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Structural, electronic and elastic properties of several metal organic frameworks as a new kind of energetic materials



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ABSTRACT

The structural, electronic and elastic properties for metal-organic frameworks (MOFs) as energetic materials are investigated using non-local density functional theory with dispersion correction. The lattice constants of MOF-EMs are reproduced well by optPBE-vdW functional. The electronic structure analysis reveals that NHN is a metal, while the others are semiconductors or insulators with band gap from 0.1 eV to 4.7 eV. NHP, CHP, CHHP and CuAN are predicted to be magnetic. We also discuss the impact sensitivities of MOF-EMs in terms of their electronic structures. The calculated bulk modulus ranges from 15.1 GPa (CuAN) to 35.0 GPa (NHN).

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1. Introduction

Metal-organic frameworks (MOFs) formed by metal ion and linked organic bridging ligands have been extensively studied for their potential applications in catalyst [1], gas storage [2], sensors [3] and drug delivery [4]. Recently, a new kind of MOFs with high nitrogen content has been synthesized by several groups [5–9]. These MOFs with high mass densities possess high heats of detonation [10] and can be considered as potential energetic materials (EMs), which are defined as an important class of materials stored with large amount of chemical energy that can be released during a short period of time. Typical energetic materials include explosives, pyrotechnics, propellants and fuels, which are widely used for civilian and military purposes [11].

Firstly, Hoopes-Weeks and colleagues synthesized one-dimensional (1D) MOF energetic materials (MOF-EMs), which are made up of line polymers with hydrazine and nitrate or perchlorate, such as NHN ($\text{Ni}(\text{N}_2\text{H}_4)_3(\text{NO}_3)_2$), NHP ($\text{Ni}(\text{N}_2\text{H}_4)_5(\text{ClO}_4)_2$), and CHP ($\text{Co}(\text{N}_2\text{H}_4)_5(\text{ClO}_4)_2$) [5]. The estimated heats of detonation were 0.75, 1.25, 1.25 kcal/g for NHN, CHP and NHP, respectively, comparable to that of 1.27 kcal/g for cyclotrimethylene trinitramine (RDX) and 1.26 kcal/g for cyclotetramethylene tetranitramine (HMX) [12]. But those MOFs are sensitive to impact. To reduce the sensitivity, they partially substituted hydrazine perchlorate with tridentate hydrazine-carboxylate anion to prepare new two-dimensional

(2D) MOF-EMs, i.e., CHHP ($\text{Co}_2(\text{N}_2\text{H}_4)_4(\text{N}_2\text{H}_3\text{CO}_2)_2(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$) and ZnHHP ($\text{Zn}_2(\text{N}_2\text{H}_4)_3(\text{N}_2\text{H}_3\text{CO}_2)_2(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$) [6]. But their heats of detonation (about 0.8 kcal/g) were also reduced.

Recently, Pang and co-workers designed and synthesized three-dimensional (3D) MOF-EMs by nitrate salt and 4-azido-1,2,4-triazole (artz) to enhance the stability and energetic properties [7]. These MOF-EMs are halogen-free because perchlorate anion may promote thyroid dysfunction and be teratogenic. Impressively, the heats of detonation are 3.62 and 1.38 kcal/g for CuAN ($\text{Cu}(\text{artz})_3(\text{NO}_3)_2$) and SAN ($\text{Ag}(\text{artz})_{1.5}(\text{NO}_3)$), respectively, which are even higher than the high-efficiency EM like CL-20 (1.5 kcal/g) [12]. Later, Gao and his colleagues prepared a new strategy for 3D MOF-EMs by reaction between Co(II) and N,N-bis(1H-tetrazole-5-yl)-amine ligand [8] or $\text{Pb}(\text{NO}_3)_2$ and 3-(tetrazol-5-yl)-triazole ligand [9]. Two Pb-based 3D MOF-EMs with lower nitrogen content (39.4% and 27.2%) are less sensitive than CuAN and SAN but possess lower heat of detonation (1.36 and 0.26 kcal/g) than CuAN and SAN [9]. The sensitivity and heat of detonation (2.66 kcal/g) for Co-based MOF-EM with higher N content (59.85%) are between that of CuAN and SAN [8].

Although these MOF-EMs have been synthesized and their structures have been determined by X-ray diffraction, little is known about their electronic, elastic and other physical properties. In this letter, we first access the accuracy of different dispersion-correction methods within density functional theory (DFT) to accurately describe the non-covalent interactions in MOFs by comparing with the experimental lattice parameters. Then we predicted the electronic and elastic properties of these new MOF-EMs, which provide vital fundamental data for the future utilization of them.

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2. Methods

DFT calculations were performed with generalized gradient approximation (GGA) [13], as implemented in the VASP [14]. The projected augmented waves (PAW) [15] potentials were used to describe the core-valence interaction. Electronic wave functions were expanded by plane wave basis with kinetic energy cutoff of 800 eV. The Brillouin zones were sampled by \mathbf{k} -point meshes with a uniform separation of 0.03 \AA^{-1} for each MOF crystal. Structural relaxation was carried out until the maximum forces on each atom are less than 0.05 eV/\AA . In addition to the standard Perdew-Burke-Ernzerhof functional (PBE) functional [13], the dispersion correction was included with Grimme's D2 scheme (PBE-D2) [16], Grimme's D3 scheme by zero damping (PBE-D3) [17], Becke-Jonson damping (PBE-D3BJ) [18], vdW-DF functional [19], vdW-DF2 functional [20] and other optimized exchange-correlation functionals based on vdW-DF (optPBE-vdW, optB88-vdW, and optB86b-vdW) [21], as implemented in the VASP by Klimeš [22]. Electronic structures of these MOFs were calculated using optPBE-vdW and the \mathbf{k} -point meshes were sampled by a uniform separation of about 0.015 \AA^{-1} . Spin-polarized calculations were performed for all systems due to the presence of transition metal atoms and possible magnetism.

The bulk modulus (B) was calculated using the three-order Birch-Murnaghan equation of state (EOS) [23] from the energy-volume relationship as expressed in Eq. (1):

$$E(V) = E_0 + BV \left[\frac{1}{B'(B'-1)} \left(\frac{V_0}{V} \right)^{B'-1} + \frac{V}{B'V_0} - \frac{1}{B'-1} \right] \quad (1)$$

where V is the cell volume, and V_0 is the equilibrium volume with the minimum energy E_0 . $E(V)$ is the energy at a given volume V . B' , the derivative of B at zero pressure, was set as 4.0.

3. Results and discussion

Figure 1 shows the crystal structures of the MOF-EMs discovered in recent experiments [5–7]. For the 1D MOF-EMs of NHN, NHP and CHP, the metal-hydrazine complexes form 1D line and interact with nitrate or perchlorate. After partial substitution of hydrazine by hydrazine-carboxylate for ZnHHP and CHHP of the 2D MOF-EMs, the metal-hydrazine complexes become 2D sheet due to the interaction between metal ion and carboxylate group and the perchlorate does not change. In the 3D MOF-EMs, metal and artz group constitute 3D framework with filled nitrate group.

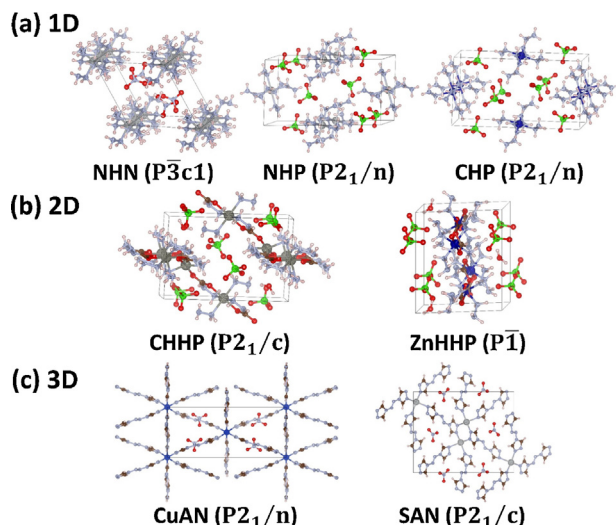


Figure 1. Crystal structures and space groups of 1D (a), 2D (b) and 3D (c) MOF-EMs.

All MOF-EMs explored here are monoclinic crystals except for NHN (trigonal) and ZnHHP (triclinic).

The assessment of various DFT methods is shown in Figure 2. As a well-known deficiency of conventional GGA [24], the standard PBE functional always overestimates the unit cell volume with an average error of 5.3% for the MOF-EMs considered. All dispersion correction schemes by Grimme show a little underestimation with average volume errors of -3.5% , -1.6% and -1.9% for PBE-D2, PBE-D3, and PBE-D3BJ, respectively. This is in agreement with our previous evaluation for EM crystals including nitromethane, HMX and PETN [25]. For those non-local correlation functionals without empirical parameters, vdW-DF with revPBE functional underestimates the strength of dispersion interaction and overestimates the lattice parameters with an average volume error of 5.7% , while vdW-DF2 partially corrects this error and reduces the average volume discrepancy to 2.5% . By optimizing the exchange functional with vdW correlation, optPBE-vdW functional gives the best performance for describing the dispersion interaction of MOF-EMs with an average volume error of only 0.1% . However, the other two functionals, i.e., optB86b-vdW and optB88-vdW, overestimate more pronouncedly, and the average volume errors for optB86b-vdW and optB88-vdW functionals reach -3.6% and -3.1% , respectively.

Based on the above results, we decide to further investigate the MOF-EMs using optPBE-vdW functional, which yields the best lattice parameters as compared with experiments. Table 1 lists the lattice parameters and mass density by optPBE-vdW method along with the experimental values. The theoretical results by other functionals can be found in Table S1 of the Supporting Information (SI). The density in Table 1 for all MOF-EMs considered here are consistent with experimental values [5]. For example, the calculated density for NHN is 2.06 g/cm^3 , in agreement with experimental value of 2.16 g/cm^3 [5]. Again, as shown in Table 1, optPBE-vdW can describe the dispersion interactions in the MOF-EMs quantitatively well. For example, along the axis which is mainly dispersion interaction in 1D MOF-EMs, the errors of lattice constant, a for NHN, a for NHP, and c for CHP are only 0.99% , 0.65% , and -0.58% , respectively. For 2D MOF-EMs, the errors for b and c of ZnHHP are -0.02% and -0.23% , respectively, which are determined by dispersion interaction between the 2D sheets paralleled to a axis. For CHHP, the error of a is 0.53% whose direction is mainly dispersion interaction between the 2D sheets paralleled to b - c plane. The same trend remains valid for the 3D MOF-EMs. From optPBE-vdW calculations, the cell volumes (V) of CuAN and SAN are 1406.7 and 1294.7 \AA^3 , respectively, which are consistent with experimental volumes of 1416.6 and 1275.8 \AA^3 . Note that all the above theoretical results are

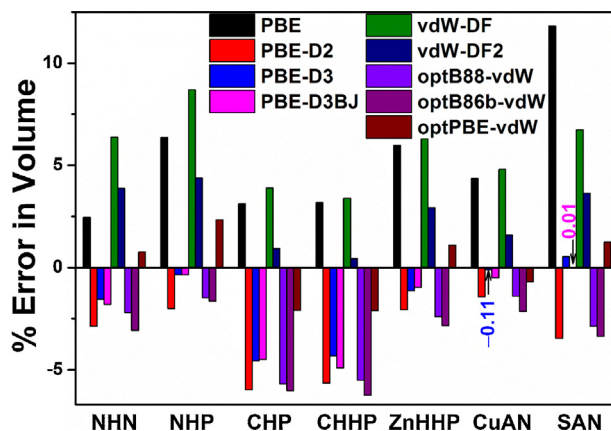


Figure 2. Errors in the calculated volume for all MOF-EMs solids compared with experimental values using different theoretical methods. Note that a very little error of 0.01% is marked for SAN using PBE-D3 with BJ damping and error of -0.11% is marked for CuAN by PBE with zero damping.

Table 1

The lattice parameters (a , b , c , α , β , γ), volume (V) and density (ρ) for selected MOF-EMs computed using optPBE-vdW functional as compared with experimental values. The space groups are given in parenthesis.

(a) NHN ($P\bar{3}_{c1}$)						
	a (Å)	c (Å)	γ ($^{\circ}$)	V (Å ³)	ρ (g/cm ³)	
Calc.	8.197	7.441	120.0	433.0	2.06	
Expt. [5]	8.117	7.531	120.0	429.7	2.16	

(b) NHP ($P2_{1/n}$)						
	a (Å)	b (Å)	c (Å)	β ($^{\circ}$)	V (Å ³)	ρ (g/cm ³)
Calc.	5.146	16.411	8.611	99.98	716.2	1.87
Expt. [5]	5.113	16.267	8.557	100.49	699.9	1.98

(c) CHP ($P2_{1/n}$)						
	a (Å)	b (Å)	c (Å)	β ($^{\circ}$)	V (Å ³)	ρ (g/cm ³)
Calc.	4.987	16.641	8.547	99.53	697.8	1.92
Expt. [5]	5.172	16.316	8.597	100.74	712.8	1.95

(d) CHHP ($P2_{1/c}$)						
	a (Å)	b (Å)	c (Å)	β ($^{\circ}$)	V (Å ³)	ρ (g/cm ³)
Calc.	9.828	10.947	10.289	115.79	996.8	1.97
Expt. [6]	9.776	11.385	10.019	114.10	1018.3	2.00

(e) ZnHHP ($P\bar{1}$)								
	a (Å)	b (Å)	c (Å)	α ($^{\circ}$)	β ($^{\circ}$)	γ ($^{\circ}$)	V (Å ³)	ρ (g/cm ³)
Calc.	7.934	9.370	13.253	89.42	91.71	106.95	941.9	2.02
Expt. [6]	7.854	9.372	13.283	90.23	92.17	107.49	931.7	2.12

(f) CuAN ($P2_{1/n}$)						
	a (Å)	b (Å)	c (Å)	β ($^{\circ}$)	V (Å ³)	ρ (g/cm ³)
Calc.	8.029	20.845	8.406	88.89	1406.7	1.55
Expt. [7]	8.011	20.461	8.644	90.64	1416.6	1.68

(g) SAN ($P2_{1/c}$)						
	a (Å)	b (Å)	c (Å)	β ($^{\circ}$)	V (Å ³)	ρ (g/cm ³)
Calc.	4.701	14.892	18.449	90.45	1294.7	2.06
Expt. [7]	4.704	14.752	18.391	91.14	1275.8	2.16

obtained at zero temperature. Accurate description of temperature effect on MOFs, like negative thermal expansion [26–28], needs further efforts by inclusion of the phonon effects and will be discussed elsewhere.

The calculated spin-polarized electronic density of states (DOS) for all MOF-EMs are depicted in Figure 3. According to the DOS, NHN is a metal, while NHP and CHP are both semiconductors with band gap of 0.6 eV (indirect) and 0.4 eV (indirect), respectively. Note that the band gap for NHP is between occupied spin-up levels and unoccupied spin-down levels. As for the 2D and 3D MOF-EMs, CHHP, ZnHHP, CuAN and SAN are semiconductors with band gap of 1.0 eV (direct), 4.7 eV (indirect), 0.1 eV (indirect) and 1.3 eV (indirect), respectively. Note that the PBE and vdW-DF functionals systematically underestimate the band gap [29]; thus the true gaps of these MOF-EMs would be larger than the theoretical values in Table 2. However, due to the large number of atoms in the unit cells, more accurate calculations using GW method are too computationally costly.

According to the band gap criterion for impact sensitivity (IS) of energetic crystals [30], an EM with smaller band gap is more sensitive (with less IS value) than that with similar structure or similar decomposition mechanism. For 1D MOF-EMs with similar structures considered in this letter, the metallic NHN should be more sensitive than semiconducting NHP and CHP. This agrees with the experimental observation that NHN is too sensitive to make effective characterization and CHP is relatively more stable [5]. According to the theoretical gap of 0.6 eV for NHP, we predict that the IS for NHP is even higher than CHP, which means NHP is more stable than CHP. For 2D MOF-EMs, CHHP with band gap of 1.0 eV is more sensitive than ZnHHP (4.7 eV). This is also in line with the experimental fact that IS of 0.8 J for CHHP is lower than that of 2.5 J for ZnHHP [6]. Finally, CuAN (with 0.1 eV gap) is more sensitive than SAN (with 1.3 eV gap) from the band gap criterion, in agreement with the experiment IS data of 22.5 J for CuAN and 30 J for SAN, respectively [7].

Our spin-polarized calculations show NHN, ZnHHP and SAN are non-magnetic while the other MOF-EMs are magnetic. The magnetic moments per unit cell (per TM atom) are $4.0 \mu_B$ ($2.0 \mu_B/\text{Ni}$), $2.0 \mu_B$ ($1.0 \mu_B/\text{Co}$), $4.0 \mu_B$ ($1.0 \mu_B/\text{Co}$), and $2.0 \mu_B$ ($1.0 \mu_B/\text{Cu}$) for NHP, CHP, CHHP and CuAN, respectively. In order to understand the magnetic properties of MOF-EMs, detailed DOS and local DOS (LDOS) for all elements in MOF-EMs are plotted in Figures S1–S7 of the SI. For NHP, LDOS shows that spin-up levels for each Ni are occupied by five electrons, while spin-down levels are occupied by three electrons, which means that each Ni atom has an on-site moment of $2.0 \mu_B$. Similarly, LDOS of CHP reveals that spin up levels for each Co are occupied by four electrons and spin down ones by three electrons (Figure S2), implying that each Co atom has spin moment of $1.0 \mu_B$. The occupied states of Co for CHHP in Figure S4 are the same as that in CHP. For CuAN, LDOS reveals that spin up levels for each Cu are occupied by five electrons and spin down ones by four electrons (Figure S6), implying each Cu atom has moment of $1.0 \mu_B$. Moreover, no s electron is found from LDOS of TM in MOF-EMs from Figures S1–S7 of SI. This suggests the s electrons are transferred to other groups of MOF-EMs.

More interestingly, detailed electronic analysis for NHN shows both the highest occupied states and lowest unoccupied states around Fermi level are originated from the hybridization between d orbitals of Ni and p orbitals of N of hydrazine group, which implies that Ni–N bond might be the reactivity center of detonation. Similar phenomena are found in NHP and CHP. Furthermore, for 2D MOF-EMs, the highest occupied levels are originated from hybridization of d orbitals of TMs and p orbitals of O of carboxylate group interacting with TMs. Only little contribution from p orbital of N of hydrazine group interacting with TMs is found. Thus, TMs interacts stronger with O of carboxylate group than that with N of hydrazine group, that is, the bond between TMs and N of hydrazine group firstly breaks as the reactivity center of decomposition. Finally, the highest occupied levels can be attributed to p orbitals of O which belongs to nitrate (NO_3) group for the 3D MOF-EMs. There is a little contribution of hybridization of d orbitals of Cu and p orbitals of N of hydrazine group interacting with Cu for CuAN, while no contribution of Ag and N of hydrazine which binds to Ag is found for SAN. This difference is attributed to closed-shell d orbitals of Ag for SAN and open-shell case of Cu for CuAN. This also explains why CuAN is more sensitive than SAN [7]. Thus, the reactivity centers of the 3D MOF-EMs are TM–N bond and nitrate group, which are different from the case of the 1D and 2D MOF-EMs.

Since the detonation of EMs usually undergoes large reduction of volume, the mechanical properties and high-pressure behavior are important for the applications of EMs. The bulk moduli (B) of MOF-EMs computed from the E - V curves using Eq. (1) are summarized in Table 2. The highest B is 35.0 GPa for NHN, and the lowest B is 15.1 GPa for CuAN; all of them are all higher than that of

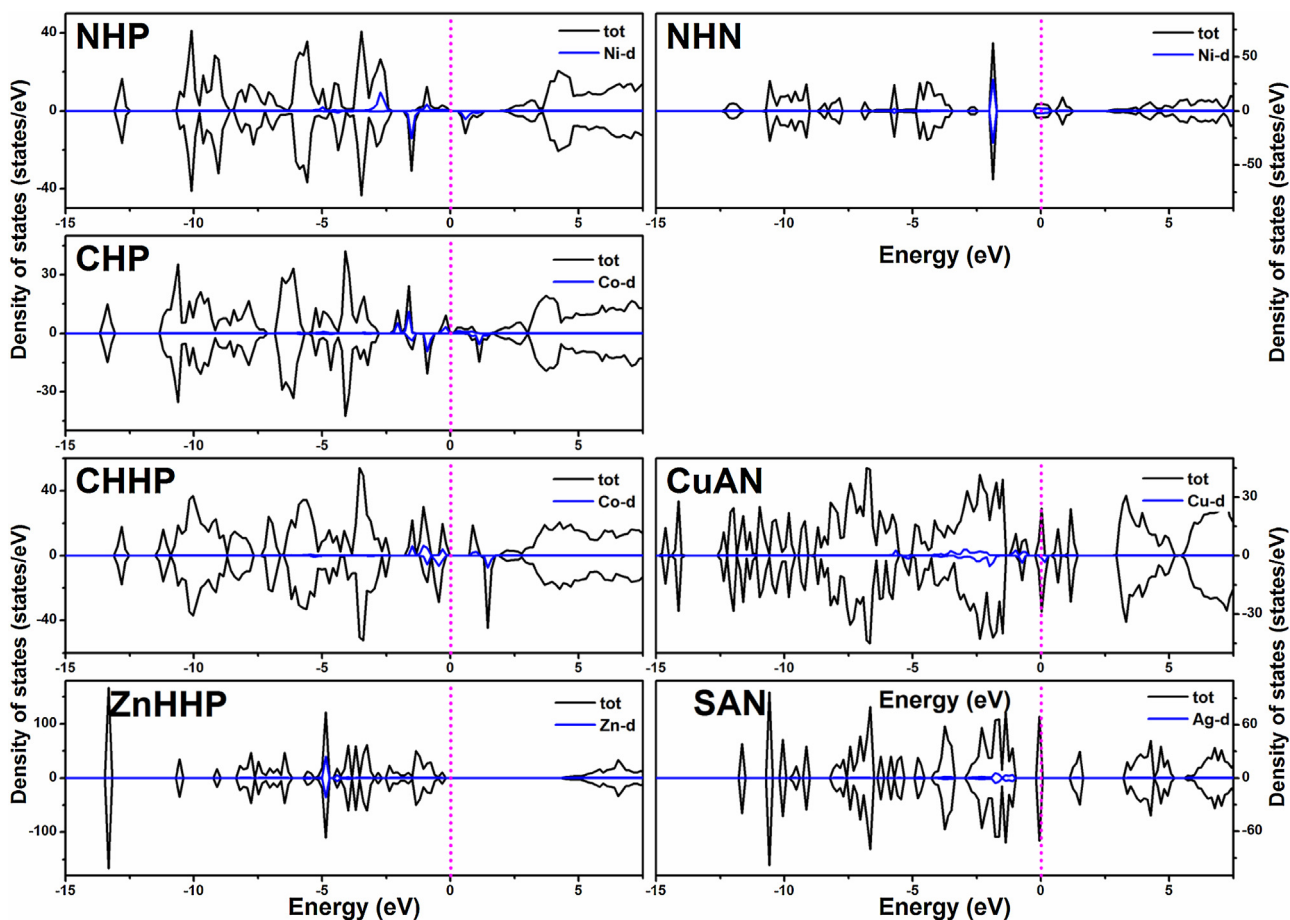


Figure 3. Spin-polarized total density of states (DOS) of crystals with black lines and local DOS (LDOS) of TM atom with blue lines in all MOF-EMs (upper: majority spin, down: minority spin). Dash lines separate the occupied and unoccupied states. The zero energy represents Fermi level.

Table 2

Bulk modulus (B), magnetic moments per unit cell (M) and band gap (E_g) for MOF-EMs estimated by optPBE-vdW functional.

	B (GPa)	M (μ_B)	E_g (eV)
NHN	35.0	0.0	metal
NHP	19.2	4.0	0.6
CHP	21.2	2.0	0.4
CHHP	22.8	4.0	1.0
ZnHHP	25.1	0.0	4.7
CuAN	15.1	2.0	0.1
SAN	25.2	0.0	1.3

traditional molecular EMs, such as 12.0 GPa for RDX [31] and 9.9 GPa for β -HMX [32].

4. Conclusions

In summary, we evaluated the accuracy of lattice parameters of seven MOF-EMs by PBE functional with empirical dispersion corrections and other non-local functionals with dispersion interactions. We found that the structural parameters of MOF-EMs can be well reproduced by optPBE-vdW functional with an average volume error of 0.1% with regard to experimental values. Then, the electronic structures and bulk moduli of MOF-EMs were predicted using optPBE-vdW calculations. Only NHN is metallic and the other MOF-EMs are semiconducting or insulating with band gap between 0.1 eV and 4.7 eV. We discussed the impact

sensitivity in terms of the band gap of MOF-EMs. We also predicted the bulk modulus that ranges from 15.1 GPa to 35.0 GPa. These theoretical results provide important data for the future utilization of these new EMs. Further theoretical investigation of thermal stability, sensitivities, temperature effect, and atomistic mechanism of detonation of these MOF-EMs are still underway and the results will be presented elsewhere.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.cplett.2015.03.058](https://doi.org/10.1016/j.cplett.2015.03.058)

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