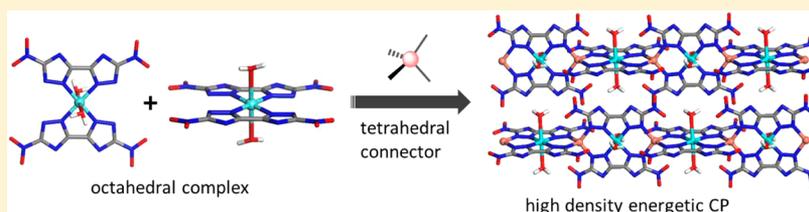


Coordination Polymerization of 5,5'-Dinitro-2*H*,2*H'*-3,3'-bi-1,2,4-triazole Leads to a Dense Explosive with High Thermal StabilitySaona Seth[†] and Adam J. Matzger^{*,†,‡,§}[†]Department of Chemistry and [‡]Department of Macromolecular Science and Engineering, University of Michigan, 930 North University Avenue, Ann Arbor, Michigan 48109, United States

Supporting Information



ABSTRACT: High-energy coordination polymers (CPs) based on nitrogen-rich ligands are an emerging class of explosives. However, modulation of the energetic properties of high-energy CPs and the establishment of their structure–function relationship remain in their infancy. In the present study, the utility of coordination polymerization as a technique to modulate the application of critical energetic properties, such as density and thermal stability, of a secondary explosive, 5,5'-dinitro-2*H*,2*H'*-3,3'-bi-1,2,4-triazole (DNBT), is presented. Ni-DNBT is a discrete octahedral complex with density lower than that of DNBT. Cu-DNBT also contains octahedral metal coordination, similar to that in Ni-DNBT, as the building unit; however, the partial reduction of Cu^{II} to Cu^I ions during the reaction and their unique geometrical preferences lead to linking of the octahedral Cu^{II} complexes by tetrahedral Cu^I ions and render the resultant material a one-dimensional polymer with high density. In fact, Cu-DNBT has the highest density among all of the DNBT-based energetics. Furthermore, Cu-DNBT exhibits thermal stability superior to that of both Ni-DNBT and DNBT. Cu-DNBT is one of the two DNBT-based energetic materials and one of the few energetics that are stable at temperatures higher than 300 °C.

INTRODUCTION

The design and synthesis of explosives with high density, good thermal stability, and low sensitivity is an important subject of contemporary research considering the central role that such materials play in a variety of civilian and military applications. The detonation velocity and pressure depend on the material density, with high density tending to increase the explosive power. Furthermore, low sensitivity to external stimuli and high thermal stability are crucial for the safe handling of energetics. Most advances to improve properties such as density, thermal stability, and sensitivity rely on the synthesis of new molecular entities based on existing motifs such as aliphatic and aromatic nitro compounds.^{1–5} New approaches are emerging that have the potential to offer a measure of control not readily achieved by organic synthesis including cocrystallization,^{6,7} salt formation,^{8–10} synthesis of energetic composites with nanoscale mixing of components,^{11–14} and coordination polymerization.^{15–28} High-energy coordination polymers (CPs) have emerged as potential next-generation energetic materials in the past few years. Whereas most applications of CPs are only possible when porosity is present,^{29–33} nonporous CPs with high heats of formation and density can serve as energetic materials.^{18,19} Energetic CPs have shown promise to offer tunable sensitivity and thermal stability depending on the nature of the metal ions or organic linkers.³⁴ In the few examples where it has been explored, energetic CPs exhibit thermal stability

different from that of constituent organic linkers.^{18,20} Tailoring the thermal stability of organic energetics through coordination polymerization remains an area ripe for exploration because so few structure–activity relationships exist.

5,5'-Dinitro-2*H*,2*H'*-3,3'-bi-1,2,4-triazole (DNBT) is a secondary explosive that can be synthesized in two steps starting from aminoguanidinium carbonate and oxalic acid.^{1,9} DNBT has a high density (1.903 g cm⁻³), high heat of formation (285 kJ mol⁻¹), and formidable detonation velocity (8413 m s⁻¹).¹ Furthermore, DNBT is less sensitive to impact compared to many of the state-of-the-art secondary military explosives [e.g., 1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane (HMX), 1,3,5-trinitroperhydro-1,3,5-triazine, and 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20)].⁷ Nitrogen-rich heterocyclic compounds, such as DNBT, have shown promise as single-component energetic materials and are also on the forefront of applications in energetic CPs. High-density energetic materials based on DNBT, which exhibit good energetic properties, have been achieved by the synthesis of nitrogen-rich organic salts⁹ and cocrystallization with azole-based energetic conformers.⁷ There are no reports, to the best of our knowledge, that exploit coordination polymerization of DNBT to modulate the energetic performance of the material. Herein,

Received: October 6, 2016

we have advantageously utilized two ionizable triazole rings with multiple potential nitrogen-donor sites of DNBT for coordination with transition-metal ions to access high-density energetic materials with high thermal stability. The structures and properties of the new energetic materials and their structure–function relationships are discussed.

The solvothermal reaction of DNBT with nickel nitrate and copper nitrate salts in dimethylformamide (DMF)/water led to Ni-DNBT and Cu-DNBT, respectively. Both materials were characterized by single-crystal X-ray diffraction analysis, and it is observed that DNBT undergoes complete deprotonation. Ni-DNBT is a discrete anionic coordination complex, in which Ni²⁺ is in an octahedral disposition and is chelated by two dianions of DNBT from the equatorial positions while the axial sites are occupied by water molecules (Figure 1b). The negative charge of

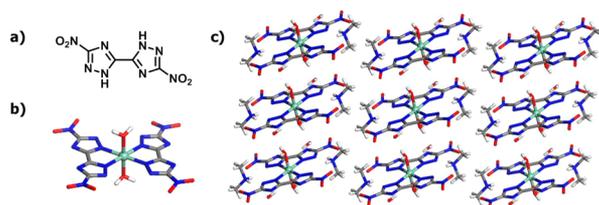


Figure 1. (a) Molecular structure of DNBT. (b) Octahedral $[\text{Ni}(\text{DNBT})_2(\text{H}_2\text{O})_2]^{2-}$ complex with two anions of DNBT chelated from the equatorial positions and two water molecules coordinated to the axial positions. (c) Packing of the anionic nickel(II) complexes, dimethylammonium ions, and uncoordinated water molecules in the crystal structure of Ni-DNBT.

the $[\text{Ni}(\text{DNBT})_2(\text{H}_2\text{O})_2]^{2-}$ complex is compensated for by dimethylammonium cations that are generated in situ via the decomposition of DMF (Figure 1c).^{35,36} The discrete metal complex Ni-DNBT crystallizes as a hydrate. The uncoordinated water is removed when the sample is dried under vacuum at room temperature. Determination of the cell parameters before (from single-crystal data; cf. the Supporting Information) and after [from the powder X-ray diffraction (PXRD) profile of the powdered material; cf. the Supporting Information] water removal at room temperature indicates a contraction of the cell volume by ca. 50 Å³ after removal of the uncoordinated water molecules from the crystal (two molecules of water per unit cell). Removal of uncoordinated water molecules under high vacuum is further supported by elemental analysis (cf. the Experimental Section). The copper complex of DNBT, obtained under reaction conditions similar to those used for the synthesis of Ni-DNBT, is a one-dimensional (1D) polymer. A fraction of the Cu^{II} ions are reduced to Cu^I under the employed reaction conditions, leading to the mixed-valent compound Cu-DNBT. As expected, two different coordination environments are observed for the copper ions with different oxidation states (Figure 2a). Each Cu^{II} ion exhibits an octahedral coordination mode similar to that observed with Ni^{II} in Ni-DNBT; i.e., two dianions of DNBT chelate at the equatorial positions, and two water molecules occupy the axial sites. The Cu^I ion, by contrast, shows tetrahedral disposition and links two neighboring octahedral Cu^{II} complexes, resulting in a 1D CP (Figure 2a). The neighboring octahedral Cu^{II} complexes in the 1D chains are oriented orthogonally by mediation of tetrahedral Cu^I ions. The negative charge of the 1D polymer $[\text{Cu}^{\text{I}}\text{Cu}^{\text{II}}(\text{DNBT})_2(\text{H}_2\text{O})_2]^-$ is counterbalanced by dimethylammonium cations present in the interstitial space (Figure 2b).

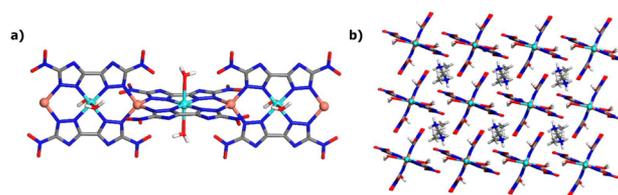


Figure 2. (a) 1D polymeric chain of Cu-DNBT consisting of an alternating arrangement of Cu^I (purple) and Cu^{II} (cyan) ions. Note the tetrahedral and octahedral coordination modes of Cu^I and Cu^{II}, respectively. (b) Presence of dimethylammonium guests in the interstitial space of the 1D polymer.

A closer look at the structure of Cu-DNBT reveals that each tetrahedral Cu^I ion is chelated by two octahedral $[\text{Cu}^{\text{II}}(\text{DNBT})_2(\text{H}_2\text{O})_2]^{2-}$ complexes. The presence of Cu^I, formed by the in situ reduction of Cu^{II} under the employed reaction condition, in Cu-DNBT renders an orthogonal arrangement of the neighboring Cu^{II} complexes, which, in turn, leads to close packing of the energetic DNBT dianions (Figures 2a and 3b). Note that the nickel complex has a crystallographic density of 1.714 g cm⁻³ at 85 K (calculated including the uncoordinated water molecules), which is less than that of the organic linker DNBT (1.903 g cm⁻³). Cu-DNBT, by contrast, has a higher crystallographic density of 2.004 g cm⁻³ (at 85 K). Considering that uncoordinated water is removed in the dry sample, the density of Ni-DNBT at room temperature is calculated to be 1.694 g cm⁻³, whereas the room temperature density for Cu-DNBT is 1.960 g cm⁻³. Clearly, different geometrical preferences of Cu^{II} and Cu^I ions within Cu-DNBT render the crystal structure of Cu-DNBT more efficiently packed, leading to a higher density (Figure 3). In fact, Cu-DNBT has the highest crystallographic density among all of the DNBT-based energetic materials.^{7,9} Packing coefficients of the DNBT dianion were calculated to compare quantitatively the efficiency with which the energetic component is packed in the crystal lattices of these complexes. Note that the packing coefficient of any component refers to the fraction of a unit cell volume occupied by that species. The calculations were performed based on the conformation adopted by the DNBT dianion in the respective metal complexes (geometries extracted directly from the crystal structures). The packing coefficients of the dianionic species in Ni-DNBT and Cu-DNBT are calculated to be 57.3% (two anions per unit cell volume of 620.9 Å³) and 66.4% (four anions per unit cell volume of 1071 Å³), respectively. The higher packing coefficient of the DNBT dianion in Cu-DNBT results in a higher energy density of the complex than in Ni-DNBT.

The performance of the DNBT-derived complexes was investigated to determine properties including thermal stability, heat of detonation, and sensitivity to impact. The thermal decomposition temperature of the complexes was determined by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). In TGA, the samples were heated from room temperature to 600 °C at a 10 °C min⁻¹ ramp rate. The energetic compound DNBT undergoes thermal decomposition at 262 °C (onset temperature; Figure 4). The discrete complex Ni-DNBT exhibits apparently different thermal behaviors in TGA and DSC. TGA reveals a continuous weight loss of Ni-DNBT with an onset temperature of 185 °C; the removal of coordinated water molecules is only partially responsible for the weight loss, and additional sublimation or decomposition must be occurring. However, no corresponding heat change is observed at this temperature in DSC. Instead, a broad exotherm above 240 °C

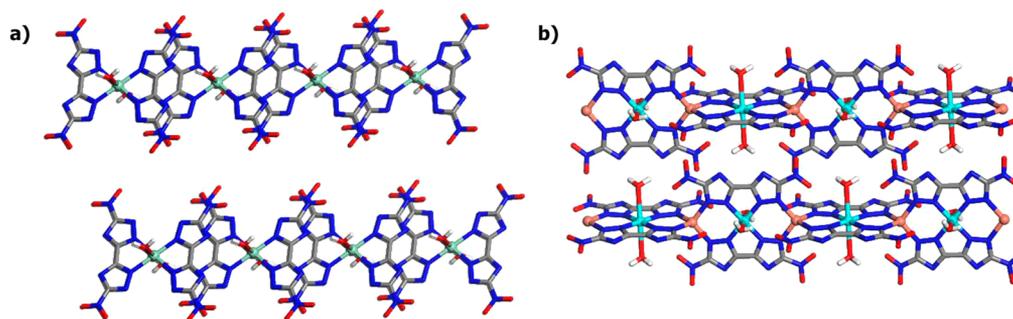


Figure 3. (a) Packing of the octahedral nickel(II) complexes in Ni-DNBT. (b) Packing of the 1D polymeric chains in Cu-DNBT. Note the orthogonal alignment of the $[\text{Cu}(\text{DNBT})_2(\text{H}_2\text{O})_2]^{2-}$ complexes in the 1D chain through chelation to tetrahedral Cu^{I} ions.

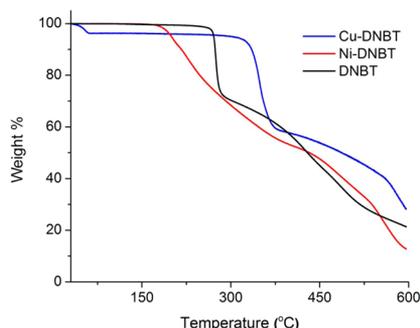


Figure 4. TGA curves of DNBT, Ni-DNBT, and Cu-DNBT.

consistent with thermal decomposition of the complex manifests. Presumably, the Ni^{II} ion induces decomposition of DNBT in the discrete complex Ni-DNBT. By contrast, the 1D CP Cu-DNBT is thermally stable up to 310 °C, as revealed by TGA and DSC (Figures 4 and 5). Cu-DNBT undergoes $\sim 3.3\%$ weight loss

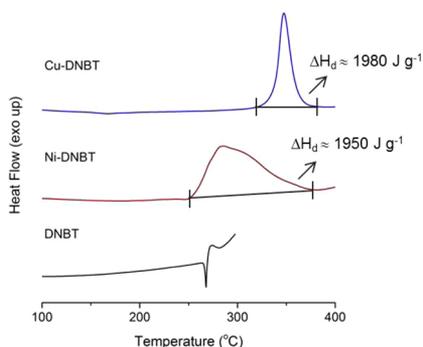


Figure 5. DSC profiles of DNBT, Ni-DNBT, and Cu-DNBT.

below 100 °C, which might be attributed to partial loss of water molecules coordinated to the metal center (water contributes to 5.5 wt % of the complex). The complex starts to decompose above 310 °C. Cu-DNBT is one of the very few energetics that exhibits thermal stability above 300 °C.^{8,18,37,38} Furthermore, the CP is thermally more stable than all of the energetic salts and cocrystals of DNBT, except the guanidinium salt, which decomposes at 335 °C.^{7,9} The high thermal decomposition temperature of Cu-DNBT indicates that the energetic linker is thermally desensitized in the polymeric structure.

The heat of detonation is another parameter to measure the performance of energetic materials. The heat released by thermal decomposition of Ni-DNBT and Cu-DNBT was determined by integrating the DSC curves to estimate the heat of detonation.

The DSC experiments were carried out at a heating rate of 5 °C min^{-1} using high-pressure hermetic pans, which can withstand pressure up to 100 bar. DNBT exhibits a sharp endotherm at 262 °C (onset temperature), corresponding to melting with subsequent decomposition, releasing heat. The heat evolution values from thermal decomposition of Ni-DNBT and Cu-DNBT are ca. 1950 and 1980 J g^{-1} , respectively.

Sensitivity is another key performance metric for energetic materials. Explosives are categorized, according to their sensitivity, into primary and secondary explosives.³⁹ Primary explosives have characteristically fast deflagration to detonation transitions when initiated via a small stimulus, and these are used as initiators in explosions. Secondary explosives are comparatively insensitive to external stimuli and release much higher heat compared to primary explosives upon detonation. Insensitivity to external stimuli is important for the safe handling and transportation of explosive materials, particularly for secondary explosives. The sensitivity of the energetic complexes to impact was measured by impact small-scale drop-testing and represented by Dh_{50} , i.e., the height for which there is 50% probability of explosion of an energetic material when a drop weight impacts the material from that height. Approximately 2 mg ($\pm 10\%$) samples were crimped in a nonhermetic DSC pan for testing. A drop weight of 5 lb. was allowed to freefall on the DSC pan containing the sample from variable distances several times to determine a reproducible Dh_{50} . DNBT was found to be insensitive to impact at a 145 cm height, the maximum height of the testing apparatus. It should be noted that the well-known secondary explosives ϵ -CL-20 and β -HMX exhibited Dh_{50} values of 29 and 55 cm, respectively, in the same apparatus.⁴⁰ Drop weight testing reveals that both coordination complexes are also insensitive to impact for the same weight and height and can, therefore, be preliminarily classified as impact-insensitive secondary explosives. However, from the DSC experiments, it is clear that the detonation of these materials can be initiated by heat. To test whether the detonation can be reliably induced by heat, the initiator experiments were carried out on a hot plate at different temperatures. Whereas Ni-DNBT detonated consistently when dropped on a hot plate at 260 °C, Cu-DNBT underwent deflagration above 340 °C.

In summary, we have utilized coordination polymerization as a tool to access high-density energetic materials from DNBT. Both of the energetic materials Cu-DNBT and Ni-DNBT contain octahedral metal complexes as a basic structural unit; the presence of mixed-valent $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$ ions in Cu-DNBT and their different geometrical preferences result in the formation of a 1D polymeric structure. Different geometrical dispositions of the metal ions in different oxidation states lead to dense packing of

the energetic component DNBT in the crystal lattice. Cu-DNBT has the highest crystallographic density among all of the DNBT-based energetic materials, and both of the complexes are impact-insensitive. Additionally, Cu-DNBT exhibits exceptional thermal stability because it is one of the few energetic materials that has a high thermal decomposition temperature, above 300 °C. Cu-DNBT, by virtue of being a 1D polymeric material, is a better energetic material than either DNBT or Ni-DNBT in terms of the density and thermal stability. Thus, it is demonstrated that coordination polymerization can be employed to synthesize powerful energetic materials of high density and thermal stability from existing energetic materials if suitable modes of coordination are exploited.

EXPERIMENTAL SECTION

Caution! No unplanned detonations were encountered during the experiments with DNBT and the complexes Cu-DNBT and Ni-DNBT. However, these materials are powerful explosives and might cause severe injury upon explosion. Proper safety protocols were followed during the experiments to prevent any explosion resulting from impact, shock, or friction.

Synthesis of Ni-DNBT. To a mixture of DNBT (Lawrence Livermore National Laboratory; 5.05 mg, 0.0223 mmol) and Ni(NO₃)₂·6H₂O (19.3 mg, 0.0665), taken in a screw-capped vial, were added 0.5 mL of DMF, 1 mL of water, and 20 μL of concentrated HNO₃. The reaction mixture was sonicated for 5 min and then heated at 85 °C for 2 days. Subsequently, the reaction mixture was allowed to cool to room temperature. Pale-green crystals were collected by filtration, washed thoroughly with a 2:1 water/DMF mixture, and dried by applying a vacuum at room temperature. Yield: 4.82 mg (66.4% based on DNBT). CHN anal. Calcd for C₁₂H₂₀N₁₈O₁₀Ni: C, 22.69; H, 3.15; N, 39.70. Found: C, 22.63; H, 3.14; N, 39.60. (The uncoordinated water molecules are removed when the sample is dried under high vacuum.) IR (solid, cm⁻¹): $\tilde{\nu}$ 3395, 3025, 2787, 2436, 1625, 1609, 1528, 1471, 1446, 1401, 1359, 1305, 1232, 1160, 1142.

Synthesis of Cu-DNBT. This complex was synthesized by employing reaction conditions similar to those used for the synthesis of Ni-DNBT using DNBT (5.02 mg, 0.0222 mmol) and Cu(NO₃)₂·2.5H₂O (10.2 mg, 0.0440 mmol). Yield: 5.46 mg (73.6% based on DNBT). CHN anal. Calcd for C₁₀H₁₂N₁₇O₁₀Cu₂: C, 18.265; H, 1.83; N, 36.23. Found: C, 18.42; H, 1.76; N, 36.22. IR (solid, cm⁻¹): $\tilde{\nu}$ 3633, 3585, 3053, 2825, 2494, 1600, 1535, 1430, 1395, 1364, 1316, 1301, 1199, 1193, 1178.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.6b02383.

X-ray crystallographic data in CIF format (CIF)

Experimental details, Fourier transform infrared spectra, and PXRD data (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: matzger@umich.edu (A.J.M.).

ORCID

Adam J. Matzger: 0000-0002-4926-2752

Author Contributions

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

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the Defense Threat Reduction Agency (Grant HDTRA1-15-1-0001). We thank Dr. Jeff Kampf for single-crystal X-ray analysis and are thankful for funding from the National Science Foundation (Grant CHE-0840456) for the Rigaku AFC10K Saturn 944+ CCD-based X-ray diffractometer. We also acknowledge Dr. Philip Pagoria of Lawrence Livermore National Laboratory for providing DNBT and Antek G. Wong-Foy for valuable discussions.

REFERENCES

- (1) Dippold, A. A.; Klapötke, T. M. Nitrogen-Rich Bis-1,2,4-triazoles – A Comparative Study of Structural and Energetic Properties. *Chem. - Eur. J.* **2012**, *18*, 16742–16753.
- (2) Bachmann, W. E.; Sheehan, J. C. A New Method of Preparing the High Explosive RDX. *J. Am. Chem. Soc.* **1949**, *71*, 1842–1845.
- (3) Kraeutle, K. J. *JANNAF Proceedings*; CPIA Publ.: Columbia, MD, 1988; p 498.
- (4) Bernstein, J. *Polymorphism in Molecular Crystals*; Oxford University Press: New York, 2002; pp 278–283.
- (5) Pagoria, P. F.; Lee, G. S.; Mitchell, A. R.; Schmidt, R. D. A Review of Energetic Materials Synthesis. *Thermochim. Acta* **2002**, *384*, 187–204.
- (6) Bolton, O.; Matzger, A. J. Improved Stability and Smart-Material Functionality Realized in an Energetic Cocrystal. *Angew. Chem., Int. Ed.* **2011**, *50*, 8960–8963.
- (7) Bennion, J. C.; McBain, A.; Son, S. F.; Matzger, A. J. Design and Synthesis of a Series of Nitrogen-Rich Energetic Cocrystals of 5,5'-Dinitro-2H,2H'-3,3'-bi-1,2,4-triazole (DNBT). *Cryst. Growth Des.* **2015**, *15*, 2545–2549.
- (8) Gao, H.; Shreeve, J. M. Azole-Based Energetic Salts. *Chem. Rev.* **2011**, *111*, 7377–7436.
- (9) Dippold, A. A.; Klapötke, T. M.; Winter, N. Insensitive Nitrogen-Rich Energetic Compounds Based on the 5,5'-Dinitro-3,3'-bi-1,2,4-triazol-2-ide Anion. *Eur. J. Inorg. Chem.* **2012**, *2012*, 3474–3484.
- (10) Yin, P.; Shreeve, J. M. From N-Nitro to N-Nitroamino: Preparation of High-Performance Energetic Materials by Introducing Nitrogen-Containing Ions. *Angew. Chem., Int. Ed.* **2015**, *54*, 14513–14517.
- (11) Zhou, X.; Torabi, M.; Lu, J.; Shen, R.; Zhang, K. Nanostructured Energetic Composites: Synthesis, Ignition/Combustion Modeling, and applications. *ACS Appl. Mater. Interfaces* **2014**, *6*, 3058–3074.
- (12) Wang, H.; Jian, G.; Zhou, W.; DeLisio, J. B.; Lee, V. T.; Zachariah, M. R. Metal Iodate-Based Energetic Composites and Their Combustion and Biocidal Performance. *ACS Appl. Mater. Interfaces* **2015**, *7*, 17363–17370.
- (13) McDonald, K. A.; Bennion, J. C.; Leone, A. K.; Matzger, A. J. Rendering Non-energetic Microporous Coordination Polymers Explosive. *Chem. Commun.* **2016**, *52*, 10862–10865.
- (14) Cudziło, S.; Kiciński, W. Preparation and Characterization of Energetic Nanocomposites of Organic Gel – Inorganic Oxidizers. *Propellants, Explos., Pyrotech.* **2009**, *34*, 155–160.
- (15) Bushuyev, O. S.; Brown, P.; Maiti, A.; Gee, R. H.; Peterson, G. R.; Weeks, B. L.; Hope-Weeks, L. J. Ionic Polymers as a New Structural Motif for High-Energy-Density Materials. *J. Am. Chem. Soc.* **2012**, *134*, 1422–1425.
- (16) Bushuyev, O. S.; Peterson, G. R.; Brown, P.; Maiti, A.; Gee, R. H.; Weeks, B. L.; Hope-Weeks, L. J. Metal–Organic Frameworks (MOFs) as Safer, Structurally Reinforced Energetics. *Chem. - Eur. J.* **2013**, *19*, 1706–1711.

- (17) Zhang, Q.; Shreeve, J. M. Metal–Organic Frameworks as High Explosives: A New Concept for Energetic Materials. *Angew. Chem., Int. Ed.* **2014**, *53*, 2540–2542.
- (18) McDonald, K. A.; Seth, S.; Matzger, A. J. Coordination Polymers with High Energy Density: An Emerging Class of Explosives. *Cryst. Growth Des.* **2015**, *15*, 5963–5972.
- (19) Zhang, S.; Yang, Q.; Liu, X.; Qu, X.; Wei, Q.; Xie, G.; Chen, S.; Gao, S. High-Energy Metal–Organic Frameworks (HE-MOFs): Synthesis, Structure and Energetic Performance. *Coord. Chem. Rev.* **2016**, *307*, 292–312.
- (20) Li, S.; Wang, Y.; Qi, C.; Zhao, X.; Zhang, J.; Zhang, S.; Pang, S. 3D Energetic Metal–Organic Frameworks: Synthesis and Properties of High Energy Materials. *Angew. Chem., Int. Ed.* **2013**, *52*, 14031–14035.
- (21) Blair, L. H.; Colakel, A.; Vrcelj, R. M.; Sinclair, I.; Coles, S. J. Metal–Organic Frameworks: MOFs as Integrated Structural Scaffolds for Pyrotechnic Materials. *Chem. Commun.* **2015**, *51*, 12185–12188.
- (22) Zhang, S.; Liu, X.; Yang, Q.; Su, Z.; Gao, W.; Wei, Q.; Xie, G.; Chen, S.; Gao, S. A New Strategy for Storage and Transportation of Sensitive High-Energy Materials: Guest-Dependent Energy and Sensitivity of 3D Metal–Organic-Framework-Based Energetic Compounds. *Chem. - Eur. J.* **2014**, *20*, 7906–7910.
- (23) Feng, Y.; Liu, X.; Duan, L.; Yang, Q.; Wei, Q.; Xie, G.; Chen, S.; Yang, X.; Gao, S. In situ Synthesized 3D Heterometallic Metal–Organic Framework (MOF) as a High-energy Density Material Shows High Heat of Detonation, Good Thermostability and Insensitivity. *Dalton Trans.* **2015**, *44*, 2333–2339.
- (24) Liu, X.; Gao, W.; Sun, P.; Su, Z.; Chen, S.; Wei, Q.; Xie, G.; Gao, S. Environmentally Friendly High-energy MOFs: Crystal Structures, Thermostability, Insensitivity and Remarkable Detonation Performances. *Green Chem.* **2015**, *17*, 831–836.
- (25) Wang, Q.; Feng, X.; Wang, S.; Song, N.; Chen, Y.; Tong, W.; Han, Y.; Yang, L.; Wang, B. Explosives: Metal–Organic Framework Templated Synthesis of Copper Azide as the Primary Explosive with Low Electrostatic Sensitivity and Excellent Initiation Ability. *Adv. Mater.* **2016**, *28*, 5766–5766.
- (26) Tang, Y.; He, C.; Mitchell, L. A.; Parrish, D. A.; Shreeve, J. M. Potassium 4,4'- Bis(dinitromethyl)-3,3'-azofurazanate: A Highly Energetic 3D Metal–Organic Framework as a Promising Primary Explosive. *Angew. Chem., Int. Ed.* **2016**, *55*, 5565–5567.
- (27) Cohen, A.; Yang, Y.; Yan, Q.-L.; Shlomovich, A.; Petrutik, N.; Burstein, L.; Pang, S.-P.; Gozin, M. Highly Thermostable and Insensitive Energetic Hybrid Coordination Polymers Based on Graphene Oxide–Cu(II) Complex. *Chem. Mater.* **2016**, *28*, 6118–6126.
- (28) Qu, X.; Zhang, S.; Yang, Q.; Su, Z.; Wei, Q.; Xie, G.; Chen, S. Silver(I)-based Energetic Coordination Polymers: Synthesis, Structure and Energy Performance. *New J. Chem.* **2015**, *39*, 7849–7857.
- (29) Suh, M. P.; Park, H. J.; Prasad, T. K.; Lim, D.-W. Hydrogen Storage in Metal–Organic Frameworks. *Chem. Rev.* **2012**, *112*, 782–835.
- (30) Li, J.-R.; Kuppler, R. J.; Zhou, H.-C. Selective Gas Adsorption and Separation in Metal–Organic Frameworks. *Chem. Soc. Rev.* **2009**, *38*, 1477–1504.
- (31) Lee, J.; Farha, O. K.; Roberts, J.; Scheidt, K. A.; Nguyen, S. T.; Hupp, J. T. Metal–Organic Framework Materials as Catalysts. *Chem. Soc. Rev.* **2009**, *38*, 1450–1459.
- (32) Yoon, M.; Srirambalaji, R.; Kim, K. Homochiral Metal–Organic Frameworks for Asymmetric Heterogeneous Catalysis. *Chem. Rev.* **2012**, *112*, 1196–1231.
- (33) Kreno, L. E.; Leong, K.; Farha, O. K.; Allendorf, M.; Van Duyne, R. P.; Hupp, J. T. Metal–Organic Framework Materials as Chemical Sensors. *Chem. Rev.* **2012**, *112*, 1105–1125.
- (34) For the effect of a metal ion or organic linker on the energetic properties, such as thermal stability and sensitivity, of isostructural energetic CPs, see refs 15 and 28.
- (35) An, J.; Shade, C. M.; Chengelis-Czegan, D. A.; Petoud, S.; Rosi, N. L. Zinc-Adeninate Metal–Organic Framework for Aqueous Encapsulation and Sensitization of Near-infrared and Visible Emitting Lanthanide Cations. *J. Am. Chem. Soc.* **2011**, *133*, 1220–1223.
- (36) Li, T.; Rosi, N. L. Screening and Evaluating Aminated Cationic Functional Moieties for Potential CO₂ Capture Applications Using an Anionic MOF Scaffold. *Chem. Commun.* **2013**, *49*, 11385–11387.
- (37) Bennion, J. C.; Vogt, L.; Tuckerman, M. E.; Matzger, A. J. Isostructural Cocrystals of 1,3,5-Trinitrobenzene Assembled by Halogen Bonding. *Cryst. Growth Des.* **2016**, *16*, 4688–4693.
- (38) Tran, T. D.; Pagoria, P. F.; Hoffman, D. M.; Cutting, J. L.; Lee, R. S.; Simpson, R. L. Characterization of 2,6-Diamino-3,5-dinitropyrazine-1-oxide (LLM-105) as an Insensitive High Explosive Material. *33rd International Annual Conference on ICT on Energetic Materials Synthesis, Production and Application*, Karlsruhe, Germany, June 25–28, 2002.
- (39) Oyler, K. D. *Green Energetic Materials*; John Wiley & Sons, Ltd.: New York, 2014; p 103.
- (40) Bolton, O.; Simke, L. R.; Pagoria, P. F.; Matzger, A. J. High Power Explosive with Good Sensitivity: A 2:1 Cocrystal of CL-20:HMx. *Cryst. Growth Des.* **2012**, *12*, 4311–4314.