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Construction of a Thermally Stable and Highly Energetic Metal-Organic Framework as Lead-Free Primary Explosives

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ABSTRACT: Two energetic compounds, i.e., 4,8-dinitraminodifurazano[3,4-*b*,*e*]pyrazine (1) and its potassium-based energetic metal-organic framework (E-MOF) (2), were prepared, and their crystal structures were confirmed by single crystal X-ray diffraction analysis. Compound 1 co-crystallizes with water molecules and shows a three-dimensional (3D) sandwich-like supramolecular structure, which is rare in the known energetic organic compounds. Compound 2 has a pillared layered structure with a pcu topology. The layered structure in the 3D framework featuring sql topology was constructed from inorganic chains {K₂O} and nitroamine groups. The crystal density of **2** is up to 2.114 g cm⁻³. This potassium-based E-MOF shows high thermal

stability, high detonation velocity, and high impact and friction sensitivities, which make it a potential high-performing primary explosive.

1. INTRODUCTION

In recent years, the research on lead-free primary explosives has aroused increasing attention since the most widely used lead-based primary explosives (e.g., lead azide (LA) and lead styphnate (LS)) have high toxicity to human beings and environment.¹⁻³ In order to offset these drawbacks, two kinds of metal-free energetic materials, namely, cyanuric triazide (CTA) and 2-diazo-4,6-dinitrophenol (DDNP), have been prepared and tried to be used as potential primary explosives.⁴⁻⁵ In spite of high detonation performance and high sensitivities, both compounds showed poor thermal stability. The design of novel energetic materials as lead-free primary explosives should consider their chemical composition, thermal stability, energetic performance, sensitivities and some other related properties. The diverse requirements of primary explosives make the development of environmentally friendly primary explosives a great challenge.⁶⁻⁷

Metal-organic frameworks (MOFs) have attracted extensive interests in various research areas including catalysis, gas adsorption and sensors, mainly due to their tunable structures and functional properties.⁸⁻¹¹ In recent years, using explosive ligands to construct energetic MOFs (i.e., E-MOFs) has been actively pursued since their energy levels and sensitivities can be controlled by reasonable assembly of metal ions and energetic ligands.¹²⁻¹³ For example, Pang and co-workers synthesized a 3D E-MOF using Cu(II) as metal centers and 4,4'-azo-1,2,4-triazole (atrz) as energetic ligand.¹⁴ This E-MOF has the high calculated detonation velocity and

low impact and friction sensitivities. The low mechanical sensitivity may be due to the strong coordination interactions between metal ions and energetic ligands. Chen and co-workers prepared a E-MOF using Cu(I) as metal center and 3-(1H-tetrazol-5-yl)-1H-triazole (H₂tztr) as energetic ligand, which exhibited high thermal stability ($T_{dec} = 355$ °C) and excellent detonation property (detonation velocity: 10400 m s⁻¹).¹⁵ Shreeve and co-workers reported an interesting 3D E-MOF, i.e., potassium 4,4'-bis(dinitromethyl)-3,3'-azofurazanate, which showed promise for primary explosive applications (Scheme 1).¹⁶ Previous studies have demonstrated that those E-MOFs composed of transition metal ions and high nitrogen ligands may have good thermal stability, while those E-MOFs composed of main group metal ions and energetic ligands may have high calculated denotation velocity and high sensitivity.¹³

Scheme 1. Molecular Structures of Some Reported Potassium-Based E-MOFs.

Previous works on potassium primary explosives:



Nowadays, the research of developing lead-free primary explosives focused on the design and construction of novel high-performing E-MOFs. Most E-MOFs adopted the potassium ion as the metal centers, and some representative examples included potassium 1,5-(dinitramino)tetrazolate,¹⁷ potassium 1,1'-dinitramino-5,5'-bis-(tetrazolate) (K₂DNABT),¹⁸ potassium 4,5bis(dinitromethyl)furoxanate,¹⁹ potassium 3-dinitromethyl-4-nitraminofurazan,²⁰ and potassium 3,4-bis(3-dinitromethylfurazan-4-oxy)furazan (K₂BDFOF)²¹ (Scheme 1). As compared to the LA and LS, these potassium-based energetic salts as primary explosives have the advantages of low toxicity, high detonation capacity and good thermal stability.²² As a result, the energetic ligands play significant roles in the construction of high-performing E-MOFs. In this context, a number of nitrogen-rich energetic ligands (e.g., triazole, tetrazole, and tetrazine) have been widely used to develop potential E-MOFs with different structures and promising properties.^{12-13,23} Compared to these nitrogen-rich energetic ligands, furazan has a relatively higher oxygen and nitrogen content which facilitates the high oxygen balance of E-MOFs. Also, the high heat of formation of furazan can enhance the detonation performance of E-MOFs.²⁴⁻²⁵

In this work, we designed and synthesized a 3D E-MOF by using potassium ions as the metal centers and nitroamine furazans as energetic ligands. A molecular fragment of 4,8-dihydrodifurazano[3,4-*b*,*e*]pyrazine (DFP) in the energetic ligand contains two furazan rings and many energetic chemical bonds (i.e., C–N, N–O and C=N bonds), which can enhance the energy level of final E-MOFs. Recently, theoretical research on 4,8-dinitraminodifurazano[3,4-

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b,e]pyrazine was reported, which showed excellent detonation performances of this compound (D = 9320 m s⁻¹, P = 40.4 GPa). The synthesis and characterization of 4,8dinitraminodifurazano[3,4-*b,e*]pyrazine is helpful for the development of novel E-MOF due to the excellent calculated performances.²⁶ Furthermore, the symmetric planar structure of DFP skeleton is beneficial to the construction of new E-MOFs with regular structures. These predictions were further confirmed through the as-synthesized E-MOF in this work. The structure, thermal stability, energetic performance, and sensitivities of this E-MOF were also studied in detail.

Scheme 2. Synthesis Route of the Energetic Ligand 4,8-Dinitraminodifurazano-[3,4-*b*,*e*]pyrazine and Its Potassium Salt



2. EXPERIMENTAL SECTION

Materials and Methods. All of the reagents were obtained from commercial resource and used as received. NMR spectra were measured on a Bruker AV II-600 MHz spectrometer (¹H NMR at 600 MHz and ¹³C NMR at 150 MHz). The ¹H NMR chemical shifts were measured relative to

DMSO- d_6 as the internal reference (DMSO- d_6 : $\delta = 2.50$ ppm). The ¹³C NMR chemical shifts were given using DMSO- d_6 as the internal standard (DMSO- d_6 : $\delta = 39.52$ ppm). C, H, N elemental analyses were carried out on a Euro EA3000 analyzer. FI-IR (KBr pellets) spectra were recorded on a Nicolet impact 410 FTIR spectrometer.

Caution: Compounds 1 and 2 must be handled by using eye protection and leather gloves. These energetic compounds must be synthesized only in small amounts, and mechanical actions involving scraping or scratching must be avoided in the synthesis process.

Synthesis of 4,8-Dinitraminodifurazano[3,4-*b*,*e*]pyrazine (1). The energetic ligand was synthesized according the route shown in Scheme 2.²⁷⁻³⁰ The key step of synthesizing 1 is the nitration reaction of 6, because the amino-groups contained in 6 were easy to lose when HNO₃ (100%) or NO₂BF₄ was used as the nitrating reagent.³¹⁻³² Compound 1 was obtained *via* the nitration of 6 with a mixed acid of nitric acid and sulfuric acid (1:5, v/v). Notably, compound 1 is prone to decompose in the reaction system. Fortunately, the purified 1 are stable at room temperature. The purified 1 was obtained by column chromatography as soon as the nitration reaction finished.

In a typical experiment, compound **6** (98 mg, 0.5 mmol) was added in portions to concentrated H_2SO_4 (2.5 mL) with stirring. The mixture was stirred for 20 min at room temperature and then cooled to -15 °C. After fuming nitric acid (0.5 mL) was added slowly to

the above solution, the mixture was stirred at -15 °C for 0.5 h. Then the reaction mixture was poured into ice water (20 mL), and extracted with diethyl ether (25 mL × 2). The combined organic phases were dried over anhydrous MgSO₄ and filtered. The filtrate was evaporated and the residue was purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 3/1 to 1/3, v/v) afforded a compound **1** (17 mg, 12% yield). IR (KBr): 3629, 3159, 3052, 2841, 1659, 1637, 1593, 1433, 1403, 1385, 1368, 1313, 1130, 1100, 963, 932, 848, 835, 820, 764, 721, 697, 585 cm⁻¹. ¹H NMR (600 MHz, DMSO-*d*₆): δ = 7.62 ppm. ¹³C NMR (150 MHz, DMSO-*d*₆): δ = 147.0 ppm. Elemental analysis, calcd (%) for C₄H₂N₁₀O₆ (286.02): C: 16.79, H: 0.70, N: 48.95; Found, C: 17.42, H: 0.98, N: 48.60.

Synthesis of Potassium 4,8-Dinitraminodifurazano[3,4-*b*,*e*]pyrazine (2). Excessive KOH was added to the combined organic phases, which were obtained by the same method given above. And then stirring at room temperature for 10 min, the mixture was filtered and washed with small amount of cold water. The solid was crystallized from H₂O afforded compound **2** (32 mg, 18% yield). IR (KBr): 1650, 1595, 1567, 1400, 1358, 1299, 1107, 992, 932, 877, 820, 819, 778, 716, 535 cm⁻¹. ¹³C NMR (150 MHz, DMSO-*d*₆): δ = 146.7 ppm. Elemental analysis, calcd (%) for C₄K₂N₁₀O₆ (361.93): C: 13.26, H: 0.00, N: 38.66, Found, C: 13.44, H: 0.22, N: 38.69.

3. RESULTS AND DISCUSSION

Structural Description. The single crystals of $1.4H_2O$ were collected by slow evaporation of water at room temperature. Single crystal X-ray diffraction revealed that

compound **1** co-crystallized with water molecules in monoclinic $P2_1/c$ (No.14) space group with a density of 1.793 g cm⁻³ at 170 K. The asymmetric unit of **1**·**4H**₂**O** contained a half energetic molecule and two water molecules (Figure S1). As shown in Figure 1, in the energetic molecule of **1**, N2, N2A and the DFP moiety stayed in a plane, while the nitro groups were hanging on the sides of the plane with a torsional angle as $112.77(2)^{\circ}$ (N1–N2–N3) and a dihedral angle as $78.02(1)^{\circ}$ (N1–N2–N3–C1).



Figure 1. The molecular structure of $1 \cdot 4H_2O$.

In the crystal of $1.4H_2O$, each energetic molecule connected to four adjacent water molecules through hydrogen bonds. The distance of N····O is in the range of 2.719(2)– 3.038(2) Å. Interestingly, in $1.4H_2O$, each water molecule interacted with three adjacent water molecules to form 2D layer structures with two types of windows, i.e., 8- and 16ring windows (Figure S2), through hydrogen bonds. If we considered the water molecules as 3-connect nodes, hydrogen atoms as 2-connected linkers, the water layers revealed 4.8^4 topology (Figure 2a). The distance of O···O is from 2.768(2) Å to 2.835(2) Å, demonstrating the existence of strong hydrogen bonds between the nearby water

molecules. On the other hand, as shown in Figure 2b, a series of energetic molecules stack in a "T" type mode to form an energetic layer. Furthermore, the energetic layers interacted with water layers through hydrogen bonds to form a sandwich-like 3D supramolecular structure (Figure 2c). This sandwich-like supramolecular structure is rarely observed in energetic materials. In most case, water molecules occupied the voids among the energetic molecule and each water molecule may interacted with several energetic molecule *via* hydrogen bonds.



Figure 2. (a) The $4 \cdot 8^4$ layer structures constructed by water molecules contained in $1 \cdot 4H_2O$ view along the *a* axis. (b) The energetic layer contained in $1 \cdot 4H_2O$ view along the *a* axis. (c) The sandwich-like 3D supramolecular structure of $1 \cdot 4H_2O$ view along the *b* axis.

Colorless crystals of **2** were grown by slow evaporation of its aqueous solution at room temperature. The single crystal X-ray diffraction displayed that compound **2** crystallizes in the monoclinic $P2_1/c$ (No.14) space group with a high density of 2.114 g cm⁻³ at 293 K, as calculated from single crystal data. The asymmetric unit of **2** contains one potassium ion and a half of energetic ligand (Figure S3a). The structure of deprotonated energetic ligand in **2** was similar to that in **1**·4**H**₂**O**, whereas the torsional angle of N1–N2–N3 decreased from 112.78(1)° to 109.77(2)° and the dihedral angle of N1–N2–N3–C2 changed from 78.02(1)° to 77.71(1)°.



Figure 3. The coordination environment of the energetic ligand in compound 2.

In the structure of **2**, each deprotonated energetic ligand is connected with eight adjacent K^+ ions through K–O and K–N bonds (Figure 3). The bond lengths of K–O and K–N are in the range of 2.724(3)–2.781(3) and 2.842(3)–3.016(3) Å, respectively. Each K^+ ion is coordinated with six adjacent atoms (three oxygen atoms and three nitrogen atoms) from six different energetic ligands (Figure S3b). Therefore, the 3D framework of **2** can also be

looked as a pillared layered structure (Figure 4a). As shown in Figure 4b, the nearby K^+ ions are connected each other via oxygen and nitrogen atom to form infinite inorganic chains (K–O–K–O), and then the inorganic chains are further connected by the nitro groups of energetic ligands to build layered structures. Then the parallel layers are pillared by DFP groups to construct the 3D framework of 2. Two different types of channel structures were observed in the framework of 2, but the windows of the channel were not big enough for further study (Figure S4).



Figure 4. (a) The 3D structure of 6 view along the *a* axis. (b) The inorganic layer contained in 6 views along the b axis. (c) The sql network of the inorganic layer. (d) The pcu topologic structure of **6**.

To gain more insights into the complicated 3D network, the topology analysis was performed.³³ If we consider each two adjacent K^+ ions as four connected nodes, the layer structure can be considered as a sql network (Figure 4c). In the whole structure, the sql networks are further pillared by DFP groups. If the DFPs are looked as two connected linkers, compound **2** has a pcu topologic structure (Figure 4d). The phase purity of compound **2** was confirmed by powder XRD. As shown in Figure S5, the main peak positions of **2** are consistent with the simulated one, demonstrating the phase purity of **2**.

To gain more insights of the interactions among the molecules contained in $1.4H_2O$ and 2, Hirshfeld surfaces associated with two-dimensional fingerprint spectra were analyzed.³⁴⁻³⁶ The red and blue spots on the Hirshfeld surface denote the high and low close contact populations, respectively. In the $1.4H_2O$, the red spots represent the strong hydrogen bonds of O-H···N and N-H···O. As shown in Figure 5a, most σ - π interactions, such as N-O, O-O, and N-C interactions, existing on the plate area of the Hirshfeld surface, may explain the "T" type packing mode of energetic molecules in 1.4H2O. The two characteristics of Hirshfeld surface are accordance well with the molecular packing modes of 1.4H₂O. From fingerprint spectra of 1.4H₂O (Figure 5c), it was observed that two sharp spikes were existent in the left bottom of the spectra, denoting the interactions of O···H and N···H, respectively. Interestingly, The interactions of N···H (8.7%) was much lower than that of O···H (28.4%), demonstrating the main interactions between energetic molecules and water molecules were O····H interactions. This is also matched well with the supramolecular structure of $1.4H_2O$. Furthermore, high ratio



of σ - π interactions (59.4% of the total weak interactions) further explained the existence of energetic layers in 1.4H₂O.



Figure 5. (a) & (b) Hirshfeld surface of $1.4H_2O$ and compound 2, respectively. (c)&(d) Fingerprint spectra of 1.4H₂O and compound 2, respectively, inset picture: the content of different interactions contributed to the Hirshfeld surface.

In the case of 2, much more red spots were observed on the Hirshfeld surface of energetic ligand implied relatively stronger interactions among the adjacent molecules than that contained in $1.4H_2O$ (Figure 5b). The red spots on the edges of the Hirshfeld surface denoted the

interactions of K···O, K···N, N···O, and N···N, respectively. The regular plate feature of Hirshfeld surface (Figure 5b) may be due to the parallel arrangement of energetic ligands in 2 along the *b*-axis. The fingerprint spectra of 2 is much different to that of $1.4H_2O$ (Figure 5d). Most weak interactions in compounds 2 are the N···O interactions (29.8% of the total weak interactions), demonstrated the high content of π - π stacking interaction of energetic ligands which was confirmed by the pillared layered structure of 2.

Thermal Stability. Both thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were employed to evaluate the thermal stability of compound **1** and **2**. TGA and DSC analyses were performed at a heating rate of 10 °C min⁻¹ under a N₂ flow. From TGA and DSC results (Figure S6 and Figure 6), it can be found that two compounds have much different thermal stabilities. Compound **1** displayed very poor thermal stability and it began to decompose when the temperature reached 74 °C. While from the TGA curve of compound **2** (Figure 6), no obvious weight loss was observed from 50 to 290 °C, indicating good thermal stability of **2** until 290 °C. Upon further heating, a sharp weight loss peak appeared and simultaneously all the weight of **2** was lost, demonstrating that **2** exploded at 290 °C. The thermal stability of **2** was also confirmed by DSC, and no any heat flow peak was observed in the DSC curve before 290 °C, which was consistent well with the TGA result. At 292 °C, a sharp heat flow peak was observed, indicating that **2** had exploded at this temperature.



Figure 6. The TGA and DSC curves of compound 2.

Energetic Properties and Sensitivity. Energetic properties of 1 and 2 were evaluated by theoretical methods.³⁷⁻³⁹ As shown in Table 1, both 1 and 2 have high nitrogen and oxygen contents, which are up to 82.5% and 65.2%, respectively. The CO-based oxygen balances of 1 and 2 are up to 5.6 and 4.4, respectively. Gaussian 09 program was used for calculating their heats of formation. Both 1 and 2 have the positive heats of formation (750.3 kJ mol⁻¹ and 277.1 kJ mol⁻¹, respectively). The high heats of formation and high density (2.114 g·cm⁻³) of 2 implied its excellent energetic properties (e.g., detonation velocity and pressure). According to the calculated results by EXPLO5 v6.02, the detonation velocities of 1 and 2 are both greater than 9000 m s⁻¹. Notably, the detonation velocity of 2 is up to 9660 m s⁻¹, which is much superior to most typical high explosives

including RDX (8795 m s⁻¹), HMX (9144 m s⁻¹), and even CL-20 (9455 m s⁻¹). Moreover, the impact and friction sensitivities of **1** and **2** were further evaluated by experimental methods.⁴⁰ The BAM drop-hammer test showed that the impact sensitivity and friction sensitivity of **2** are 2 J and 1 N, respectively, demonstrating its very high mechanical sensitivities. As compared to the typical primary explosive $Pb(N_3)_2$, it is clear that **2** exhibited the higher energetic performance and comparable mechanical sensitivities towards the impact and friction.

Compounds	1	2	$Pb(N_3)_2$
Formula	$C_4H_2N_{10}O_6$	$C_4 K_2 N_{10} O_6$	PbN ₆
M [g mol ⁻¹]	286.0	361.9	291.3
$T_{dec}[^{o}C]^{a}$	74	292	315
$\Omega_{ m CO}\left[\% ight]^b$	5.6	4.4	-11.0
N [%] ^c	49.0	38.7	28.9
$N + O [\%]^d$	82.5	65.2	28.9
$\rho [g \text{ cm}^{-3}]$	1.803 ^e	2.114^{f}	4.800
$\Delta H_{f} [kJ mol^{-1}]^{g}$	750.3	277.1	450.1
$D [m s^{-1}]^h$	9153	9660	5877
$P [GPa]^i$	36.5	36.8	33.4
IS $[J]^{i}$	1	2	2.5-4.0
$\mathrm{FS}\left[\mathrm{N} ight]^k$	24	1	0.1–1

 Table 1. Physicochemical and energetic properties of compounds 1 and 2.

^{*a*}Decomposition temperature (onset temperature at a heating rate of 10 °C min⁻¹). ^{*b*}Oxygen balance for $C_aH_bO_cN_d$, 1600(c-a-b/2)/MW (based on CO). ^{*c*}Nitrogen content. ^{*d*}Nitrogen and oxygen content. ^{*e*}Density measured by using a gas pycnometer at room temperature. ^{*f*}Crystal density at 293 K. ^{*g*}Heat of formation (calculated with Gaussian 09 program package).

^{*h*}Detonation velocity calculated with EXPLO5 v6.02. ^{*i*}Detonation pressure calculated with EXPLO5 v6.02. ^{*j*}Impact sensitivity. ^{*k*}Friction sensitivity.

4. CONCLUSION

In summary, two energetic compounds, i.e., $1.4H_2O$ and the E-MOF 2 were designed and synthesized. In the crystal structure of $1.4H_2O$, the energetic ligand molecules interact with adjacent energetic ligands *via* σ - π interactions to form an energetic layer, while each water molecule interacts with nearby water molecules via hydrogen bonds to form a water layer. The regular water layers observed in $1.4H_2O$ are very rare in the energetic organic molecules. The energetic layers and water layers of $1.4H_2O$ are further packing to construct a sandwich-like 3D supramolecular structure. In compound 2, potassium ions and energetic ligands are connected each other through a 6,8-connection mode to form a 3D framework with pcu topology. Compound 2 has the high crystal density (2.114 g·cm⁻³), high thermal stability (T_d: 292 °C), high detonation velocity (9660 m s⁻¹), and the high impact and friction sensitivities (2 J and 1 N, respectively). The excellent detonation performances, high thermal stability associated with high mechanical sensitivities make compound 2 a potential high-performing primary explosive.

ASSOCIATED CONTENT

Supporting Information. NMR, additional structural figures, and computational methods are available free of charge via the Internet at <u>http://pubs.acs.org</u>.

X-ray data in CIF format (CIF)

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Notes

The authors declare no competing financial interest.

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Construction of a Thermally Stable and Highly Energetic Metal-Organic Framework as Lead-Free Primary Explosives

A 3D energetic metal-organic framework featuring pillared layered structure and pcu topology was prepared. This compound exhibited high crystal density, high thermal stability, high detonation velocity, and high sensitivities, which makes it a potential high-performing primary explosive.

