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COMMUNICATION

Metal-Organic Frameworks: MOFs as integrated structural scaffolds for pyrotechnic materials

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Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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A new approach to formulating pyrotechnic materials is presented whereby constituent ingredients are bound together in a solid-state lattice. This reduces the batch inconsistencies arising from the traditional approach of combining powders by ensuring the key ingredients are 'mixed' in appropriate quantities and are in intimate contact. Further benefits of these types of material are increased safety levels as well as simpler logistics, storage and manufacture. A systematic series of new frameworks comprising fuel and oxidiser agents (group 1 and 2 metal nodes & terephthalic acid derivatives as linkers) has been synthesised and structurally characterised. These new materials have been assessed for pyrotechnic effect by calorimetry and burn tests. Results indicate that these materials exhibit the desired pyrotechnic material properties and the effect can be correlated to the dimensionality of the structure. A new approach to formulating pyrotechnic materials is proposed whereby constituent ingredients are bound together in a solid-state lattice. A series of Metal-Organic Framework frameworks comprising fuel and oxidiser agents exhibits the desired properties of a pyrotechnic material and this effect is correlated to the dimensionality of the structure.

Pyrotechnics are ubiquitous in modern life, with usage ranging across airbags, flares, matches, oxygen candles and display. However the approach to their manufacture has barely changed over the centuries that we have been using them. Research into pyrotechnic materials is further motivated by a need to improve safety and flexibility of manufacture, logistics, storage and performance consistency. They are categorised alongside propellants and explosives as "Energetic Materials" and at the simplest level, a pyrotechnic material consists of two primary constituents - an oxidiser, commonly metal nitrates or perchlorates and a reducing agent or fuel which can be comprised of non-metals

e.g. C or S, metals e.g. Mg or Al and carbohydrates e.g. lactose.¹ Further ingredients are binders, propellants and agents producing effects such as colour, sound or smoke.² A pyrotechnic device is therefore a mixture of functional materials in the solid state, in contrast to explosives which are typically single molecules that undergo rapid decomposition. For pyrotechnics to produce the desired effect ingredients must be intimately mixed, but industry still follows simplistic manufacturing approaches. Ingredients are either dry mixed or wet mixed where the former tumbles powders together or sieves,^{3,4} whilst wet mixing blends a slurry with horizontal and vertical mixers and various blades. These methods do not ensure the homogeneous composition necessary for pyrotechnics to function ideally or guarantee batch consistency. Newer mixing methods for energetics (but not pyrotechnics) have been devised, such as the use of nanoparticles⁵ and resonant acoustic mixing,⁶ however they suffer from the same issues in ensuring that particles mix intimately.

We present an alternative approach to traditional mixing of the ingredients of a pyrotechnic device. By incorporating components in a single crystalline lattice true intimate blending at the molecular level can be achieved in the solid state. This approach not only achieves precisely the desired stoichiometric (or otherwise) ratios but also reduces the components in a physical mixture, thereby minimising batch variation. This can be achieved by coordination of components in a single functional framework material. Metal-organic frameworks (MOFs) have been recognized as useful materials for applications in gas storage, gas purification, catalysis, and as sensors.⁷ The use of MOFs in the energetic materials field was unknown until recent explosive chemical sensors developments where the porosity of the framework absorbs and traps explosive compounds and triggers a detectable response.⁸ It was recently reported that MOFs could incorporate known explosive compounds in the framework and create structural reinforcement that stabilizes the unstable components. Hope-Weeks et al.⁹ reported two hydrazine-perchlorate 1D materials, $[\text{Ni}(\text{NH}_2\text{NH}_2)_5(\text{ClO}_4)_2]_n(\text{NHP})$ and $[\text{Co}(\text{NH}_2\text{NH}_2)_5(\text{ClO}_4)_2]_n(\text{CHP})$, which have linear polymeric structures and are possibly the most powerful metal-based energetic materials known. Pang and co-workers¹⁰ extended this approach to enhance framework structural reinforcement and made the 3D energetic

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Electronic Supplementary Information (ESI) available: Full experimental details are provided, both as an appendix to this paper and at DOI:10.5258/SOTON/376152. Crystallographic data has been deposited with CCDC (1046525-1046535). See DOI: 10.1039/x0xx00000x

MOFs ($\text{Cu}(\text{atrz})_3(\text{NO}_3)_2$)_n and ($\text{Ag}(\text{atrz})_{1.5}(\text{NO}_3)$)_n¹¹. Klapötke et al.¹² have investigated the incorporation of compounds containing high levels of nitrogen into salts and coordination polymers with the intention of introducing stability to these materials whilst also providing a means to manufacturing 'greener' energetic materials. Rather than stabilising known energetic materials, we take traditional fuels and oxidisers used by the industry and incorporate them in an integrated scaffold. In doing so, one can systematically modify both components ie metal nodes and linkers, to fine-tune pyrotechnic effect. Table 1 summarises the system design, where Group 1 and 2 metal nitrates form nodes that couple with terephthalic or tetrafluoroterephthalic acid linkers. Alkaline earth metals nitrates were chosen due to potential to mimic zinc nitrate in a MOF5 synthesis¹³ and the burn colour changing within the group (reflected by shading in table 1). Dicarboxylic acid moieties of terephthalic acids and fluorinated analogues enable them to act as linkers. Terephthalic acid has a known pyrotechnic effect so the hypothesis is that incorporation of a fluorinated linker generates a response similar to industry use of fluorinated compounds eg PTFE. Therefore synthesis of all 36 combinations would generate a systematic library capable of probing pyrotechnic effect.

Metal Nitrate	Linker
Potassium nitrate	Terephthalic acid (1)
Rubidium nitrate	Isophthalic acid (2)
Cesium nitrate	Phthalic acid (3)
Calcium nitrate tetrahydrate	Tetrafluoroterephthalic acid (4)
Strontium nitrate	Tetrafluoroisophthalic acid (5)
Barium nitrate	Tetrafluorophthalic acid (6)

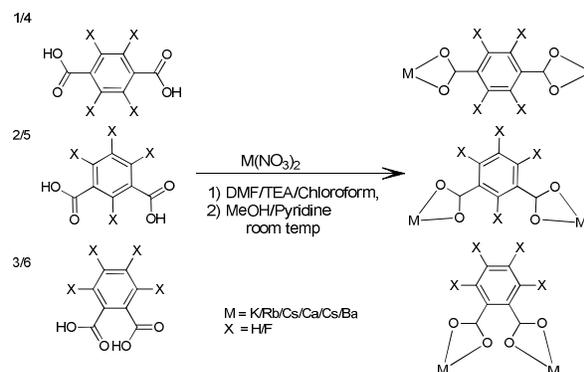
Table 1. The components used to form the homologous series.

Scheme 1 depicts a generalised synthesis procedure with two possible routes. At room temperature route 1 uses the appropriate metal nitrate and acid in dimethylformamide (DMF) with triethylamine (TEA) as a deprotonating agent to precipitate the product, which was left in chloroform for 24 hours to allow DMF exchange. Route 2 replaces DMF/TEA with methanol/pyridine.

A summary and full experimental details of compounds synthesised, route taken and structures determined is given as ESI. Group 2 compounds are generally easier to synthesise than Group 1 analogues and this may be attributed to the fact that they have a greater polarisability and therefore have a greater coordination number potential (6-8) while group 1 metals are more constrained (6). Moreover, products with fluorinated linkers are more readily synthesised via the MeOH route. The resulting crystal structure types determined are depicted in figure 1. Table 1 also shows that a number of syntheses also generate material, which either cannot be isolated from the starting components or other final products, or, if they do result in what appears to be a pure final phase, only as a powder form, which cannot be solved with available powder diffraction methods.

The majority of the 16 structures arose from the MeOH/pyridine synthesis and with fluorinated linkers. Coupling of Ca and Sr with 1 resulted in Ca1_2 and Sr1_2 (CATPAL¹⁴ & LOCCA¹⁵).¹⁶ Both comprise 1D chains and the same coordination ($\text{M}(\text{OH}_2)_4(\text{COO})_3$). They are topologically similar, but not isostructural as Ca1_2 has one water molecule above the M-COO plane and three below while

Sr1_2 has two above and two below. 3D similarity arises from each chain hydrogen bonding to four others similarly in both structures. Sr1_1 also formed two known structures (a = IJOVEJ¹⁷ & b = NOCLOH¹⁸). The Sr1_1a building units are $\text{Sr}(\text{OH}_2)(\text{COO})_5$ whereas for Sr1_1b they are $\text{Sr}(\text{DMF})(\text{COO})_5$. Both crystal structures form 3D frameworks but while Sr1_1a arises from cross-linking sheets of $\text{Sr}(\text{OH}_2)(\text{COO})_5$, Sr1_1b is comprised of cross-linked 1D chains.



Scheme 1. Synthetic scheme.

The fluorinated terephthalic materials are unique as they all form products affording crystal structures. Group 1 metals all coordinate with a distorted trigonal prism geometry and form 3D topologies. In K4_2, (PIPDOJ)¹⁹ $\text{K}(\text{COO})_5$ units link to create 2D sheets which are cross-linked to create the 3D structure. Rb4_2 and Cs4_2 are isostructural - Rb/Cs(COO)₆ units link to create 2D sheets that cross-link to form a 3D structure. Isophthalic and phthalic acid linkers fail to produce a crystal structure with any of the group 1 metals.

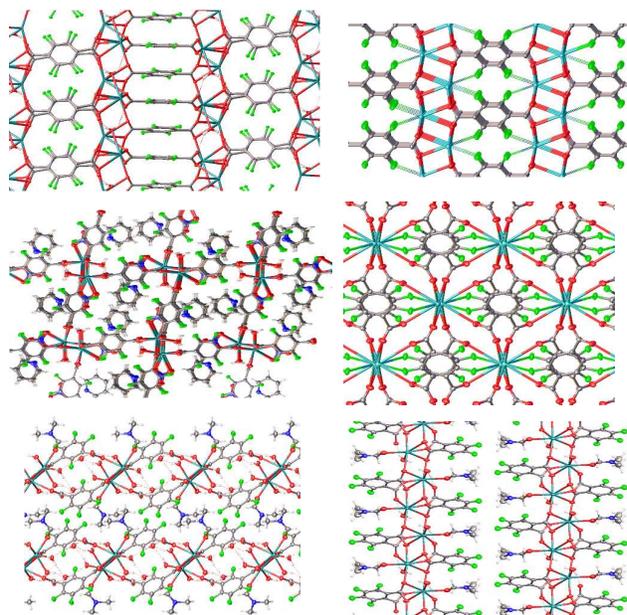
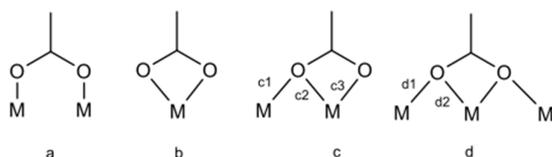


Figure 1. Pyrotechnic MOF structures determined a) Ba4_1/2, b) K4_2, c) Ca/Sr4_2, d) Rb/Cs4_2, e) Sr5_1, f) Sr6_1; _1 indicates a structure arising from route 1 synthesis, while _2 refers to route 2.

The group 2 metals are structurally more prolific as regards fluorinated linkers, with all forming products and most generating crystal structures. The metal centres have a strong preference for coordinating in a biaugmented triangular prism geometry. Ca4_2 and Sr4_2 are isostructural - Ca/Sr(OH₂)(COO)₄ units combine to form 1D chains cross-linked in two directions to create a 3D MOF. Pyridine resides in the pores of this structure. Ba4_1/2 comprises Ba(OH₂)(COO)₆ units linking to create 2D sheets which cross-link to form a 3D structure, notably via both synthesis methods. Sr5_1 consists of monomeric Sr(OH₂)₃(DMF)(COO)₃ units with two Sr centres connected by linkers to form a 1D chain. Terminal water molecules prevent the formation of 2D covalent sheets, favouring a structure mediated by hydrogen bonding to create supramolecular sheets. Conversely Sr5_2 forms 2D sheets via Sr(OH₂)(NO₃)(COO)₅ and Sr(NO₃)(COO)₅ units. Ca6_2 forms 1D chains composed of monomeric Ca(NO₃)(COO)₅ units with two Ca centres linking to form a network connectivity similar to Sr5_1. Sr6_1 comprises Sr(OH₂)(DMF)(COO)₅ units, while Sr6_2 comprises Sr(OH₂)(COO)₆ and Sr(OH₂)(COO)₅ units and in both cases these link together to create 2D sheets. Ba6_2 forms 2D sheets constructed by cross-linked Ba(OH₂)(COO)₅ units and resembles Sr6_1 as both possess a solvent molecule spacer between acids above and below the 2D sheets.



Scheme 2. RCOO⁻ coordination modes a) bridging b) chelating c) chelating & a bridging oxygen d) two oxygens chelating & bridging.

Powder XRD patterns (see ESI sections 3.3 & 4.3) demonstrate bulk purity and isostructurality between Ca4_2 and Sr4_2 and also Rb4_2 and Cs4_2. In order to compare across structural families the carboxylate coordination has been classified (scheme 2)⁸. The classifications describe connectivity of linker groups and in combination with type of building unit and dimensionality (table 2) enable a description and comparison of networks.

Product	Building Units	Linker Connectivity	1D,2D,3D [§]
Ca1_2	Ca(OH ₂) ₄ (COO) ₃	(d1, d2, t, br) x2	1D
Sr1_1a	Sr(OH ₂) ₂ (COO) ₅	(a) x3, c1, c2, c3, (br) x2	3D
Sr1_1b	Sr(DMF)(COO) ₅	c1, c2, c3, (d1, d2) x2, t	3D
Sr1_2	Sr(OH ₂) ₄ (COO) ₃	(d1, d2) x2, (t) x4	1D
Ca4_2	Ca(OH ₂)(NO ₃)(COO) ₄	(b, d1, d2) x2, t	3D
Sr4_2	Sr(OH ₂)(NO ₃)(COO) ₄	(b, d1, d2) x2, t	3D
Ba4_1/2	Ba(OH ₂)(COO) ₆	(a) x3 (d1, d2) x2, br	3D
K4_2	K(COO) ₅	(d1x2, d2) x2	3D
Rb4_2	Rb(COO) ₆	(a) x6	3D

Cs4_2	Cs(COO) ₆	(a) x6	3D
Sr5_1	Sr(OH ₂) ₃ (DMF)(COO) ₃	c1, c2, c3, *, (t) x4	1D
Sr5_2	Sr(OH ₂)(NO ₃)(COO) ₅	(a, d1, d2) x2, t	2D
Ca6_2	Ca(NO ₃)(COO) ₅	(a) x3, c1, c2, c3	1D
Sr6_1	Sr(OH ₂)(DMF)(COO) ₅	(a, d1, d2) x2, (t) x2	2D
Sr6_2	Sr(OH ₂) ₂ (COO) ₆ ,	(a) x4, (c1) x2, (br) x2	2D
	Sr(OH ₂) ₂ (COO) ₅	(a) x4, c2, c3, t, br	
Ba6_2	Ba(OH ₂) ₃ (COO) ₅	(a, d1, d2) x2, t, br	2D
		(x2)	

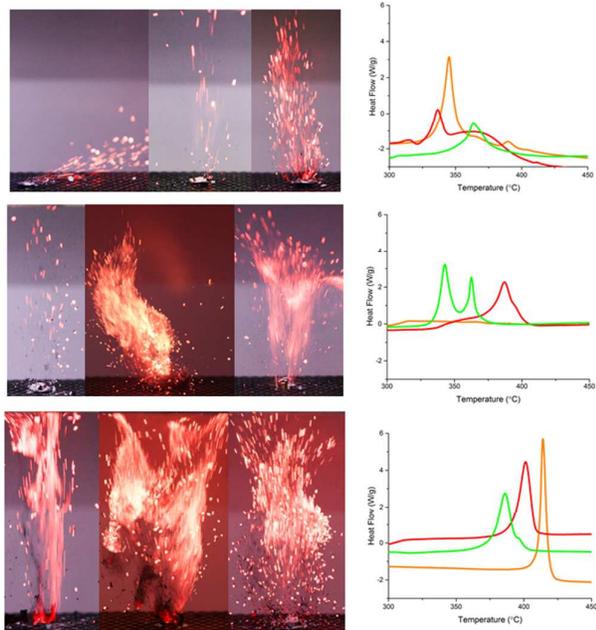
Table 2. Crystal structure geometry and network connectivity: t represents terminal water coordination and br a bridging mode.

[§] The 3D networks could be assigned topologies using the same approach applied to MOFs, however this becomes impractical when applied to 2 & 1D networks, so an adapted scheme based on the carboxylate coordination was applied to all structures.

Terminal coordination by water generally results in reduced dimensionality and impedes the formation of a 3D network. In the fluorinated 1D structures c and d type coordination prevails, whereas for higher dimensionality bonding modes are more diverse. The geometry of linker groups within the framework varies significantly depending on whether they are fluorinated. This is observed in the torsion angles between the carboxylate and aromatic ring, where in Ca1 and Sr1 they are coplanar as opposed to ranging from 45° to 85° in fluorinated cases. It is assumed that the sterically favoured orientation is coplanar but interactions with fluorine groups cause the linker to rotate, which results in the framework becoming more susceptible to higher dimensionality. Even in Ba4_1/2 where linkers lie roughly parallel within a sheet, on moving from one sheet to the next they rotate by 73° which, as a result of 1,4 substitution, drives the formation of a 3D network.

The thermal behaviour of these compounds was investigated by DSC (see ESI sections 3.4 & 4.4) and shows fluorinated linkers to be more reactive while alkali metal structures have lower quality pyrotechnic effect. The structural reinforcement provided by incorporating pyrotechnic ingredients in 3D frameworks is known to be a contributing factor to their high thermal stability.^{10, 12, 20} Figure 2 depicts burn tests and corresponding DSC measurements and shows that tetrafluorophthalic acid linker **6** has the most dramatic effect. Also descending the group (Ca>Sr>Ba) increases pyrotechnic effect. The effect is clearly linked to structure – 3D networks formed by **4** are very stable and have least effect, whilst lower dimensionality networks ie 1D chains in **5** and 2D sheets in **6** are less reinforced and more effective pyrotechnics. The enthalpy of combustion from DSC is greater for lower dimensionality, thus supporting the hypothesis linking structure to pyrotechnic effect.

Figure 2. Burn tests in relation to DSC results. Top row Ca4, Sr4, Ba4, DSC4; middle row Ca5, Sr5, Ba5, DSC5; bottom row Ca6, Sr6, Ba6, DSC6 (DSC Ca, = orange, Sr = red, Ba = green).



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In summary, thirteen alkaline earth metal and three alkali metal coordination polymers have been structurally characterised, eleven of which are novel and all exhibiting pyrotechnic effects. With this approach, the typical pyrotechnic mix (metal nitrate oxidiser, organic fuel) has been transformed into an integrated MOF, containing fuel (both metal and organic) and a fluorinated oxidiser in a single structure. Using a fluorinated linker produces a strong pyrotechnic effect that can be linked to the dimensionality of the framework. There is a fine balance between cross-linking 1D chains so that ingredients are intimately mixed, whilst at the same time ensuring that the structure is not so stable that the pyrotechnic effect is reduced. We therefore conclude that these materials offer the necessary structural tunability within an integrated scaffold for ingredients to produce an appreciable effect and thus may be the basis for a next generation of pyrotechnics, for example it is entirely possible that using this molecular construction method, further modifications can be developed, permitting incorporation of more complex entities, such as dyestuffs for release during burning. Clearly, this approach is directed by our starting materials, which are directly related to current pyrotechnic processes, but it is likely that given a different selection of starting materials, different, but more effective pyrotechnic MOFs can be constructed. Given these basic results, it will be possible to move forward and determine more specific physico-chemical characteristics, such as friction and impact tests for safety and directly useful parameters, e.g well-defined spectral characteristics. It was also intended that the incorporation of group I and II metals would introduce colour into the burn, however this was not very prominent and further work will aim to incorporate chlorine into the framework so that metal chloride decomposition products, which have characteristic colours, form on burning.

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