 241 s at an even lower O/F ratio of 1.50, which is considered beneficial for propulsion applications in which the oxidizer density is low compared to high-density metals and fuels. A mixture of 20% Co(**AIm**)$_2$, 60% aluminum and 20% AN by weight exhibited an even higher peak I_{sp} value of 252 s with the O/F ratio of 1.00. Similar results were obtained for Co(**VIm**)$_2$ in mixture with aluminum powder, with the calculated maximum I_{sp} of 242 s at an O/F ratio of 1.5 and 20% by weight HMOF content. As in the case of Co(**AIm**)$_2$, the addition of AN increased the I_{sp}. For example, a mixture of 20% Co(**VIm**)$_2$, 60% Al and 20% AN by weight exhibited a peak I_{sp} of 253 s at an O/F ratio of 1.00, again very similar to hydrazine hypergols. High I_{sp} values were also observed for mixtures of Co(**VIm**)$_2$ with magnesium powder, with or without AN and AP additives, in the range of 220-234 s. The values are consistent with the lower I_{sp} for this metal of 219 s (see SI).

   In summary, we have provided the first demonstration of MOFs being used as additives to induce hypergolic behavior, *i.e.* spontaneous and rapid ignition in contact with an oxidizer, to non-hypergolic metal materials. We have shown the ability to use previously reported hypergolic MOFs, isostructural to popular ZIF-8 and ZIF-67 materials, as triggers for hypergolic ignition of magnesium and aluminum powders, as well as zinc powder. The rapid ignition behavior was retained in the presence of conventional oxidizers used in aerospace technologies, such as ammonium nitrate and perchlorate. While the observed ability to use MOFs for inducing hypergolic ignition of non-hypergolic materials is unprecedented, we note that the observed IDs for blends containing aluminum – the conventionally used fuel in solid booster rockets,[27,28] are below the lower limit of 50 ms for propulsion applications. This observation, along with calculated specific impulse that matches currently used hydrazine-based hypergols, suggests a route to use hypergolic MOFs in the development of new and cost-effective hypergolic propellants.

Author Contributions
The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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