Propellants, Explosives, Pyrotechnics

DOI: 10.1002/prep.201700101

New Application of Hydroxyl Groups: Ligands for High Density Metal Organic Frameworks

Hui Su,[a] Yalu Dong,[a] Yao Du,[a] Pengcheng Zhang,[a] Panpan Peng,[a] Shenghua Li,*[a] Jichuan Zhang,[a] and Siping Pang*[a]

Abstract: Energetic metal organic frameworks (MOFs) with energetic anions as ligands can be used as new-generation explosives. Many powerful anions have been introduced into energetic MOFs to improve the properties; however, the hydroxyl as a common group for energetic MOFs has rarely been studied. In this article, we present two examples of energetic MOFs ($[Cu(atz)(NO_3)(OH)]_n$) and $[Zn(ata)(OH)]$ (atz = 4-amino-1,2,4-triazole; ata = 5-amino-1H-tetrazole) with the hydroxyl group as the ligand. Crystal structure analyses reveal that the two compounds possess compact two-dimensional (2-D) structures with densities up to 2.41 g cm^{-3} and 2.54 g cm^{-3}, respectively. These two compounds have excellent physicochemical properties. The results demonstrate that a hydroxyl group as the ligands could commendably increase the densities of energetic MOFs, thereby enhancing the detonation performance. It is anticipated this work will open a new direction for the development of energetic MOFs.

Keywords: Energetic · Metal Organic Frameworks · Hydrothermal · Density · Hydroxyl

1 Introduction

Development of superior energetic materials is becoming increasingly important in materials science research [1–6]. High-energy MOFs (HE-MOFs) which make use of high nitrogen content azole heterocycles and their derivatives as ligands are a unique class due to their interesting structures. These energetic ligands [7] and the abundant oxygen-containing anions [8] have been a huge advantage to obtain HE-MOFs with high heat of detonation. HE-MOFs have porous frame materials, which may be beneficial for convective transport [9–11] and thus will influence the energetic performance. In addition, all the sensitive anions are trapped inside the frame structure [8], making the energetic MOFs mechanically insensitive. From these inherent advantages [7–8], it is predicted that HE-MOFs could also become suitable candidates for energetic materials.

Most HE-MOFs have 1D channels [8] incorporating electronegative anions for charge balance. As an important part of HE-MOFs, these groups [12] exert a huge influence on the properties of the MOFs backbone. In order to improve the performances of these polymers, many other more powerful groups have been introduced into HE-MOFs for their high oxygen content and high energy (such as dinitramide ions [12], azides [13] and perchlorates [14]). For example, a dinitramide ion could improve [12] the oxygen balance and density when compared to a nitro group, while the introduction of an azido ligand enhances the nitrogen content. Since HE-MOFs are an emerging class of energetic material and possess very regular channels, introducing a dinitramide ion could increase [12] the sensitivity to mechanical stimulation, perhaps owing to excess compression of functional groups onto a limited backbone. Some powerful anions (azides or perchlorates) could cause serious environmental pollution [15–17], which restrict the range of application. Hence, finding suitable groups for high-energy MOFs remains a challenge.

The hydroxyl group is a common group for energetic materials and it may improve the oxygen balance and the densities. For example, the introduction [18] of the hydroxyl group to 5-aminotetrazole could increase the density from 1.502 g cm^{-3} (5-aminotetrazole) to 1.695 g cm^{-3} (1-hydroxy-5-aminotetrazole), while the density of 1-hydroxy-5-aminotetrazole was also higher than that of the corresponding 1,5-diaminotetrazole (1.571 g cm^{-3}). Organic explosives [19] with hydroxyl groups do not show superiority in improving the heat of detonation, or other properties, when compared to those of other groups. However, the hydroxyl group is an easily ionized functional group with strongly electrophilic characteristics, which may strengthen [20] hydrogen bonds, obviously improving [21–23] for the density of energetic materials. For example, the density of TNP (2, 4, 6-trinitrophenol) is 1.763 g cm^{-3} and the density of TNT (2, 4, 6-Trinitrotoluene) is 1.643 g cm^{-3}. Improving the densities may be beneficial to the detonation properties since detonation pressure and velocity are two principal detonation

---

[a] *H. Su, Y. Dong, Y. Du, P. Zhang, P. Peng, S. Li, J. Zhang, S. Pang*
School of Materials Science & Engineering, Beijing Institute of Technology, Beijing 100081, PR China
**e-mail: lishenghua@bit.edu.cn*
pangsp@bit.edu.cn

Supporting information for this article is available on the WWW under https://doi.org/10.1002/prep.201700101 parameters, and are proportional to the initial density of pure or mixtures of energetic compounds. Although a lot of MOFs with the hydroxyl group as the ligand have a remarkably high density (such as 2.223 g cm^{-3} for $\{[Cu_6(atz)_6(H_2O)_2(\mu_3\text{-}OH)_2(SO_4)_5]\cdot 5.25H_2O\}_n$ [24]; 2.189 g cm^{-3} for $\{[Cu_2(atz)_2(\mu\text{-}OH)_2(SO_4)]\cdot 3H_2O\}_n$ [24]; 2.296 g cm^{-3} for $\{[Cu_7(atz)_6(H_2O)_6(\mu_3\text{-}OH)_2(SO_4)_6]\cdot 2H_2O\}_n$ [24]; 2.873 g cm^{-3} for $\{[Zn_4SO_4(OH)_6(C_2N_2H_8)_{0.5}]\cdot 3H_2O\}_n$ [25] ($C_2N_2H_8$=ethylenediamine) and 2.805 g cm^{-3} for $\{[Zn_4SO_4(OH)_6(C_2N_2H_8)_{0.5}]_7\cdot 18H_2O\}_n$ [25]), there has been no research on potential MOFs as energetic materials due to the lack of an energetic ligand which rapidly releases heat during combustion.

Herein, we present two examples of energetic MOFs with the hydroxyl group as the ligand. Two energetic MOFs, $[Cu(atz)(NO_3)(OH)]_n$ [26] and [Zn(ata)(OH)] [27] (atz = 4-amino-1,2,4-triazole; ata = 5-amino-1H-tetrazole), were prepared using a coordination chemistry strategy. Crystal structure analyses revealed that the above compounds possess compact two-dimensional (2-D) structures with densities up to 2.41 g cm^{-3} and 2.54 g cm^{-3}, respectively. Their relatively high densities are presumably due to the hydroxyl groups; these MOFs have close layer-by-layer stacking in the solid state, resulting in a high density. In addition, the above framework results in superior insensitivity, thermostability and a high theoretical detonation pressure. Moreover, all of these properties indicate that the two compounds have the potential to be insensitive explosives.

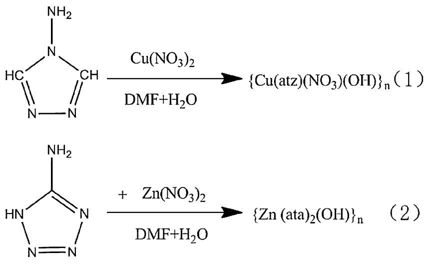
2 Experimental Section

2.1 Chemical and Materials

Copper dinitrate trihydrate and dimethylformamide were all purchased from Beijing Chemical Reagent Company without further purification. atz, ata and Zinc nitrate hexahydrate was purchased from Sigma-Aldrich corporation.

2.2 Synthesis of the Energetic metal Organic Framework

The copper complex MOFs species, $[Cu(atz)(NO_3)(OH)]_n$, (1), was synthesized using a hydrothermal method – a simple reaction of copper dinitrate trihydrate with atz in water (Scheme 1). atz (0.084 g, 10 mmol) was suspended in 10 mL dimethylformamide, with stirring at room temperature until the solution is clear and transparent. The solvent was removed and the solution transferred into a 50 mL volumetric flask. A solution of copper dinitrate trihydrate (0.483 g, 20 mmol) in 20 mL water was added whilst keeping the temperature at 90 °C. In order to speed up the reactions, one drop of dense nitric acid (about 0.03 mL) was added. The reaction mixture was left standing for 36 h at 90 °C. Dark blue bulk crystals (suitable for X-ray structure determination) of target product from a clear green solution were acquired. The solid was collected by filtration, washed with deionized water, and vacuum dried at 60 °C. The crystal structure of (1) is confirmed by X-ray analysis to be equal to the one reported by Liu, et al [26]. Elemental analysis of $C_2H_5CuN_5O_4$ (226.66) (%): calculated – C 10.60, H 2.22, N 30.91; experimental – C 10.33, H 2.78, N 31.65.



Scheme 1. Synthesis and coordination mode for 1 and 2

The zinc complex, [Zn(ata)(OH)], (2), was synthesized using the same hydrothermal method - a simple reaction of zinc nitrate hexahydrate with ata (Scheme 1). The crystal structure of (2) is confirmed by X-ray analysis to be equal to the one reported by Wang et al [27]. ata (0.085 g, 10 mmol) was suspended in 10 mL dimethylformamide, with stirring at room temperature until the solution was clear and transparent. The solvent was removed and the solution transferred into a 50 mL hydrothermal reaction vessel. A solution of zinc nitrate hexahydrate (0.483 g, 20 mmol) in 20 mL water was added whilst keeping the temperature at 160 °C. The reaction mixture was left standing for 40 h at 160 °C. Colourless bulk crystals (suitable for X-ray structure determination) were acquired. The solid was collected by filtration, washed with deionized water, and vacuum dried at 60 °C. Elemental analysis of CH_3ON_5Zn (166.45) (%): calculated – C 7.2, H 1.8, N 54.1; experimental – C 7.6, H 2.8, N 52.7.

3 Results and Discussion

3.1 Crystal Structure

Nitrogen-rich 2-D porous MOF, (1), belongs to the triclinic P-1 space group where hydroxyl groups bridge linear –Cu–O–Cu- chains, interconnected together by atz ligands. The crystal structure of (1) is confirmed by X-ray analysis to be equal to the one reported by Liu [26], et al. As depicted in Figure 1, the asymmetric unit is made up of two Cu(II) species, two atz ligands, two hydroxyl groups and two nitrate anions. The Cu atom exhibits two different coordination modes when binding to atz ligands. The first mode is a hexadentate Cu(1) atom coordinated by two O atoms from two symmetric hydroxyl groups (Cu(1)–O(3) = 1.94 Å), two O atoms from two symmetric nitrate groups (Cu(1)–O(3) = Cu(1)–O(2) = 2.57 Å) and two N atoms from two atz ligands. Another is Cu(2) atoms in a disparate environment, where hexadentate Cu(2) atoms are bridged by two O atoms from two symmetric hydroxyl groups (Cu(2)–O(3) = Cu(2)–O(4) =

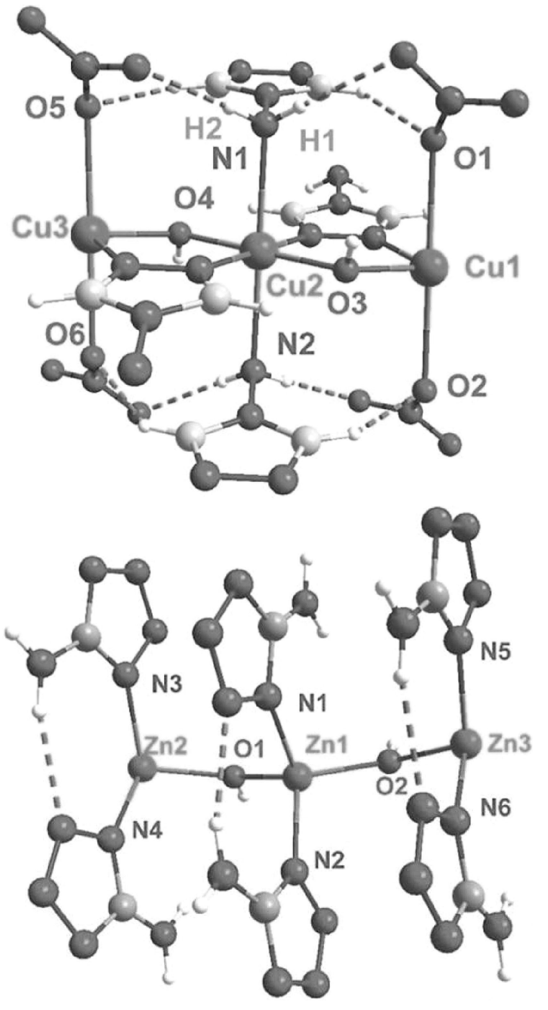


Figure 1. Coordination environment of M (II) ions in title compound ((1) = up, (2) = down; for (1) M: Cu and (2) M: Zn; with some hydrogen atoms are omitted for clarity).

1.95 Å) and four N atoms from four atz ligands. The hydroxyl groups act as a bridge to link two adjacent Cu atoms, forming –Cu-O–Cu- chains (Cu(1)–O(3) = Cu(2)–O(4)–Cu(3)). In the structure of (1), the nitrate groups and the Contains hydrogen(C – H, N–H) groups of the atz ligands form diverse hydrogen bonding (e.g., dashed line, Figure 1). The N–H···O hydrogen-bonding distances (O…N distances) vary from 2.90 Å to 3.1 Å, which is considerably approach with previously reported distances (2.8 Å–3.0 Å) [28] indicating hydrogen-bonding interactions. Two different copper coordination environments make up compound (1) and form a 2-D compacted polymeric sheet. Portions of the 2-D sheet polymer appear to be arranged in a "ladder" motif (Figure 2). The adjacent layers are linked by weak interlayer O–H···O hydrogen-bonding (dashed line, Figure 2), yielding a stable 3-D supramolecular network.

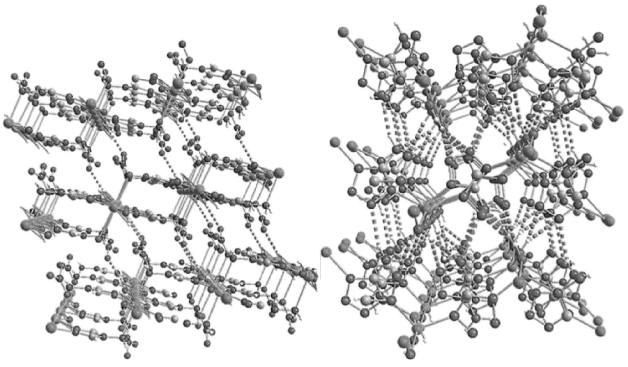


Figure 2. 3-D supramolecular network of the title compounds ((1) = left, (2) = right, with some hydrogen atoms omitted for clarity).

Single-crystal structural analysis indicates that (2) is a grid-like coplanar 2-D layer with hydroxyl groups bridging linear –Zn–O–Zn– chains, interconnected by ata ligands (Figure 1). The crystal structure of (2) is confirmed by X-ray analysis to be analogous to the one reported by Wang [27] with similar coordination mode and different space group. The Zn atoms exhibit just one (tetradentate) coordination mode, formed by two O atoms from two symmetric hydroxyl groups (Zn(1)–O(1) = Zn(1)–O(2) = 1.94 Å) and two N atoms from two ata ligands (Zn(1)–N(1) = Zn(1)–N(2) = 2.00 Å). Just like (1), the 2-D layers are stabilized by the intramolecular N–H···N hydrogen bonding interactions (dashed line, Figure 1). The 2-D layers of (2) are further interlinked by the strong N–H···N and O–H···N hydrogen bonding interactions (dashed line, Figure 2) and stack into a 3D supramolecular framework.

According to single-crystal structural analysis, (1) and (2) possess high densities (2.41 g cm^{-3} for (1) and 2.54 g cm^{-3} for (2)), which are presumably a result of the hydroxyl groups. As shown in Figure 1, the hydroxyl groups and metallic ion array features regular intervals with powerful –Cu–O–Cu– or –Zn–O–Zn– chain connection. It should be noted that the minimum distance between two adjacent metallic ions for (2) is extremely short (3.37 Å), lower than for the MOFs with the same ligands and metal ions reported to date, including $Zn_2(ata)_3$ (6.0 Å) [27] and $[Zn(ata)_2(NO_3)]_n$ (6.1 Å and CCDC: 1028765). Similarly, (1) possesses extremely short distances (3.4 Å), as (2). It is possible that two adjacent metallic ions are close due to strong coordinate bonds and the small size of hydroxyl groups, thus illustrating the hydroxyl groups play an important role, compacting the structure and increasing the density. Extensive hydrogen bonds (dashed line, Figure 2) between the layers results in close layer stacking, giving a high density.

3.2 Evaluation of Physicochemical Properties

To evaluate the possibility of compounds (1) and (2) as suitable explosives, the physicochemical properties of density, oxygen balance, nitrogen content and sensitivity were investigated. As show in Table 1, the density of (1) and (2) is

Table 1. Physicochemical properties of MOFs and some energetic materials.

Property	ρ [a] [g cm^{-3}]	*N* [b] [%]	Ω_{CO2} [c] [%]	T_{dec} [d] [°C]	ΔH_{det} [e] [kJ g^{-1}]	*D* [f] [km s^{-1}]	*P* [g] [GPa]	*IS* [h] [J]	*FS* [i] [N]	*ESD* [j] [J]
1	2.41	30.91	−24.72	288	3.158	7.459	29.71	11	180	12.13
2	2.54	54.1	−33.60	338	2.553	8.628	39.67	>40	>360	>24.75
TNT [k]	1,65	18.5	−73.96	244	3.751	7.178	20.5	15	353	0.57
RDX [k]	1.81	37.80	−21.60	210	5.796	8.600	33.92	7.5	120	0.2
HMX [k]	1.95	37.8	−21.60	287	5.520	8.900	38.39	7.4	–	0.2
CL-20 [l]	2.04	38.36	0	221	6.164	9730	44.4	4	48	0.13
$[Cu(Htztr)]_n$ [k]	2.44	49.08	−56.09	355	16.553	10.40	56.48	32	>360	>24.75
$Pb(Htztr)_2(H_2O)$ [m]	2.519	39.40	−45.03	340	5.683	7.715	31.57	>40	>360	–
Pb(H2tztr)(O) [m]	3.511	27.20	−28.86	318	1.066	8.122	40.12	>40	>360	–
CHHP [k]	2.00	23.58	−13.01	231	3.137	6.205	17.96	0.8	–	–
ZnHHP [k]	2.12	23.61	−49.99	293	2.927	7.016	23.58	–	–	–

[a] Density. [b] Nitrogen content. [c] Oxygen balance. [d] The onset decomposition temperature (DSC). [e] the heat of detonation. [f] The detonation velocity (calculated by EXPLO5 v6.01). [g] detonation pressure (calculated by EXPLO5 v6.01). [h] Impact sensitivity. [i] Friction sensitivity. [j] Electrostatic sensitivity. [k] Properties are taken from Ref [31]. [l] Properties are taken from ref. [12] [m] Properties are taken from Ref [32].

2.41 g cm^{-3} and 2.54 g cm^{-3}, respectively. The density of (1) and (2) is higher than that of the organic explosives TNT (1.65 g cm^{-3}) and RDX (1.81 g cm^{-3}) (Table 1), but is also higher than that of the MOFs with the same ligands and metal ions reported to date (Figure 3), including $[Cu(atz)_3(NO_3)_2]_n$ (1.811 g cm^{-3}) [29], $[Cu(atz)_2(NO_3)_2]_n$ (2.072 g cm^{-3}) [26], $Zn_2(ata)_3$ (1.68208 g cm^{-3}) [27] and $[Zn(ata)_2(NO_3)]_n$ (2.12076 g cm^{-3} and CCDC: 1028765).

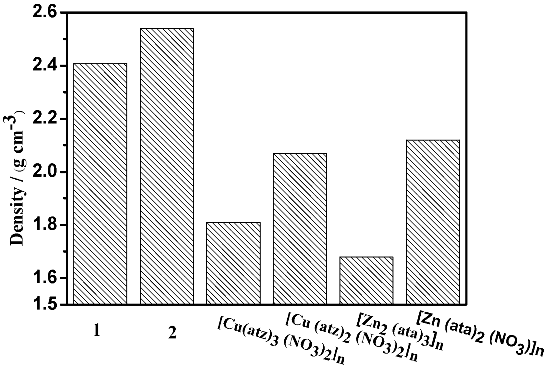


Figure 3. Bar chart representation of the literature density values for the MOFs with the same ligands and metal ions reported to date.

In addition, the oxygen balance and nitrogen content for (1) and (2) is acceptable. The nitrogen content of (2) is 54.10 %, assuring halogen free, low smoking and friendly to the environment products. For compound (1), the sensitivities (IS = 11 J; FS = 180 N; EDS = 12.13 J) are lower than those of traditional energetic materials such as RDX (IS = 7.5 J; FS = 120 N; EDS = 0.2 J) (Table 1). In addition, compound (2) is an insensitive energetic material. In contrast, the extreme sensitivities to electrostatic discharge [30–31] of RDX (0.2 J) and CL-20 (0.13 J) (Table 1) are exceedingly dangerous because external disturbance can easily set them off.

3.3 Thermostabilities

The thermostabilities of (1) and (2) were investigated using thermogravimetric analysis. The decomposition temperatures of (1) and (2) were measured to be 288 °C and 338 °C, respectively (Figure 4), which is higher than that of RDX (210 °C, Table 1), one of the most energetic materials commonly employed. From Figure 4, we learn about materials that leave very few solid residues after combustion (28 % for (1) and 46 % for (2)), which is an important characteristic for environmentally friendly energetic materials.

3.4 Computational Assessment

To estimate the heat of detonation (ΔH_{det}) of the above materials, and to see how they compare to those of common energetic materials, a precise rotating-oxygen bomb calorimeter [31] was used for energetic MOFs. Approximately 500 mg of the samples were pressed with an oxygen bomb [33], which is a well-defined amount of benzoic acid (calculated: 1000 mg) pressed to form a tablet, ensuring better combustion. The recorded data is the average of six single measurements. The experimental results for the constant volume combustion energies ($\Delta_c U$) of energetic compounds (1) and (2) are 5949.8 J g^{-1} and 7109.3 J g^{-1}, respectively. On the basis of the formula $\Delta_c H_{\theta m} = \Delta_c U_{\theta m} + [ng\ (products) - ng\ (reactants)]\ RT$ (where ng is the total molar amount of gases in the products or reactants, $R = 8.314\ J mol^{-1} K^{-1}$, $T = 298.15\ K$), the standard molar enthalpies of combustion ($\Delta_c H_{\theta m}$) can be derived as being 1340.95 kJ mol^{-1} for (1) and 1171.51 kJ mol^{-1} for (2). The combustion reaction Equations are listed as (1) and (2):

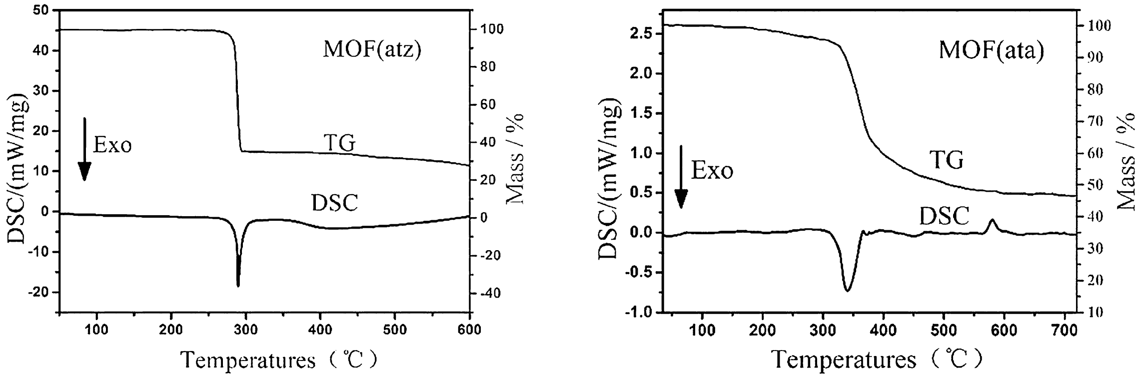


Figure 4. The DSC-TG curve for (1) left; and (2) right.

$$C_2H_5O_4N_5Cu + 1.75\ O_2 = CuO + 2\ CO_2 + 2.5\ H_2O + 2.5\ N_2 \tag{1}$$

$$CH_3ON_5Zn + 1.75\ O_2 = ZnO + CO_2 + 1.5\ H_2O + 2.5\ N_2 \tag{2}$$

The standard molar enthalpies of formation of the combustion products are obtained from the literature. According to Hess's law, the standard molar enthalpies of formation ($\Delta_f H_{\theta m}$) of (1) and (2) at 298.15 K are calculated as $-192.49\ kJ\,mol^{-1}$ and $64.81\ kJ\,mol^{-1}$, respectively. In accordance with the maximum heat release principle, for (1), water, nitrogen, carbon and carbon dioxide were assumed to be the final products of decomposition of the organic part of the framework, and the formation of copper was assumed to be governed by the deficiency of oxygen. For (2), hydrogen, nitrogen and carbon were assumed to be produced primarily due to the deficiency of oxygen and the formation of zinc oxide was based mainly on the maximum heat release principle. The complete detonation reactions are described by Equations (3) and (4).

$$C_2H_5O_4N_5Cu = Cu + 0.75\ CO_2 + 2.5\ H_2O + 2.5\ N_2 + 1.25\ C \tag{3}$$

$$CH_3ON_5Zn = ZnO + 1.5\ H_2 + 2.5\ N_2 + C \tag{4}$$

In the theoretical case, the heat of detonation (ΔH_{det}) of compounds (1) and (2) at 298.15 K are calculated as $3157.6\ J\,g^{-1}$ and $2552.9\ J\,g^{-1}$, respectively. Detonation velocity (D) and detonation pressure (P) are perhaps the most important parameters which illustrate the detonation characteristics of energetic materials. Detonation performances of the related energetic MOFs here were evaluated by the empirical Kamlet-Jacobs [34] formula, as:

$$D = 1.01\ \Phi^{1/2}\ (1 + 1.30\rho) \tag{5}$$

$$P = 1.558\ \Phi\ \rho^2 \tag{6}$$

$$\Phi = 31.68\,N\ (MQ)^{1/2} \tag{7}$$

D represents detonation velocity ($km\,s^{-1}$) and P is detonation pressure (GPa), ρ is the density of explosive ($g\,cm^{-3}$). Φ, N, M and Q are characteristic parameters of an explosive. Φ is an intermediate quantity, which has no practical meaning. N is the moles of detonation gases per gram of explosive, M is the average molecular weight of these gases and Q is the heat of detonation ($kcal\,g^{-1}$). The complete detonation reactions are described by Equations 1 and 2. The formation of metal oxides as solid was assumed to be governed by the deficiency of oxygen.

The physical properties of the compounds and relevant compounds are listed in Table 1. As shown in Table 1, although the detonation velocity of (2) was measured to be $8.628\ km\,s^{-1}$, which is lower than or approximately equal to that of the main explosives (RDX: $8.600\ km\,s^{-1}$; HMX: $8.900\ km\,s^{-1}$), the detonation pressure of (2) is higher than that of those materials (TNT: 20.5 GPa; RDX: 33.92 GPa; HMX: 38.39 GPa; Table 1). Among them, the detonation pressure of (2) is lower than that of the recently reported $[Cu(Htztr)]_n$ (theoretical calculation) but is higher than for the majority of energetic MOFs reported to date: $[Pb(Htztr)_2(H_2O)]_n$ (31.57 GPa), CHHP (17.96 GPa) and ZnHHP (23.58 GPa) (Table 1). The relatively high detonation pressure of (2) could result from its high density and abundant detonation products, which are closely related to the volume of the detonation gases. The relatively high detonation pressure is presumably caused by the high density of (2).

3.5 Detonation Performance

Compared to the energetic materials reported previously, excellent density of the title energetic MOFs are proved, with particularly high density of $2.41\ g\,cm^{-3}$ and $2.54\ g\,cm^{-3}$ for (1) and (2), respectively, which are insensitive to external stimulus. The heat of detonation of compound (1) is in the lower level of conventional explosives and energetic MOFs listed in Table 1, and the favourable values of D and P are probably due to the excellent oxygen balance and high density. In spite of the lower heat of detonation of compound (2), the excellent detonation pressure may be due to the high density up to 2.54 g cm^{-3}. In addition, the introduction of hydroxyl groups to energetic MOFs does not shown an improvement to the heat of detonation, nevertheless, hydroxyl groups with strongly electrophilic characteristic and small size may reduce the distances between bridging hydroxyls and two metallic ion, which may benefit the density of energetic MOFs.

4 Conclusions

In conclusion, two high density energetic MOFs have been synthesized with hydroxyl groups as the ligands. The properties of the two MOFs have been measured or calculated, revealing that the species possess high densities for energetic MOFs. As two high energy density materials, complexes (1) and (2) exhibit favourable physicochemical properties, such as high decomposition temperatures, favourable oxygen balance and low sensitivities. Specifically, compound (2) exhibits explosive performances with the highest detonation pressure of 39.67 GPa, equal with that of HMX, one of the most energetic materials commonly used. The present work provides a possible application of hydroxyl groups to influence the density of energetic materials, and exciting results can be expected after further work.

Acknowledgements

The authors acknowledge financial support from the National Natural Science Foundation of China (21576026 and U1530262) and the opening project of State Key Laboratory of Science and Technology (Beijing Institute of Technology, ZDKT12-03).

References

[1] T. M. Klapötke, D. G. Piercey, J. Stierstorfer, The taming of CN_7^-: the azidotetrazolate 2-oxide anion. *Chem.-Eur. J.* **2011**, *17*, 13068–13077.

[2] T. M. Klapötke, F. A. Martin, J. Stierstorfer, C2N14: An energetic and highly sensitive binary azidotetrazole. *Angew. Chem., Int. Ed.* **2011**, *50*, 4227–4229.

[3] Y. H. Joo, J. M. Shreeve, High-density energetic mono- or bis (Oxy)-5-nitroiminotetrazoles. *Angew. Chem., Int. Ed.* **2010**, *49*, 7320–7324.

[4] P. Yin, J. Zhang, C. He, D. A. Parrish, J. M. Shreeve, Polynitro-substituted pyrazoles and triazoles as potential energetic materials and oxidizers. *J. Mater. Chem. A* **2014**, *2*, 3200–3208.

[5] Y. C. Li, C. Qi, S. H. Li, H. J. Zhang, C. H. Sun, Y. Z. Yu, S. P. Pang, 1, 1′-Azobis-1, 2, 3-triazole: A high-nitrogen compound with stable N8 structure and photochromism. *J. Am. Chem. Soc.* **2010**, *132*, 12172–12173.

[6] C. Qi, S. H. Li, Y. C. Li, Y. Wang, X. K. Chen, S. P. Pang, A novel stable high-nitrogen energetic material: 4, 4′-azobis (1, 2, 4-triazole). *J. Mater. Chem.* **2011**, *21*, 3221–3225.

[7] O. S. Bushuyev, P. Brown, A. Maiti, R. H. Gee, G. R. Peterson, B. L. Weeks, L. J. Hope-Weeks, Ionic polymers as a new structural motif for high-energy-density materials. *J. Am. Chem. Soc.* **2012**, *134*, 1422–1425.

[8] S. Li, Y. Wang, C. Qi, X. Zhao, J. Zhang, S. Zhang, S. Pang, 3D Energetic Metal–Organic Frameworks: Synthesis and Properties of High Energy Materials. *Angew. Chem., Int. Ed.* **2013**, *52*, 14031–14035.

[9] Y. He, R. Krishna, B. Chen, Metal-organic frameworks with potential for energy-efficient adsorptive separation of light hydrocarbons. *Energy Environ. Sci.* **2012**, *5*, 9107–9120.

[10] Q. Zhai, Q. Lin, T. Wu, L. Wang, S. Zheng, X. Bu, P. Feng, High CO2 and H2 uptake in an anionic porous framework with amino-decorated polyhedral cages. *Chem. Mater.* **2012**, *24*, 2624–2626.

[11] H. B. Zhang, M. J. Zhang, P. Lin, V. Malgras, J. Tang, S. M. Alshehri, Y. Yamauchi, S. W. Du, J. Zhang. A Highly energetic N-rich metal-organic framework as a new high-energy-density materia. *Chem. Eur. J.* **2016**, *22*, 1141–1145.

[12] J. Zhang, Y. Du, K. Dong, H. Su, S. Zhang, S. Li, S. Pang, Taming dinitramide anions within an energetic metal-organic framework: A new strategy for synthesis and tunable properties of high energy materials. *Chem. Mater.* **2016**, *28*, 1472–1480.

[13] J. Liu, D. Fu, J. Zhuang, C. Duan, X. You, Linear trinuclear and one-dimensional copper(II) complexes containing co-bridging end-on azido and triazole ligands. Crystal structures and magnetic properties of $[Cu_3(atrz)_2(N_3)_6]$ and $[Cu(atrz)_2(N_3)]NO_3$ (atrz = 4-amino-1,2,4-triazole). *J. Chem. Soc., Dalton Trans.* **1999**, 2337–2342.

[14] Z. Mi, S. Chen, Z. Jing, L. Yang, T. Zhang, Innovative concept of designing primary explosives by introducing polymers: preparation and investigation of $\{[Ca(CHZ)_2](ClO_4)_2\}_n$ (CHZ = carbohydrazide). *Eur. J. Inorg. Chem.* **2016**, 3978–3983.

[15] Y. Zhang, J. X. Chen, L. L. Wen, Y. Tang, H. Zhao, Effects of salinity on simultaneous reduction of perchlorate and nitrate in a methane-based membrane biofilm reactor. *Environ. Sci. Pollut. Res.* **2016**, *23*, 24248–24255.

[16] B. C. Terry, T. R. Sippel, M. A. Pfeil, I. E. Gunduz, S. F. Son, Removing hydrochloric acid exhaust products from high performance solid rocket propellant using aluminum-lithium alloy. *J. Hazard. Mat.* **2016**, *317*, 259–266.

[17] I. L. Blanc-Louvry, P. Laburthe-Tolra, V. Massol, F. Papin, J. P. Goulle, G. Lachatre, J. M. Gaulier, B. Proust, Suicidal sodium azide intoxication: an analytical challenge based on a rare case. *Forensic Sci. Int.* **2012**, *221*, e17–e20.

[18] D Fischer, T. M. Klapötke, D. G. Piercey, J. Stierstorfer, Synthesis of 5-aminotetrazole-1N-oxide and Its azo derivative: a key step in the development of new energetic materials. *Chem. Eur. J.* **2013**, *19*, 4602–4613.

[19] H. Du, H. Liu, Y. Liu, J. Zhang, F. Wang, X. Gong, DFT studies on detonation properties, pyrolysis mechanism, and stability of the nitro and hydroxyl derivatives of benzene. *Chin. J. Chem.* **2011**, *29*, 455–462.

[20] H. Zhang, F. Chen, F. Zhao, C. Meng, Structural and electronic properties of 2, 4, 6-trinitrophenol (TNP). *J. Mol. Struct.: THEOCHEM* **2008**, *857*, 33–37.

[21] L. Meng, Z. Lu, X, Wei, X. Xue, Y. Ma, Q. Zeng, G. Fan, F. Nie, C. Zhang, Two-sided effects of strong hydrogen bonding on the stability of dihydroxylammonium 5, 5′-bistetrazole-1, 1′-diolate (TKX-50). *CrystEngComm* **2016**, *18*, 2258–2267.

[22] J. Zhang, Q. Zhang, T. T. Vo, D. A. Parrish, J. M. Shreeve, Energetic salts with π-stacking and hydrogen-bonding interactions lead the way to future energetic materials. *J. Am. Chem. Soc.* **2015**, *137*, 1697–1704.

[23] P. Yin, D. A. Parrish, J. M. Shreeve, Energetic multifunctionalized nitraminopyrazoles and their ionic derivatives: ternary hydrogen-bond induced high energy density materials. *J. Am. Chem. Soc.* **2015**, *137*, 4778–4786.

[24] E. Yang, X. Wang, C. Zhang, N. Yang, Z. Liu, X. Zhao, Three new MOFs with unusual CuII6 cluster, linear CuII chain and triangular CuII3 core motifs tuned by sulfonate group: Synthesis, structures and magnetic properties. *Sci. China Chem.* **2013**, *5*, 465–474.

[25] A. Rujiwatra, G. J. Mander, C. J. Kepert, M. J. Rosseinsky, Synthesis and Characterization of Subcell-Supercell Related Ethylenediamine-Pillared Zinc Hydroxy sulfates. *Cryst. Growth Des.* **2005**, *5*, 183–189.

[26] Z. Liu, Y. Su, E. Yang, X. Zhao, Structural transformation from a coplanar layer to a linear chain by switchable coordination of exocyclic amino group. *Inorg. Chem. Commun.* **2012**, *26*, 56–59.

[27] X. Wang, J. Chen, J. Liu, Photoluminescent Zn (II) metal-organic frameworks built from tetrazole ligand: 2D four-connected regular honeycomb (4363)-net. *Cryst. Growth Des.* **2007**, *7*, 1227–1229.

[28] R. Vargas, J. Garza, R. A. Friesner, H. Stern, B. P. Hay, D. A. Dixon, Strength of the N–H···O=C and C–H···O=C Bonds in Formamide and N-Methylacetamide Dimers. *J. Phys. Chem. A* **2001**, *105*, 4963–4968.

[29] M. M. Dîrtu, C. Neuhausen, A. D. Naik, A. Rotaru, L. Spinu, Y. Garcia, Insights into the origin of cooperative effects in the spin transition of $[Fe(NH_2trz)_3](NO_3)_2$: The role of supramolecular interactions evidenced in the crystal structure of $[Cu(NH_2trz)_3](NO_3)_2{\cdot}H2O$. *Inorg. Chem.* **2010**, *49*, 5723–5736.

[30] N. Fischer, D. Fischer, T. M. Klapötke, D. G. Piercey, J. Stierstorfer, Pushing the limits of energetic materials-the synthesis and characterization of dihydroxylammonium 5, 5′-bistetrazole-1, 1′-diolate. *J. Mater. Chem.* **2012**, *22*, 20418–20422.

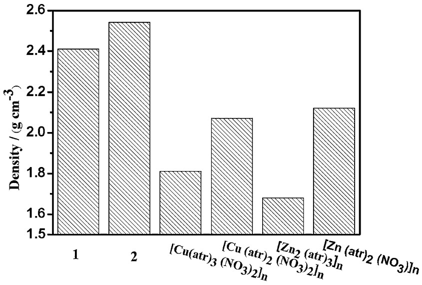
[31] X. Y. Liu, W. J. Gao, P. P. Sun, Z. Y. Su, S. p. Chen, Q. Wei, G. Xie, S. L. Gao. Environmentally friendly high-energy MOFs: crystal structures, thermostability, insensitivity and remarkable detonation performances. *Green Chemistry* **2015**, *17*, 831–836.

[32] W. J. Gao, X. Y. Liu, Z. Y. Su, S. Zhang, Q. Yang, Q. Wei, S. P. Chen, G. Xie, X. Y. Yang, S. L. Gao, High-energy-density materials with remarkable thermostability and insensitivity: syntheses, structures and physicochemical properties of Pb (II) compounds with 3-(tetrazol-5-yl) triazole. *J. Mater. Chem. A* **2014**, *2*, 11958–11965.

[33] X. Yang, S. Chen, S. Gao, H. Li, Q. Shi, Construction of a rotating-bomb combustion calorimeter and measurement of thermal effects. *Instrum. Sci. Technol.* **2002**, *30*, 311–321.

[34] M. J. Kamlet, S. J. Jacobs, Chemistry of detonations. I. A simple method for calculating detonation properties of C–H–N–O explosives. *J. Chem. Phys.* **1968**, *48*, 23–35.

Received: April 13, 2017
Revised: August 5, 2017



H. Su, Y. Dong, Y. Du, P. Zhang, P. Peng, S. Li, J. Zhang, S. Pang**

1 – 8

New Application of Hydroxyl Groups: Ligands for High Density Metal Organic Frameworks