Angewandte
Highlights

Energetic Materials

DOI: 10.1002/anie.201310014

Metal–Organic Frameworks as High Explosives: A New Concept for Energetic Materials**

*Qinghua Zhang and Jean'ne M. Shreeve**

coordination polymers · energetic materials · heat of detonation · metal–organic frameworks · porous structures

In memory of Malcolm M. Renfrew

Metal–organic frameworks (MOFs) represent a fascinating class of porous crystalline materials with ordered pores and channels.[1] In general, they can be readily prepared by the self-assembly of metal ions or metal-containing clusters with organic ligands through coordination bonds between metal center and organic linker. Because of their intriguing structures and unique properties, the investigation of MOFs has attracted considerable interest, and their potential applications have been explored in various fields, such as gas storage, catalysis, molecular sensing, separation, and nonlinear optical materials.[2,3] Recently, several investigators have demonstrated the possibility of using nitrogen-rich MOFs as high explosives.[4,5] Although they remain to be systematically exploited, the exceptional energetic performance of several reported energetic MOFs has revealed their great potential as new-generation high explosives.

The concept of energetic metal–organic polymers is not strictly new. In the field of energetic materials, a great number of metal-based explosives, including metal salts and complexes, have been used as initiating primary explosives for many decades; many are composed of metal ions (including Pb^{2+} and Ag^{+}) and energetic anions (such as N_3^- and NO_3^-) or energetic ligands (e.g., hydrazine). In the case of energetic bidentate or multidentate ligands, many energetic metal–organic frameworks can be formed through coordination interactions between metal ions and energetic ligands. By virtue of this strategy, a variety of energetic MOFs with diverse structures and topologies have been synthesized and utilized as energetic materials for commercial and military applications,[6–9] although they have not been called "energetic MOFs" in the literature. Depending upon the metal ion geometry and the binding mode of the bridging energetic ligands, the network structures of energetic MOFs can be designed in one, two, or three dimensions (1D, 2D, or 3D; Figure 1). Apart from metal ions and ligand geometries, other factors, such as temperature, solvent, pH, and stoichiometry, may also play a significant role in modulating the network topologies and the dimensionalities of the target energetic MOFs. In this sense, the concept of designing energetic MOFs as high explosives has provided a unique architectural platform for developing new-generation energetic materials.

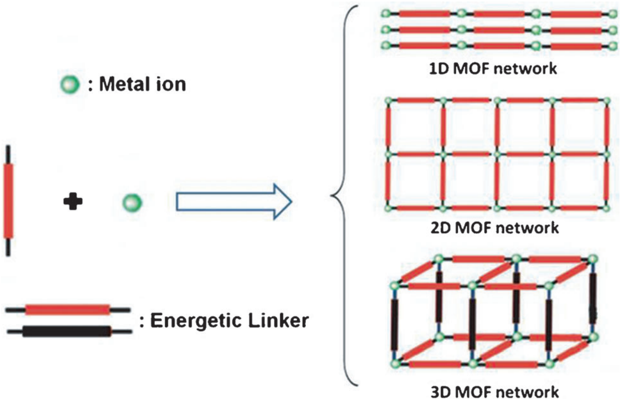

Figure 1. Design strategy for energetic MOFs with 1D, 2D, and 3D network structures.

Recently, in pursuit of greener energetic materials, an interesting energetic metal–organic coordination polymer of zinc(II) hydrazine azide, $[Zn(N_2H_4)_2(N_3)_2]_n$, was reported.[10] This material has a 1D framework structure, in which the Zn^{II} ion is hexacoordinated with two azido ligands by μ_1-azido bridges and four hydrazine molecules, which act as bidentate ligands. The nitrogen content of this energetic 1D MOF material is 65.6%, and its heat of combustion is 5.45 $MJ\,kg^{-1}$. By virtue of a similar self-assembly strategy, energetic cobalt- and nickel-based MOFs have been reported, in which hydrazine, as the sole inner-sphere bridging ligand, can efficiently link adjacent metal centers to form linear polymeric backbone structures.[4b] Three energetically unstable MOF materials, namely nickel hydrazine perchlorate (NHP), cobalt hydrazine perchlorate (CHP), and nickel hydrazine nitrate (NHN), were obtained. Single-crystal X-ray diffraction (XRD) demonstrated that both NHP and CHP formed linear structures of continuous parallel polymeric chains with every subsequent metal atom bridged to the previous one by

---

[*] Dr. Q. Zhang, Prof. Dr. J. M. Shreeve
Department of Chemistry, University of Idaho
Moscow, ID 83844-2343 (USA)
E-mail: jshreeve@uidaho.edu
Dr. Q. Zhang
Institute of Chemical Materials
China Academy of Engineering Physics
Mianyang 621900 (China)

[**] Financial support by the ONR (N00014-12-1-0536).

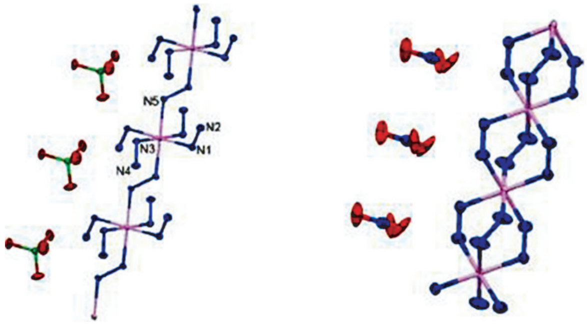

Figure 2. 1D crystal structures of nickel hydrazine perchlorate (NHP; left) and nickel hydrazine nitrate (NHN; right). Ellipsoids set at 50% probability. Reproduced with permission from Ref. [4b]. Copyright (2012), American Chemical Society.

a single hydrazine molecule (Figure 2, left), whereas NHN has a triply bridging hydrazine cage in the polymeric structure in which all hydrazine ligands bridge successive nickel centers (Figure 2, right). Both NHP and CHP exhibit good energetic properties and their heats of detonation (ΔH_{det}) are comparable to that of CL-20. Unfortunately, these nickel- and cobalt-based 1D MOFs are highly sensitive to flame, spark, and impact, which also precludes their commercial use.

To explore the potential of advanced MOFs for further energetic applications, two novel energetic cobalt- and zinc-based coordination architectures, $[Co_2(N_2H_4)_4\text{-}(N_2H_3CO_2)_2]\text{-}[ClO_4]_2\cdot H_2O$ (CHHP) and $[Zn_2(N_2H_4)_3\text{-}(N_2H_3CO_2)_2]\text{-}[ClO_4]_2\cdot H_2O$ (ZnHHP), which showed polymeric 2D sheet structures, were reported.[4a] Different from the linear polymers NHP and NHN, which were described above, partial ligand substitution of hydrazine by the tridentate hydrazine carboxylate anion afforded new 2D-layered structures. Crystallographic studies showed that nitrogen-rich CHHP formed a sheet polymer that is composed of distorted octahedral metal centers with mixed coordination spheres, in which each cobalt ion bears three hydrazine ligands and two hydrazine carboxylate ligands, whereas at the same time every hydrazine carboxylate ligand is a tridentate ligand that bridges two cobalt ions in the polymeric sheet structure. The final sheet was a 2D network of a mixed-ligand cobalt MOF. Similarly, energetic ZnHHP also formed a 2D polymeric sheet structure, in which the zinc ion was octahedrally coordinated with four equatorial hydrazine ligands and two axial bonds to the oxygen atoms of the hydrazine carboxylate moiety. Both CHHP and ZnHHP exhibit good thermal stabilities (decomposition temperatures of 231 °C and 293 °C, respectively), and their calculated crystal ion densities are $\geq 2.0\ g\,cm^{-3}$ at 150 K. Compared to the highly sensitive 1D MOFs NHP and NHN, the 2D structures of CHHP and ZnHHP resulted in a considerable reduction of sensitivity, while retaining or even increasing the energy content relative to typical metal-based explosives. Therefore, these energetic 2D MOFs are promising candidates for replacing heavy-metal primers, such as lead azide.

Compared with 1D and 2D MOFs, energetic 3D structures possess more complicated connection modes and enhanced structural reinforcement. The latest contribution that addresses the preparation of 3D energetic MOFs described two energetic MOFs, $[Cu(atrz)_3(NO_3)_2]_n$ and $[Ag(atrz)_{1.5}(NO_3)]_n$, which were synthesized by a hydrothermal reaction in which 4,4′-azo-1,2,4-triazole (atrz) was used as an energetic multidentate ligand to link the metal ions (copper or silver ion).[5] Compared to hydrazine, atrz has six potentially coordinating nitrogen atoms in the molecule, thereby meeting the geometric needs for a 3D architecture. Both 3D MOFs are air-stable and insoluble in most organic solvents, such as dimethyl sulfoxide, methanol, and acetone.

Crystallographic studies revealed that $[Cu(atrz)_3(NO_3)_2]_n$ possessed a 3D porous MOF structure. Each atrz moiety served as a bidentate ligand bridging two Cu^{II} centers, thereby forming a 3D equilateral triangular porous framework (Figure 3 a). Interestingly, the pores along the *a* axis are filled with nitrate anions. The species, $[Ag(atrz)_{1.5}(NO_3)]_n$, also has a 3D irregular porous MOF structure, in which two types of pores are formed because the atrz ligand exhibited bonding to silver atoms in two different coordination modes (Figure 3 b). In this 3D structure, two types of pores (A and B) are formed parallel to the crystallographic *a* axis, and the bigger pores (A) host the NO_3^- anion (Figure 3 b). Two 3D energetic MOFs, $[Cu(atrz)_3(NO_3)_2]_n$ and $[Ag(atrz)_{1.5}(NO_3)]_n$, exhibited high densities (1.68 and 2.16 $g\,cm^{-3}$, respectively) and good thermal stabilities (decomposition temperatures of 243 and

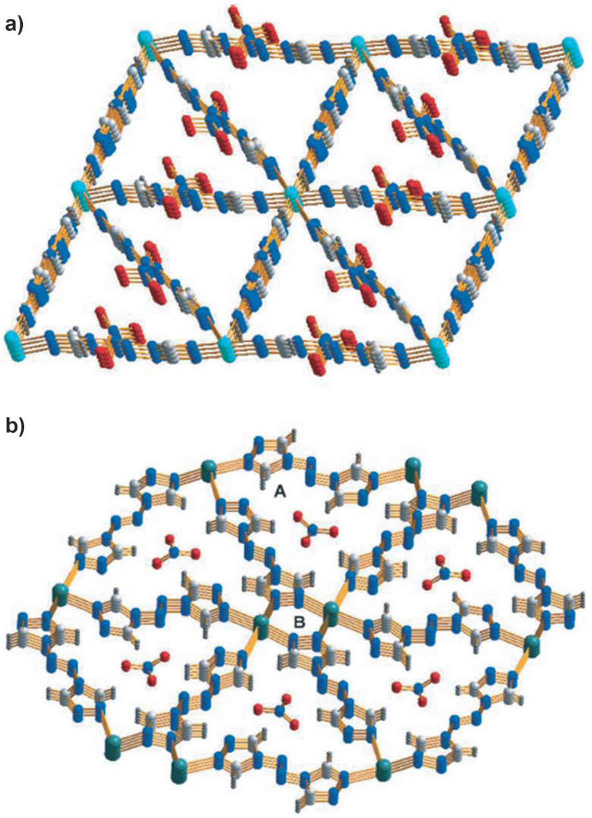

Figure 3. 3D porous framework structures of a) $[Cu(atrz)_3(NO_3)_2]_n$ and b) $[Ag(atrz)_{1.5}(NO_3)]_n$ depicted along the crystallographic *a* axis. The nitrate anions have been omitted for clarity. Reproduced with permission from Ref. [5]. Copyright (2013), Wiley-VCH.

257 °C, respectively). The strong structural reinforcement and extensive coordination networks in 3D frameworks may be responsible for their high thermal stabilities. More importantly, these energetic 3D MOF materials exhibit much lower sensitivity towards impact, friction, and electrostatic discharge than 1D and 2D energetic MOFs, while possessing higher heats of detonation (ΔH_{det}) than all of the previously reported energetic MOFs.[4,10] The concept of 3D energetic MOFs thus provides a new insight for future developments of new-generation high-performance primary explosives.

Overall, the construction of new energetic MOFs with 1D, 2D, or 3D structures has been achieved by the self-assembly of energetic bidentate or multidentate ligands with non-toxic metal ions. By virtue of this strategy, a new class of energetic materials with porous framework structures, especially 3D energetic MOFs, is emerging. The ordered multidimensional framework structures are expected to possess the desired physical (high density) and chemical properties (high thermal stability, high energetic output, and low sensitivity). For 3D energetic MOFs, in particular, the choice of metal ions and the structural modification of energetic ligands will significantly influence the structures of the resulting MOFs and ultimately the energetic properties of the material. There is no doubt that this new concept will provide a great opportunity for developing new-generation green primary explosives; the properties and energetic performance of the target material should be reasonably predictable. We are convinced that this newly emerging field is bubbling with opportunities, and that significant progress will be made in the years ahead.

Received: November 18, 2013

---

[1] a) L. E. Kreno, K. Leong, O. K. Farha, M. Allendorf, R. P. V. Duyne, J. T. Hupp, *Chem. Rev.* **2012**, *112*, 1105 – 1125; b) M. C. Das, S. Xiang, Z. Zhang, B. Chen, *Angew. Chem.* **2011**, *123*, 10696 – 10707; *Angew. Chem. Int. Ed.* **2011**, *50*, 10510 – 10520.

[2] S. S. Nagarkar, B. Joarder, A. K. Chaudhari, S. Mukherjee, S. K. Ghosh, *Angew. Chem.* **2013**, *125*, 2953 – 2957; *Angew. Chem. Int. Ed.* **2013**, *52*, 2881 – 2885.

[3] a) Y. Bae, R. Q. Snurr, *Angew. Chem.* **2011**, *123*, 11790 – 11801; *Angew. Chem. Int. Ed.* **2011**, *50*, 11586 – 11596; b) C. Wang, D. Liu, W. Lin, *J. Am. Chem. Soc.* **2013**, *135*, 13222 – 13234.

[4] a) O. S. Bushuyev, G. R. Peterson, P. Brown, A. Maiti, R. H. Gee, B. L. Weeks, L. J. Hope-Weeks, *Chem. Eur. J.* **2013**, *19*, 1706 – 1711; b) O. S. Bushuyev, P. Brown, A. Maiti, R. H. Gee, G. R. Peterson, B. L. Weeks, L. J. Hope-Weeks, *J. Am. Chem. Soc.* **2012**, *134*, 1422 – 1425.

[5] S. Li, Y. Wang, C. Qi, X. Zhao, J. Zhang, S. Zhang, S. Pang, *Angew. Chem.* **2013**, *125*, 14281 – 14285; *Angew. Chem. Int. Ed.* **2013**, *52*, 14031 – 14035

[6] Z. Yan, M. Li, H. Gao, X. Huang, D, Li, *Chem. Commun.* **2012**, *48*, 3960 – 3962.

[7] C. Yang, U. Kaipa, Q. Z. Mather, X. Wang, V. Nesterov, A. F. Venero, M. A. Omary, *J. Am. Chem. Soc.* **2011**, *133*, 18094 – 18097.

[8] B. Szafranowska, J. Beck, *Eur. J. Inorg. Chem.* **2013**, 3167 – 3177.

[9] a) M. Joas, T. M. Klapötke, J. Stierstorfer, N. Szimhardt, *Chem. Eur. J.* **2013**, *19*, 9995 – 10003; b) Y. Garcia, O. Kahn, L. Rabardel, B. Chansou, L. Salmon, J. P. Tuchagues, *Inorg. Chem.* **1999**, *38*, 4663 – 4670.

[10] B. Wu, L. Yang, S. Wang, T. Zhang, J. Zhang, Z. Zhou, K. Yu, *Z. Anorg. Allg. Chem.* **2011**, *637*, 450 – 455.