

## Supporting Information

### **Energetic Mn(II)/Ni(II) Coordination Compounds in Catalyzing RDX and HMX Decomposition and Enhancing Combustion**

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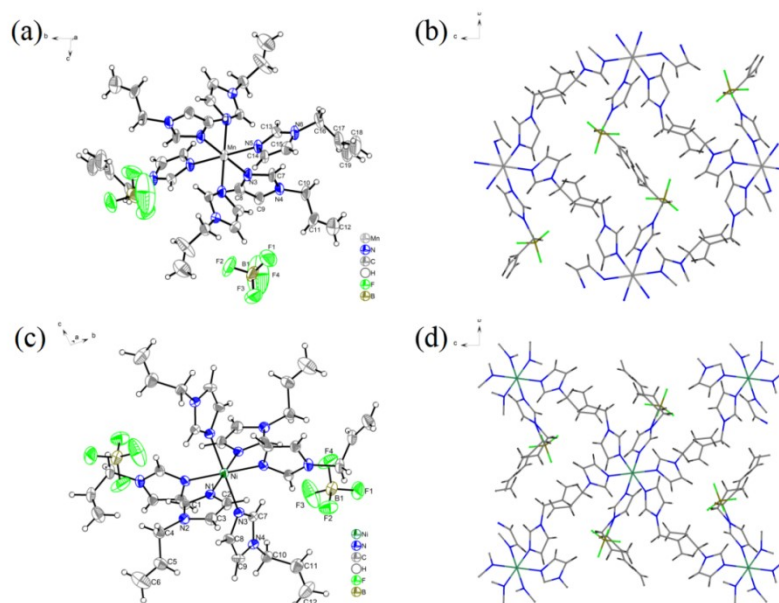
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## S1. Preparation and Characterization Methods of Materials

### S1.1 Preparation and experimental methods

Synthesis of Ni-ABF: Briefly, an aqueous solution of AIM (1.30 g, 12 mmol in 10 mL H<sub>2</sub>O) was added dropwise to an aqueous solution of Ni(NO<sub>3</sub>)<sub>2</sub> (0.58 g, 2 mmol in 10 mL H<sub>2</sub>O) under stirring. The mixture was kept at 60 °C for 10 min to allow coordination. Subsequently, an aqueous solution of NaBF<sub>4</sub> (0.44 g, 4 mmol in 10 mL H<sub>2</sub>O) was added dropwise, inducing immediate precipitation. The crude product was collected by filtration, washed thoroughly with ultrapure water and ethanol, and dried under vacuum at 60 °C for 12 h to obtain the powdered sample. Single crystals suitable for X-ray diffraction were grown from the filtrate by slow evaporation at 25 °C in the dark over 7 days.

Mn-ABF and Ni-ABF employ identical experimental protocols, with the detailed characterization methods outlined below. The specific test conditions for single-crystal X-ray diffraction are as follows: single-crystal X-ray diffraction data were collected at a constant temperature of 293 K on a Rigaku AFC-10/Saturn 724+ CCD diffractometer. Graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) was used as the source, with the generator operated at 50 kV and 40 mA. Diffraction data were collected in  $\omega$ -scan mode over the full angular range required for structural refinement. Powder X-ray Diffraction (PXRD): Data were collected with Cu K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ), a step size of  $0.02^\circ$ , a scan time of 1 s/step, and a  $2\theta$  scanning range of  $5^\circ\sim 80^\circ$ . TG/DSC: All tests were performed under a 50 mL/min high-purity nitrogen flow, using alumina sample pans, with a sample mass of 2~3 mg. Measurements were conducted over a temperature range of  $30 \text{ }^\circ\text{C}\sim 500 \text{ }^\circ\text{C}$  at a heating rate of 10 K/min. X-ray Photoelectron Spectroscopy (XPS): Spectra were recorded with Al K $\alpha$  radiation (1486.6 eV). All binding energies were calibrated against the C 1s peak at 284.8 eV for charge correction. A pass energy of 160 eV was used for survey scans, and 40 eV for high-resolution core-level scans.



**Fig. S1** Molecular structures and stacking diagrams of Mn-ABF(a-b) and Ni-ABF(c-d)

## S1.2 The Catalytic Effects of Mn-ABF and Ni-ABF on RDX and HMX

Differential scanning calorimetry (DSC) tests were conducted using a TA-SDT650 under an air atmosphere and heating rates of 5/10/15/20 °C·min<sup>-1</sup>. DSC curves were obtained for RDX, HMX, RDX+Mn-ABF, RDX+Ni-ABF HMX+Mn-ABF and HMX+Ni-ABF at different heating rates.

To investigate the effects of Mn-ABF and Ni-ABF on the combustion behavior of RDX/AP/Al and HMX/AP/Al composite materials, 500 mg of RDX/AP/Al, HMX/AP/Al, RDX/AP/Al+1, RDX/AP/Al+2, HMX/AP/Al+1, and HMX/AP/Al+2 samples were placed in quartz tubes, with each tube containing a 14-mm-long sample. The samples were then ignited using an electric heating wire, and the combustion process was recorded using high-speed photography.

Combustion environment: All combustion tests were conducted in a laboratory fume hood qualified for combustion experiments, in full compliance with relevant laboratory safety and management regulations. Ignition method: A direct current power supply was used as the ignition system, and ignition was achieved via a nickel-chromium alloy wire. Definition of initial recording time: In the high-speed photography recording, the moment when the DC power supply is turned on is defined as the initial starting time of combustion, and the moment when the sample finishes burning is defined as the end time.

## S2. Mn-ABF of X-ray crystallographic data

Table S1. X-ray crystallographic data for Mn-ABF

Parameter	Mn-ABF
Compounds	Mn(AIM) <sub>6</sub> (BF <sub>4</sub> ) <sub>2</sub>
Formula	MnB <sub>2</sub> F <sub>8</sub> C <sub>36</sub> H <sub>46</sub> N <sub>12</sub>
CCDC	2545128
Formula weight	875.41
Temperature/K	118.95
Crystal system	monoclinic
Space group	P2 <sub>1</sub> /n
<i>a</i> /Å	8.4551(14)
<i>b</i> /Å	14.660(2)
<i>c</i> /Å	17.989(17)
<i>α</i> /°	90.00
<i>β</i> /°	104.662(17)
<i>γ</i> /°	90.00
Volume/Å <sup>3</sup>	2157.2(7)
<i>Z</i>	2
<i>ρ</i> /(g/cm <sup>3</sup> )	1.348
<i>F</i> (000)	906
Goodness-of-fit on F <sup>2</sup>	1.034
<i>R</i> <sub>1</sub> ( <i>I</i> ≥ 2σ( <i>I</i> ))	0.1252

$R_1(\text{all data})$	0.2161
$wR_2(I \geq 2\sigma(I))$	0.3069
$wR_2(\text{all data})$	0.3692

The Mn-ABF crystal belongs to the triclinic crystal system with space group  $P2_1/n$ . Its unit cell parameters ( $a=8.4551 \text{ \AA}$ ,  $b=14.660 \text{ \AA}$ ,  $c=17.989 \text{ \AA}$ ;  $\alpha=90.00^\circ$ ,  $\beta=104.662^\circ$ ,  $\gamma=90.00^\circ$ ) exhibit typical non-orthogonality, with a unit cell volume of  $2157.2 \text{ \AA}^3$ . Each unit cell contains only one formula unit ( $Z=2$ ), yielding a calculated density of  $1.452 \text{ g/cm}^3$ . The structural analysis exhibits excellent reliability metrics ( $\text{Goof}=1.034$ ,  $R_1=0.1252$ ), indicating that the Mn(II) ion likely resides at the symmetry center within this centrally symmetric structure. The precise determination of its coordination configuration with AIM ligands and the stacking arrangement of  $\text{BF}_4^-$  anions provides a robust structural foundation for understanding its coordination chemistry and material properties.

### S3. Bond length and bond angle data for Mn-ABF

Table S2. Bond angles of Mn-ABF.

Bonds	Length( $\text{\AA}$ )
Mn1-N1	2.267(7)
Mn1-N3	2.263(8)
Mn1-N5	2.285(7)
N1-C2	1.375(12)
N1-C1	1.309(11)
N6-C16	1.484(12)
N6-C13	1.339(11)
N6-C15	1.360(12)
N3-C7	1.329(11)
N3-C8	1.385(12)
N5-C14	1.365(11)
N5-C13	1.326(11)
C4-N2	1.473(11)
C7-N4	1.340(11)
N4-C10	1.497(12)
N4-C9	1.369(12)
C3-N2	1.385(12)
N2-C1	1.338(11)
F2-B1	1.329(16)
F3-B1	1.401(17)
B1-F1	1.360(16)
B1-F4	1.249(18)

Table S3. Bond lengths of Mn-ABF.

Bond Angle	Angle(°)
N1-Mn1-N5	87.8(3)
N3-Mn1-N1	89.2(3)
N3-Mn1-N5	91.2(3)
C2-N1-Mn1	125.3(6)
C1-N1-Mn1	128.6(7)
C7-N3-Mn1	128.6(7)
C8-N3-Mn1	127.3(6)
C14-N5-Mn1	127.4(6)
C13-N5-Mn1	127.1(6)
F2-B1-F3	103.6(13)
F2-B1-F1	110.7(12)
F1-B1-F3	105.9(11)
F4-B1-F2	112.3(14)
F4-B1-F3	112.5(16)
F4-B1-F1	111.4(16)

#### S4. Ni-ABF of X-ray crystallographic data

Table S4. X-ray crystallographic data for Ni-ABF.

Parameter	Ni-ABF
Compounds	Ni(AIM) <sub>6</sub> (BF <sub>4</sub> ) <sub>2</sub>
Formula	NiB <sub>2</sub> F <sub>8</sub> C <sub>36</sub> H <sub>18</sub> N <sub>12</sub>
CCDC	2529542
Formula weight	881.19
Temperature/K	115.95
Crystal system	monoclinic
Space group	P2 <sub>1</sub> /c
<i>a</i> /Å	8.4400(8)
<i>b</i> /Å	14.2634(14)
<i>c</i> /Å	18.063(5)
$\alpha$ /°	90.00
$\beta$ /°	104.819(15)
$\gamma$ /°	90.00
Volume/Å <sup>3</sup>	2102.2(6)
<i>Z</i>	2
$\rho$ /(g/cm <sup>3</sup> )	1.392
<i>F</i> (000)	916
Goodness-of-fit on F <sup>2</sup>	1.047
<i>R</i> <sub>1</sub> ( <i>I</i> ≥ 2σ( <i>I</i> ))	0.0664
<i>R</i> <sub>1</sub> (all data)	0.1128
<i>wR</i> <sub>2</sub> ( <i>I</i> ≥ 2σ( <i>I</i> ))	0.1259

The Ni-ABF crystal belongs to the triclinic crystal system with space group P-1. Its unit cell parameters ( $a=8.4400 \text{ \AA}$ ,  $b=14.2634 \text{ \AA}$ ,  $c=18.063 \text{ \AA}$ ;  $\alpha=90.00^\circ$ ,  $\beta=104.819^\circ$ ,  $\gamma=90.00^\circ$ ) exhibit typical non-orthogonality, with a unit cell volume of  $881.19 \text{ \AA}^3$ . Each unit cell contains only one formula unit ( $Z=2$ ), yielding a calculated density of  $1.482 \text{ g/cm}^3$ . The structural analysis exhibits excellent reliability metrics (GooF=1.047,  $R_1=0.0664$ ), indicating that the Ni(II) ion likely resides at the symmetry center within this centrally symmetric structure. The precise determination of its coordination configuration with VIM ligands and the stacking arrangement of  $\text{BF}_4^-$  anions provides a robust structural foundation for understanding its coordination chemistry and material properties.

### S5. Bond length and bond angle data for Ni-ABF

Table S5. Bond angles of Ni-ABF.

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N6-C16	1.484(12)
N6-C13	1.339(11)
N6-C15	1.360(12)
N3-C7	1.329(11)
N3-C8	1.385(12)
N5-C14	1.365(11)
N5-C13	1.326(11)
C4-N2	1.473(11)
C7-N4	1.340(11)
N4-C10	1.497(12)
N4-C9	1.369(12)
C3-N2	1.385(12)
N2-C1	1.338(11)
F2-B1	1.329(16)
F3-B1	1.401(17)
B1-F1	1.360(16)
B1-F4	1.249(18)

Table S6. Bond lengths of Ni-ABF.

Bond Angle	Angle( $^\circ$ )
N1-Mn1-N5	87.8(3)
N3-Mn1-N1	89.2(3)
N3-Mn1-N5	91.2(3)
C2-N1-Mn1	125.3(6)

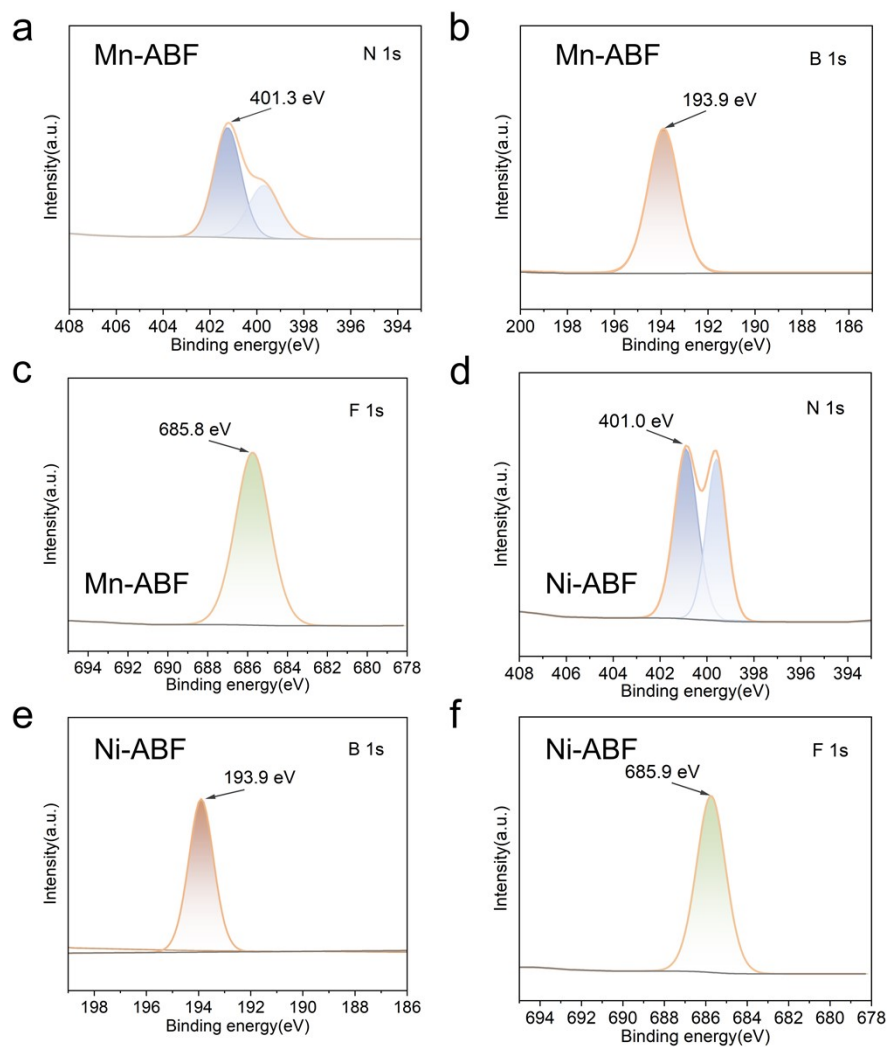
C1-N1-Mn1	128.6(7)
C7-N3-Mn1	128.6(7)
C8-N3-Mn1	127.3(6)
C14-N5-Mn1	127.4(6)
C13-N5-Mn1	127.1(6)
F2-B1-F3	103.6(13)
F2-B1-F1	110.7(12)
F1-B1-F3	105.9(11)
F4-B1-F2	112.3(14)
F4-B1-F3	112.5(16)
F4-B1-F1	111.4(16)

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### S6. Calculation details for Mn-ABF and Ni-ABF

All density functional theory calculations in this work were performed using the Gaussian 16 software package. Geometry optimization, frequency analysis and frontier molecular orbital energy calculation were conducted with the unrestricted B3LYP (UB3LYP) hybrid functional, and a mixed basis set scheme was applied: the central metal atoms (Mn for Mn-ABF, Ni for Ni-ABF) were described by the def2-TZVP basis set, C/H/N atoms from the vinylimidazole ligands were described by 6-31G(d), and B/F atoms from the tetrafluoroborate counterions were described by 6-31+G(d). Ni-ABF follows the identical protocol with only adjustments to the initial atomic coordinates, charge and spin multiplicity. The ESP calculations were performed on isolated molecules in the gas phase and therefore do not incorporate the effects of crystal packing.

## S7. Bond length and bond angle data for Ni-ABF



**Fig. 1** (a-c) The XPS spectra of Mn-ABF. (d-f) The XPS spectra of Ni-ABF.