Supporting Information

Catalytic Ignition of [BMIM]DCA-H_2O_2 Propellant with $Cu(vim)_2(DCA)_2$ Complex

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Content

Computational Details

Characterization of single crystal X-ray diffraction

Based on the coherent diffraction of X-rays by the periodic arrangement of atoms in the crystal, the crystal structure of the compound is analyzed by recording the position and intensity of the diffraction points. In the structural analysis, the non-hydrogen atoms were initially positioned by difference Fourier synthesis, and the full matrix least squares refinement was performed by SHELXS-97 program. Hydrogen atoms adopt theoretical hydrogenation and participate in refinement based on the riding model. The experiment first determined the crystal system, orientation matrix and unit cell parameters of the single crystal. The data were corrected for Lorentz polarization and absorption to reduce systematic errors. Subsequently, SHELXL-97 was used to optimize the atomic parameters to make them consistent with the measured diffraction data, and the crystallographic data were verified by PLATON-99 to complete the whole process from structural optimization to verification. The crystallographic data of the complexes $M(vim)_2(DCA)_2$ (M = Mn, Fe, Co, Cu) are listed in **Table S1**, and the relevant bond lengths and bond angles are summarized in **Tables S2-S5**.

Heat of Formation

The heat of formation (ΔH_f) of the complex is calculated by the following reaction:[1]

$$M(s) + C(s) + H_2(g) + O_2(g) + N_2(g) \rightarrow C_aH_bM_cO_dN_e \qquad (1)$$

CP2K 2023.1 software was used to complete the calculation.[2] The electronic interaction is described by the PBE0 mixed functional,[3] and the dispersion effect is corrected by the Grimme D3 method.[4] The plane wave cutoff energy is set to 400 eV. The DZVP-MOLOPT-SR-GTH basis set is used for structural optimization,[5] and the pob-TZVP basis set is used for single point energy calculation.[6] The input file is generated by Multiwfn software.[7] The ΔH_f calculation results of the complex $M(vim)_2(DCA)_2$ (M = Mn, Fe, Co, Cu) are shown in **Table S6**.

In order to explore the effect of the interaction between the complex and [BMIM]DCA on the thermodynamic properties of the propellant system. Through the following **Equations 1-4**，The ΔH_f (complex : fuel = x : y = 0.1 : 0.9) of the mixture of $M(vim)_2(DCA)_2$ (M = Mn, Fe, Co, Cu) and [BMIM]DCA was calculated. The ΔH_f of [BMIM]DCA was obtained from the literature.[8]

$$n_{complex} = \frac{x}{M_{complex}} \qquad (1)$$

$$n_{IL} = \frac{y}{M_{IL}} \qquad (2)$$

$$n_{sum} = n_{complex} + n_{IL} = \frac{x}{M_{complex}} + \frac{y}{M_{IL}} \qquad (3)$$

$$\Delta_f H_{mix} = \frac{n_{complex}}{n_{sum}} * \Delta_f H_{complex} + \frac{n_{IL}}{n_{sum}} * \Delta_f H_{IL} \qquad (4)$$

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Table S1 Crystallographic data and structure refinement details for Complex $M(vim)_2(DCA)_2$.

Complex	**Mn**	**Fe**	**Co**	**Cu**
Formula	$C_{14}H_{12}MnN_{10}$	$C_{14}H_{12}FeN_{10}$	$C_{14}H_{12}CoN_{10}$	$C_{14}H_{12}CuN_{10}$
fw	375.28	376.19	379.27	383.88
T/K	117.60(10)	117.3(2)	117.70(10)	118.2(4)
Crystal system	triclinic	triclinic	orthorhombic	triclinic
Space group	*P-1*	*P-1*	*Cmca*	*P-1*
a (Å)	6.5511(7)	6.4991(14)	7.311(2)	6.5205(16)
b (Å)	7.5013(8)	7.4621(16)	16.584(5)	7.4284(17)
c (Å)	8.9897(8)	9.0329(18)	14.201(4)	8.7894(19)
α (deg)	104.611(8)	106.411(19)	90.00	105.140(19)
β (deg)	94.881(8)	94.875(18)	90.00	96.923(19)
γ (deg)	95.641(8)	96.013(18)	90.00	95.675(19)
V (Å^3)	422.64(7)	414.88(15)	1721.8(9)	404.16(16)
Z	1	1	4	1
ρ (g·cm^{-3})	1.474	1.506	1.463	1.577
Abs coeff (mm^{-1})	0.801	0.929	1.016	1.372
F (000)	191	192	772	195
GOF	1.100	0.999	1.108	1.083
Data/restraints/parameters	1618/0/115	1564/0/115	902/0/71	1535/0/115
$R_1(I > 2\sigma(I))^a$	0.0411	0.0787	0.0790	0.0488
$wR_2(I > 2\sigma(I))^b$	0.0794	0.1198	0.2092	0.0946
$R_1(all\ data)^a$	0.0485	0.1197	0.0963	0.0559
$wR_2(all\ data)^b$	0.0874	0.1446	0.2291	0.1034

$^aR_1 = \sum\|F_0| - |F_c\|/\sum|F_0|$. $^bwR_2 = \{\sum[w(F_0^2 - F_c^2)^2]/\sum[w(F_0^2)^2]\}^{1/2}$.

Table S2 Selected bond lengths and bond angles of Complex Mn(vim)$_2$(DCA)$_2$.

Atom	Length (Å)	Atom	Length (Å)
Mn1-N3	2.228(2)	N4-C6	1.310(3)
Mn1-N3[1]	2.228(2)	N4-C7	1.308(3)
Mn1-N1	2.222(2)	N3-C6	1.150(3)
Mn1-N1[1]	2.222(2)	C1-N1	1.319(3)
Mn1-N5[2]	2.269(2)	N1-C2	1.385(3)
Mn1-N5[3]	2.269(2)	N5- Mn1[4]	2.269(2)
N2-C1	1.353(3)	N5-C7	1.154(3)
N2-C3	1.378(3)	C3-C2	1.342(4)
N2-C4	1.420(3)	C4-C5	1.302(3)
Atom	**Angle (°)**	**Atom**	**Angle (°)**
N3[1]-Mn1-N3	180.000(1)	C1-N2-C3	106.9(2)
N3-Mn1-N5[2]	90.84(8)	C1-N2-C4	124.8(2)
N3-Mn1-N5[3]	89.16(8)	C3-N2-C4	128.1(2)
N3[1]-Mn1-N5[3]	90.84(8)	C7-N4-C6	119.4(2)
N3[1]-Mn1-N5[2]	89.16(8)	C6-N3-Mn1	163.14(19)
N1-Mn1-N3[1]	89.46(8)	N1-C1-N2	111.7(2)
N1[1]-Mn1-N3[1]	90.54(8)	C1-N1-Mn1	126.49(15)
N1-Mn1-N3	90.54(8)	C1-N1-C2	104.7(2)
N1[1]-Mn1-N3	89.46(8)	C2-N1-Mn1	128.73(16)
N1-Mn1-N1[1]	180.000(1)	C7-N5-Mn1[4]	150.98(17)
N1[1]-Mn1-N5[3]	92.10(8)	N3-C6-N4	174.2(3)
N1-Mn1-N5[2]	92.10(8)	N5-C7-N4	174.0(2)
N1[1]-Mn1-N5[2]	87.90(8)	C2-C3-N2	106.0(2)
N1-Mn1-N5[3]	87.90(8)	C5-C4-N2	124.5(2)
N5[2]-Mn1-N5[3]	180.00(9)	C3-C2-N1	110.7(2)

Noted: [1]1-X,2-Y,2-Z; [2]+X,1+Y,+Z; [3]1-X,1-Y,2-Z; [4]+X,-1+Y,+Z

Table S3 Selected bond lengths and bond angles of Complex $Fe(vim)_2(DCA)_2$.

Atom	**Length (Å)**	**Atom**	**Length (Å)**
Fe1-N3[1]	2.161(5)	N3-C6	1.171(7)
Fe1-N3	2.161(5)	N4-C6	1.306(7)
Fe1-N1[1]	2.161(5)	N4-C7	1.324(6)
Fe1-N1	2.161(5)	N1-C2	1.382(7)
Fe1-N5[2]	2.199(4)	N1-C1	1.308(6)
Fe1-N5[3]	2.199(4)	C2-C3	1.361(7)
N2-C4	1.407(6)	C7-N5	1.146(6)
N2-C3	1.370(7)	C4-C5	1.331(8)
N2-C1	1.364(7)	N5-Fe1[4]	2.199(4)

Atom	**Angle (°)**	**Atom**	**Angle (°)**
N3-Fe1-N3[1]	180.000(1)	C2-N2-C4	127.6(5)
N3-Fe1-N1[1]	90.74(18)	C1-N2-C4	125.3(5)
N3[1]-Fe1-N1[1]	89.26(18)	C1-N2-C3	107.0(5)
N3-Fe1-N1	89.26(18)	C6-N3-Fe1	163.3(4)
N3[1]-Fe1-N1	90.74(18)	C6-N4-C7	118.1(5)
N3-Fe1-N5[2]	92.02(16)	C2-N1-Fe1	127.2(4)
N3[1]-Fe1-N5[2]	87.98(16)	C1-N1-Fe1	126.2(4)
N3[1]-Fe1-N5[3]	92.02(16)	C1-N1-C2	106.6(5)
N3-Fe1-N5[3]	87.98(16)	N3-C6-N4	174.1(6)
N1-Fe1-N1[1]	180.000(1)	C3-C2-N1	108.9(5)
N1[1]-Fe1-N5[2]	91.54(16)	N5-C7-N4	173.6(6)
N1-Fe1-N5[2]	88.46(16)	C5-C4-N2	124.9(6)
N1[1]-Fe1-N5[3]	88.46(16)	C7-N5-Fe1[4]	155.0(4)
N1-Fe1-N5[3]	91.54(16)	C2-C3-N2	106.6(5)
N5[3]-Fe1-N5[2]	180.000(1)	N1-C1-N2	110.9(6)

Noted: [1]2-X,1-Y,1-Z; [2]+X,-1+Y,+Z; [3]2-X,2-Y,1-Z; [4]+X,1+Y,+Z

Table S4 Selected bond lengths and bond angles of Complex $Co(vim)_2(DCA)_2$.

Atom	Length (Å)	Atom	Length (Å)
$Co1-N1^1$	2.094(6)	N4-C6	1.317(6)
Co1-N1	2.094(6)	$N4-C6^4$	1.317(6)
Co1-N3	2.138(5)	C2-N1	1.376(10)
$Co1-N3^2$	2.138(5)	N2-C1	1.351(9)
$Co1-N3^3$	2.138(5)	N2-C4	1.427(9)
$Co1-N3^1$	2.138(5)	N1-C1	1.310(9)
C3-C2	1.355(12)	C6-N3	1.150(7)
C3-N2	1.362(10)	C4-C5	1.295(11)
Atom	**Angle (°)**	**Atom**	**Angle (°)**
$N1-Co1-N1^1$	180.0(3)	$N3^1-Co1-N3$	180.0(3)
N1-Co1-N3	89.20(17)	C2-C3-N2	106.9(7)
$N1^1-Co1-N3^2$	90.80(17)	$C6^4-N4-C6$	116.8(6)
$N1^1-Co1-N3$	90.80(17)	C3-C2-N1	109.4(7)
$N1-Co1-N3^2$	89.20(17)	C3-N2-C4	128.7(6)
$N1-Co1-N3^3$	90.80(17)	C1-N2-C3	106.3(6)
$N1^1-Co1-N3^3$	89.20(17)	C1-N2-C4	124.9(6)
$N1-Co1-N3^1$	90.80(17)	C2-N1-Co1	126.7(5)
$N1^1-Co1-N3^1$	89.20(17)	C1-N1-Co1	128.0(5)
$N3^3-Co1-N3^2$	180.0(3)	C1-N1-C2	105.3(6)
$N3^1-Co1-N3^2$	89.9(2)	N3-C6-N4	175.9(5)
$N3-Co1-N3^2$	90.1(2)	C6-N3-Co1	160.8(4)
$N3^3-Co1-N3^1$	90.1(2)	N1-C1-N2	112.1(6)
$N3^3-Co1-N3$	89.9(2)	C5-C4-N2	124.2(7)

Noted: ^{1}-X,-Y,-Z; ^{2}-X,+Y,+Z; ^{3}+X,-Y,-Z; ^{4}1-X,+Y,+Z

Table S5 Selected bond lengths and bond angles of Complex $Cu(vim)_2(DCA)_2$.

Atom	**Length (Å)**	**Atom**	**Length (Å)**
Cu1-N4	1.999(3)	N2-C2	1.319(4)
Cu1-N4^1	1.999(3)	C1-N1	1.149(4)
Cu1-N1^1	2.002(3)	C6-N5	1.415(5)
Cu1-N1	2.002(3)	C6-C7	1.305(4)
N4-C3	1.321(4)	N5-C5	1.376(4)
N4-C4	1.392(4)	C5-C4	1.342(5)
C3-N5	1.354(4)	C2-N3	1.157(4)
N2-C1	1.310(4)		
Atom	**Angle (˚)**	**Atom**	**Angle (˚)**
N4^1-Cu1-N4	180.000(1)	C1-N2-C2	121.1(3)
N4^1-Cu1-N1^1	90.17(12)	N1-C1-N2	173.4(4)
N4-Cu1-N1^1	89.83(12)	C7-C6-N5	124.4(3)
N4^1-Cu1-N1	89.83(12)	C3-N5-C6	124.2(3)
N4-Cu1-N1	90.17(12)	C3-N5-C5	107.3(3)
N1-Cu1-N1^1	180.00(16)	C5-N5-C6	128.2(3)
C3-N4-Cu1	126.1(2)	C4-C5-N5	106.6(3)
C3-N4-C4	105.7(3)	N3-C2-N2	173.8(3)
C4-N4-Cu1	128.2(3)	C1-N1-Cu1	168.6(3)
N4-C3-N5	110.8(3)	C5-C4-N4	109.6(3)

Noted: ^{1}1-X,2-Y,1-Z

Table S6 Heat formation of complex.

Complex	ΔH_f(s, 298 K, KJ·mol^{-1})
$Mn(vim)_2(DCA)_2$	-657.3
$Fe(vim)_2(DCA)_2$	-614.0
$Co(vim)_2(DCA)_2$	-548.0
$Cu(vim)_2(DCA)_2$	-482.2

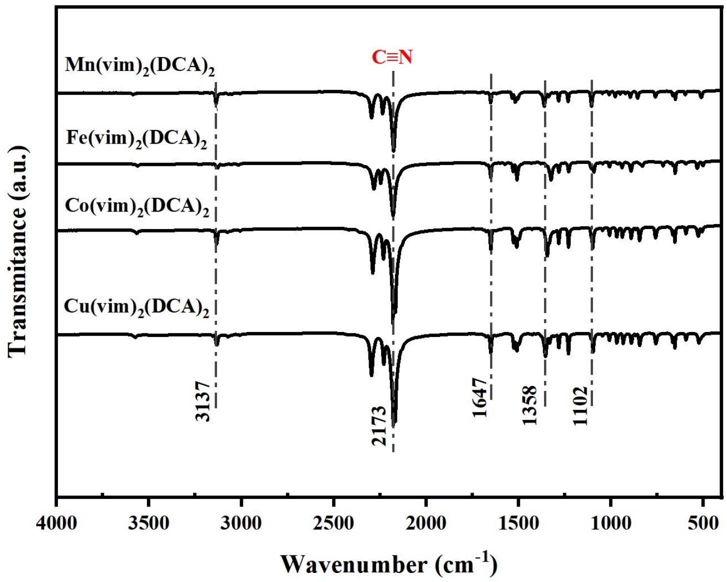

Fig. S1 FT-IR spectra of $M(vim)_2(DCA)_2$ (M = Mn, Fe, Co, Cu).

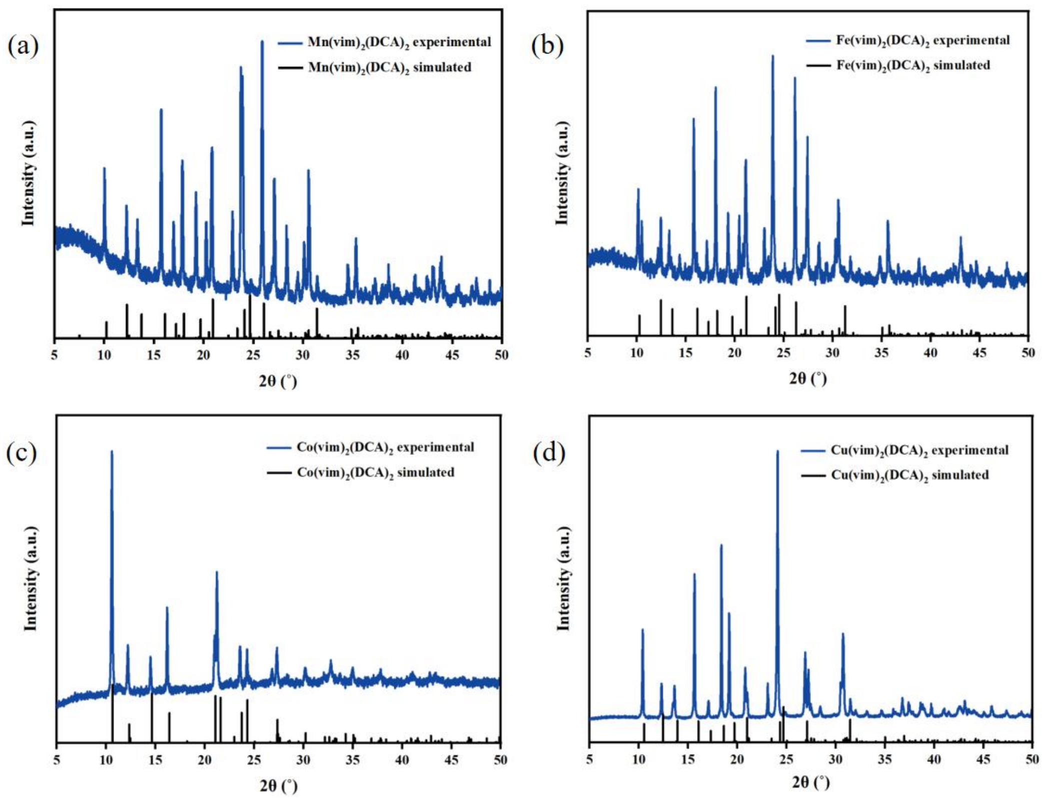

Fig. S2 PXRD patterns for (a) $Mn(vim)_2(DCA)_2$, (b) $Fe(vim)_2(DCA)_2$, (c) $Co(vim)_2(DCA)_2$ and (d) $Cu(vim)_2(DCA)_2$.

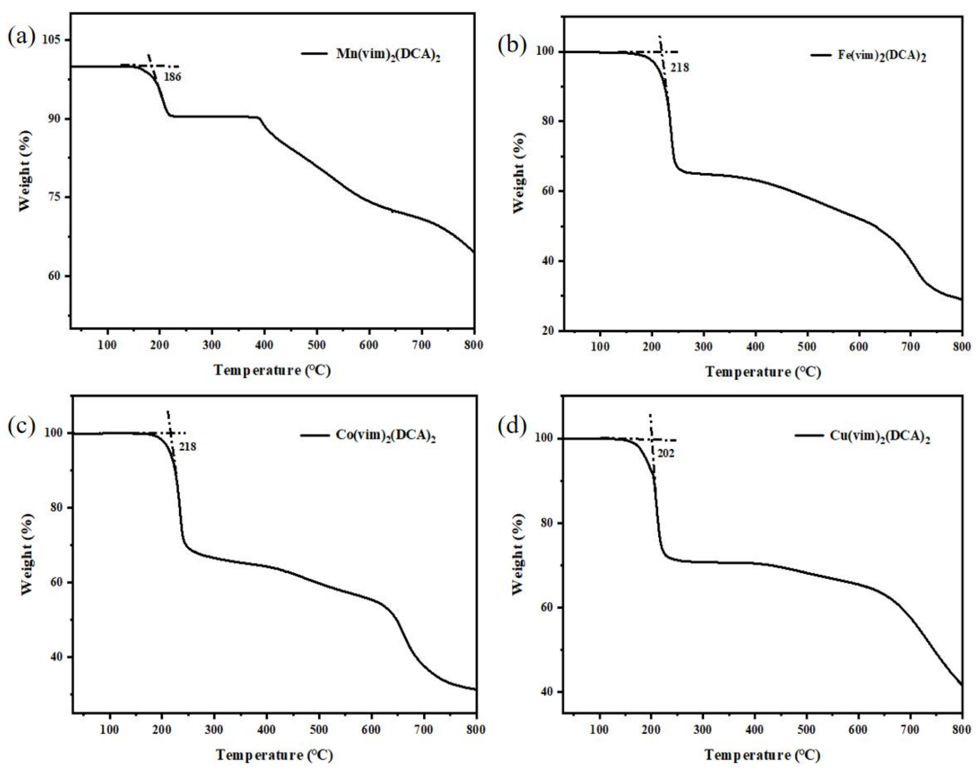

Fig. S3 TG curves of (a) $Mn(vim)_2(DCA)_2$, (b) $Fe(vim)_2(DCA)_2$, (c) $Co(vim)_2(DCA)_2$ and (d) $Cu(vim)_2(DCA)_2$.

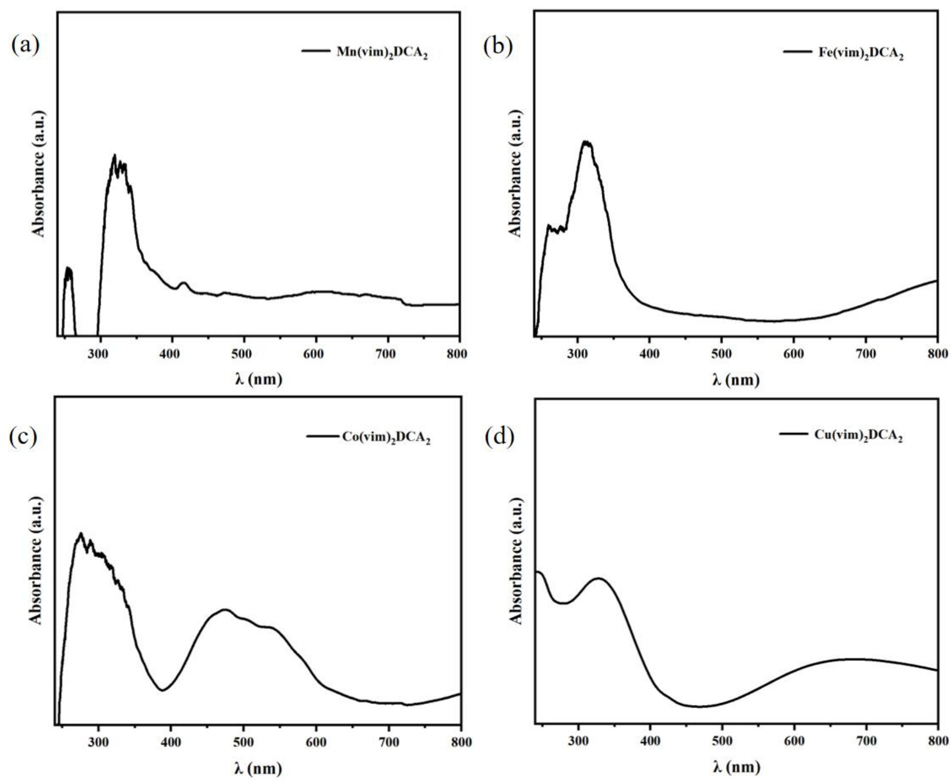

Fig. S4 UV-Vis absorption spectra of (a) $Mn(vim)_2(DCA)_2$, (b) $Fe(vim)_2(DCA)_2$, (c) $Co(vim)_2(DCA)_2$ and (d) $Cu(vim)_2(DCA)_2$.

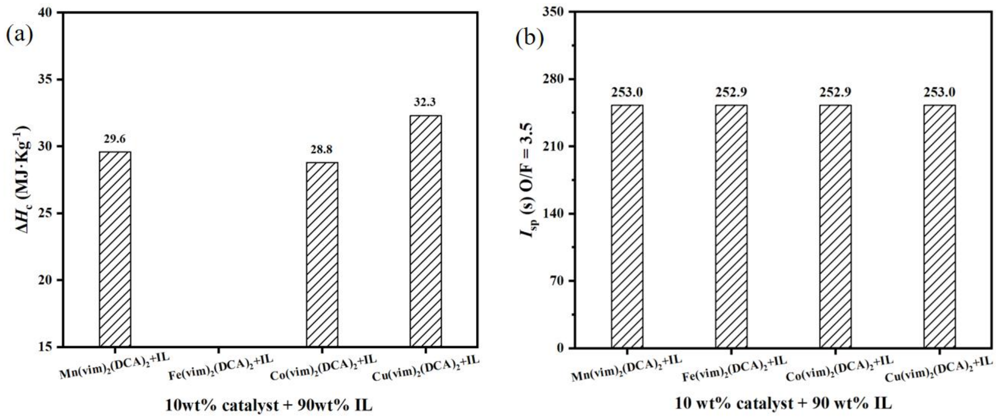

Fig. S5 (a) Enthalpy of combustion and (b) specific impulse (O/F = 3.5) of 10 wt% catalyst + 90 wt% IL.

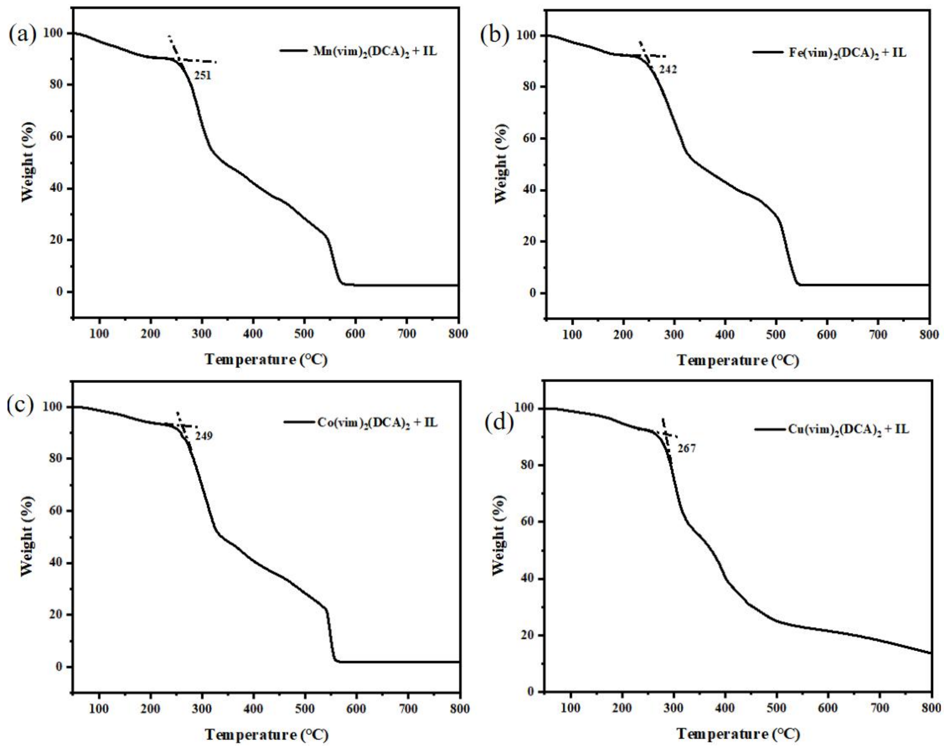

Fig. S6 TG curves of (a) 10 wt% $Mn(vim)_2(DCA)_2$ + 90 wt% [BMIM]DCA, (b) 10 wt% $Fe(vim)_2(DCA)_2$ + 90 wt% [BMIM]DCA, (c) 10 wt% $Co(vim)_2(DCA)_2$ + 90 wt% [BMIM]DCA and (d) 10 wt% $Cu(vim)_2(DCA)_2$ + 90 wt% [BMIM]DCA.

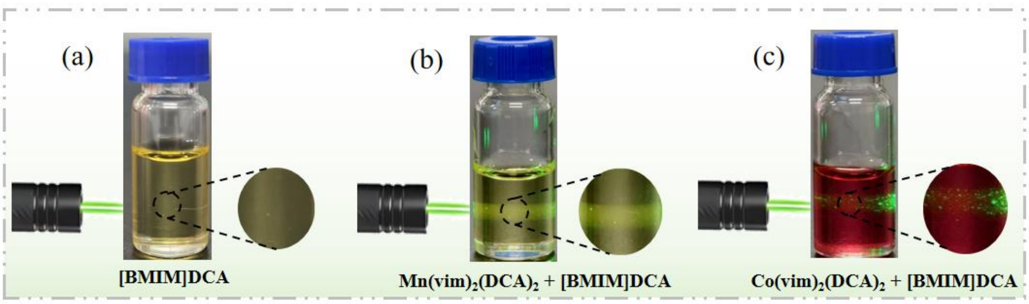

Fig. S7 Tyndall effect of (a) [BMIM]DCA, (b) $Mn(vim)_2(DCA)_2$ + [BMIM]DCA and (c) $Co(vim)_2(DCA)_2$ + [BMIM]DCA.

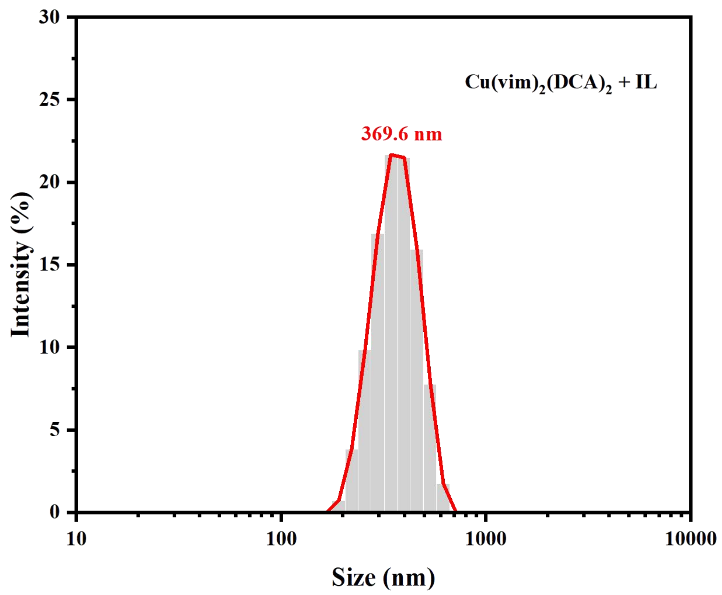

Fig. S8 Particle size distributions of $Cu(vim)_2(DCA)_2$ + [BMIM]DCA .

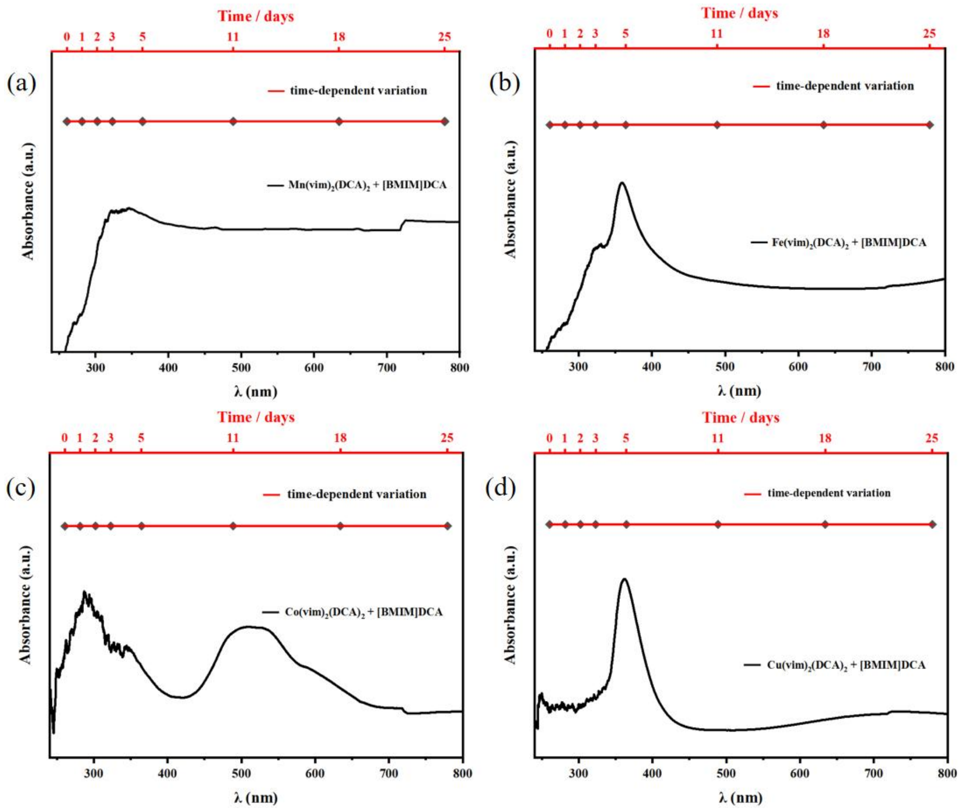

Fig. S9 UV-Vis absorption spectra of (a) $Mn(vim)_2(DCA)_2$ + [BMIM]DCA and its absorbance with time at 346 nm, (b) $Fe(vim)_2(DCA)_2$ + [BMIM]DCA and its absorbance with time at 362 nm, (c) $Co(vim)_2(DCA)_2$ + [BMIM]DCA and its absorbance with time at 288 nm, (d) $Cu(vim)_2(DCA)_2$ + [BMIM]DCA and its absorbance with time at 359 nm.

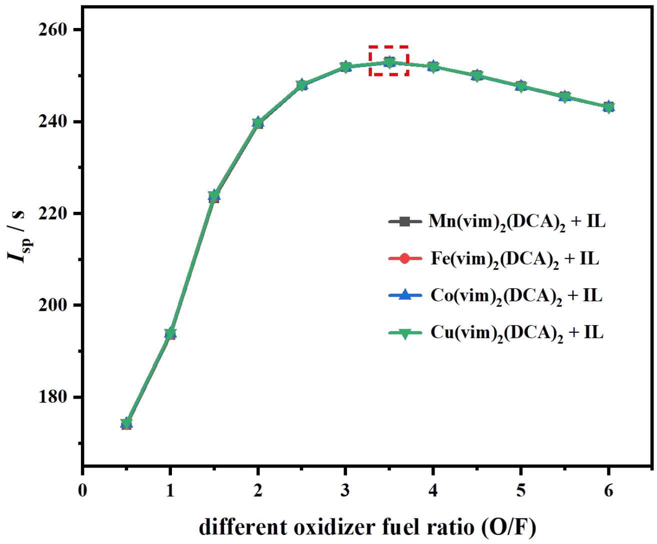

Fig. S10 Specific impulse of 10 wt% $M(vim)_2(DCA)_2$ (M = Mn, Fe, Co, Cu) + 90 wt% [BMIM]DCA mixed fuel in the O/F range of 0.5-6.

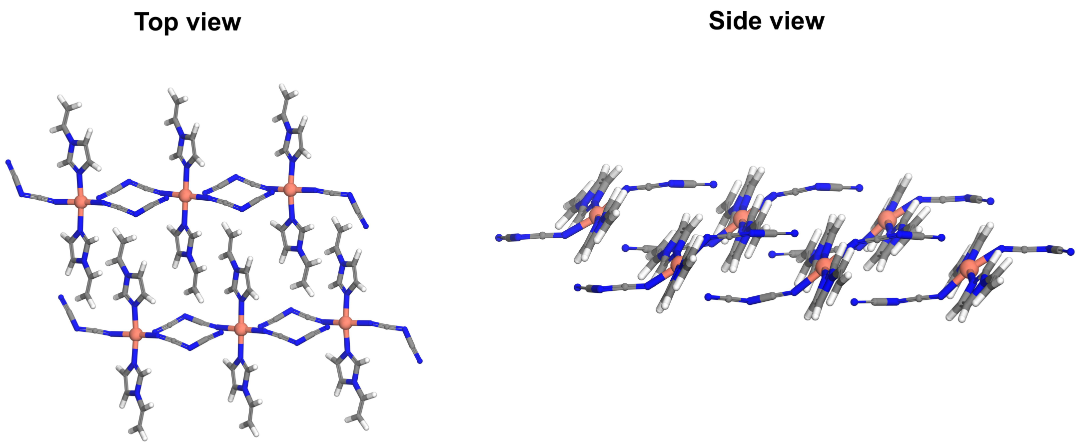

Fig. S11 DFT-optimized configuration of $Cu(vim)_2(DCA)_2$.