Electronic Supplementary Information

Pentazolate-Based Bowl-Shaped Molecular Container

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Contents

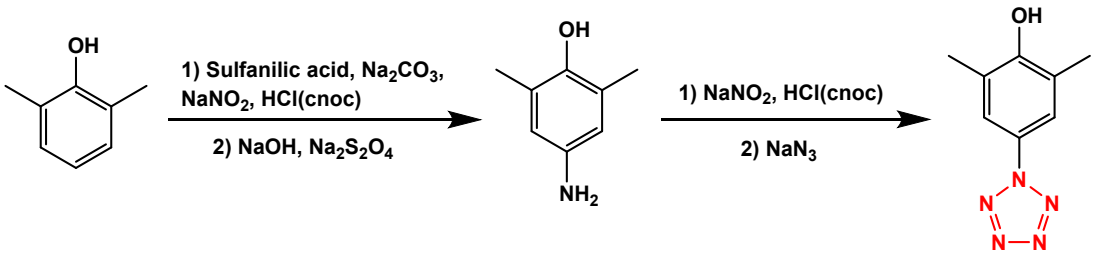
1. Experimental Section

General information: All the starting materials and solvents were of analytical grade, obtained from commercial suppliers and used without further purification.

Caution! Several compounds, like sodium azide (NaN_3) and the precursor compound aryl-pentazole, are highly energetic and more likely to explode when heated. Metal-pentazole salts are sensitive to impact and friction. Besides, NaN_3 is highly toxic. Appropriate safety precautions, like protective gloves and coats, face shield and explosion-proof baffle must be followed to ensure safety. Small-scale reactions are encouraged.

1.1 Synthesis of 3,5-dimethyl-4-hydroxyphenylpentazole

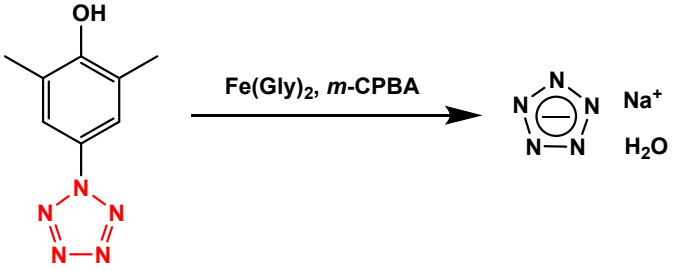
In this work, the precursor compound 3,5-dimethyl-4-hydroxyphenylpentazole was prepared on the basis of the previous study, schematic diagram shown in Scheme S1.[1]



Scheme S1. Synthesis of 3,5-dimethyl-4-hydroxyphenylpentazole.

1.2 Synthesis of $[Na(H_2O)(N_5)]\cdot 2H_2O$

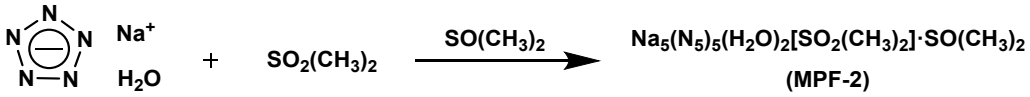
$[Na(H_2O)(N_5)]\cdot 2H_2O$ was synthesized according to the methods described in our previous report, schematic diagram shown in Scheme S2.[2]



Scheme S2. Synthesis of $[Na(H_2O)(N_5)]\cdot 2H_2O$.

1.3 Synthesis of $Na_5(N_5)_5(H_2O)_2[SO_2(CH_3)_2]\cdot SO(CH_3)_2$ (MPF-2)

$[Na(H_2O)(N_5)]\cdot 2H_2O$ (147mg, 1mmol) and $SO_2(CH_3)_2$ (MSM) (18.8mg, 0.2mmol) at a molar ratio of 5:1 was added into $SO(CH_3)_2$ (DMSO), and stirred for several minutes at room temperature until completely dissolved. After filtration, the collected filtrate was volatilized at ambient temperature, then the colourless crystal of **MPF-2** was obtained from the solution.



Scheme S3. Synthesis of **MPF-2**.

2. Thermal Properties

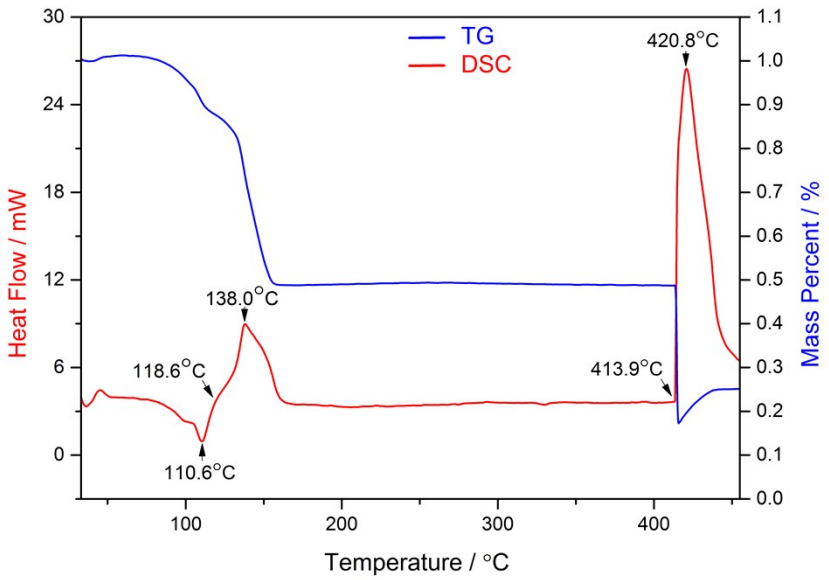


Figure S1. TG-DSC curves of **MPF-2** at rate of 10 $K\cdot min^{-1}$.

Thermal properties of **MPF-2** are evaluated at a heating rate of $10^oC\cdot min^{-1}$ under a N_2 atmosphere in the temperature ranging from 30 °C to 455 °C, and the TG/DSC curves of **MPF-2** are shown in Figure S1. TG-DSC curves indicated **MPF-2** went through three stages as the temperature increased. With the loss of weight, **MPF-2** experienced the process of first absorbing heat, then releasing heat twice. When the temperature rises, water molecules and small organic molecules escape from **MPF-2**, further causing the skeleton to collapse and more molecules to break away. Therefore, the DSC curve shows an endothermic peak (the

peak temperature is 110.6 °C), and the TG curve shows the rate of weight loss increases gradually. As the temperature rises further, the pentazole anions begin to decompose. The DSC curve shows an exothermic peak (the peak temperature is 138 °C), and the weight begins to decrease sharply in the TG curve. As the temperature continues to rise to 400 °C, there are no changes in the TG-DSC curves. Finally, a tremendous exothermic peak is observed (the exothermic peak temperature is 420.8 °C), probably due to the drastic explosion of residual nitrogen compounds.

3. Crystal Structure Data

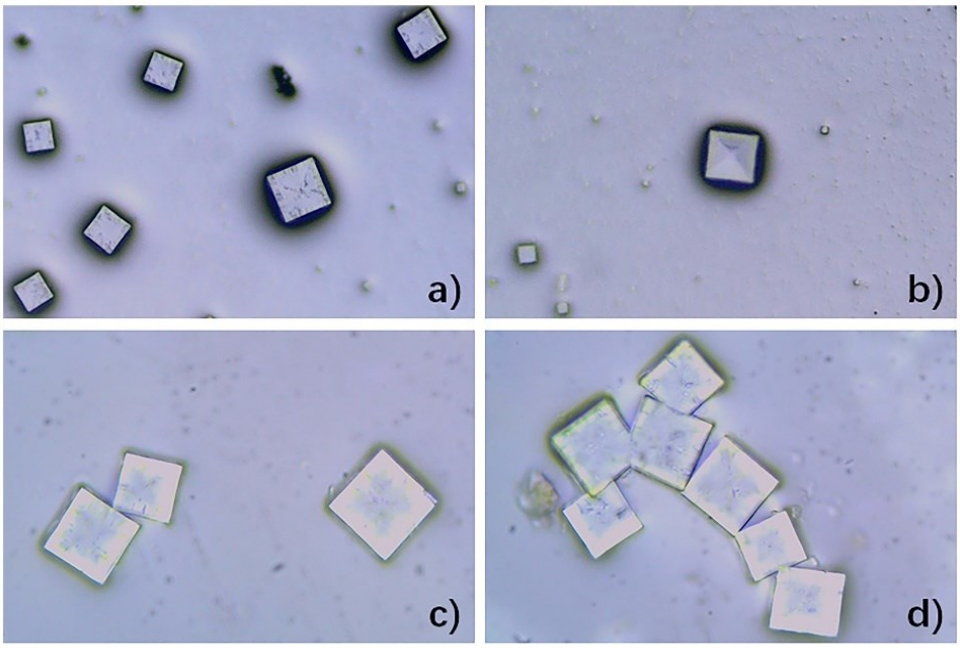


Figure S2. The crystals photographs of **MPF-2**.

a), b) were taken by low-powered microscope and c), d) were taken by high-power microscope.

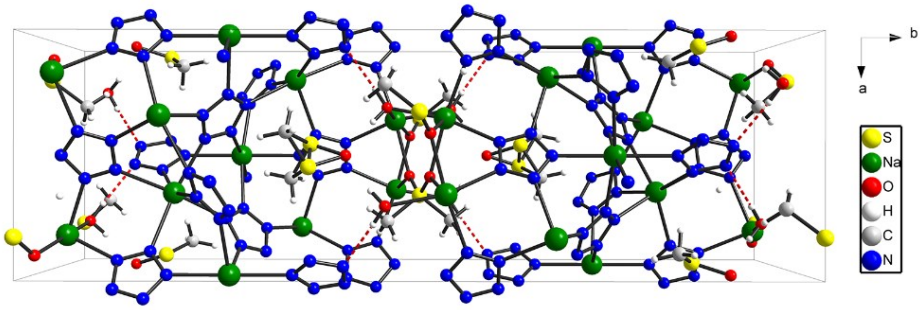


Figure S3. Unit cell view of **MPF-2** along the *c*-axis.

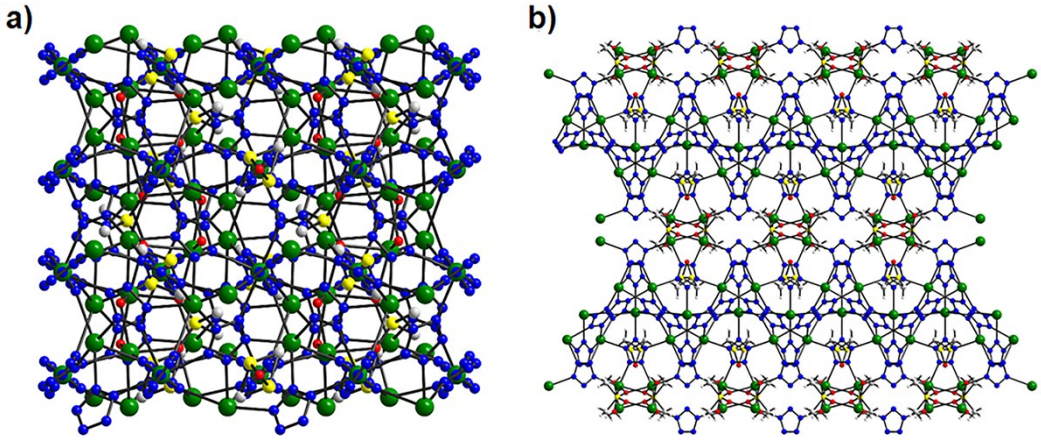


Figure S4. (a) The 3D framework of **MPF-2** along the *b*-axis. H atoms are omitted. (b) The 3D framework of **MPF-2** along the *c*-axis.

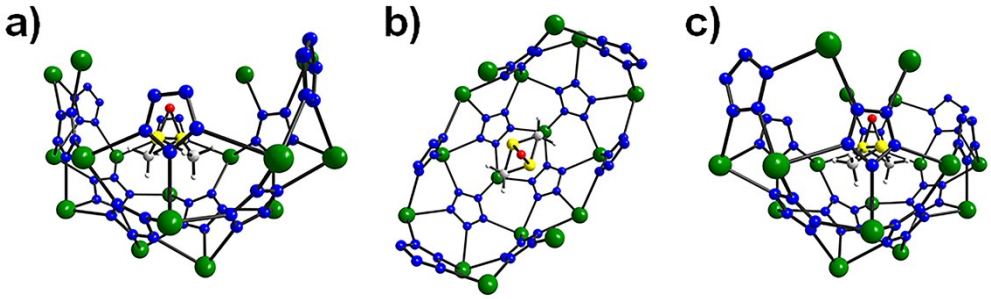


Figure S5. (a)-(c) The bowl-shaped molecular container in MPF-2 along the *a*-, *b*- and *c*-axis.

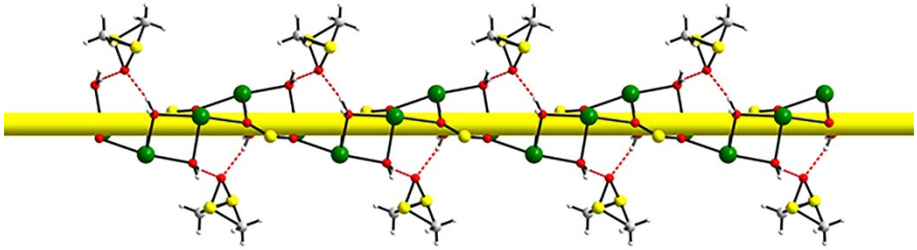


Figure S6. DMSO molecules are held in the Na-O chains by hydrogen bonds.

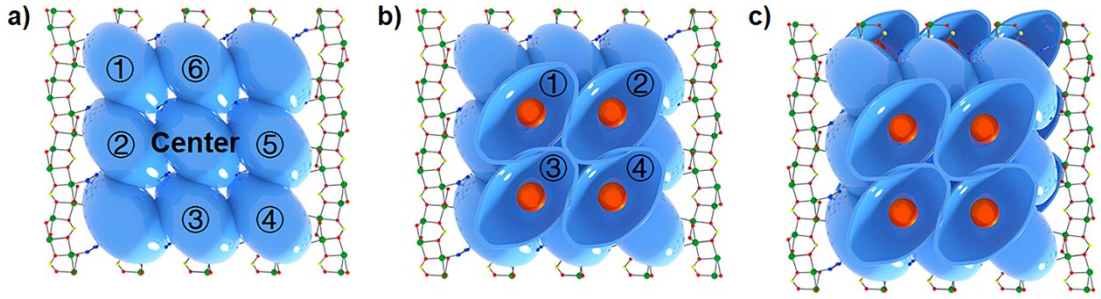


Figure S7. Schematic drawing of the spatial arrangement of the nanocages in **MPF-2**.

Single crystal X-ray diffraction (XRD) data were collected with synchrotron radiation (λ = 0.9077 Å) at the Beamline I711, MAX IV Laboratory, Lund, Sweden. Data reduction and empirical absorption correction were applied with CrysAlisPro, and the structure was solved and refined by SHELX. All non-hydrogen atoms were located from the single crystal X-ray diffraction data. Crystallographic details of the structure refinement are given in Table S1, S2 and S3. The atomic coordinates and equivalent isotropic displacement parameters can be found in the cif file.

Table S1. Crystal data and structure refinement for **MPF-2**.

Empirical formula	$Na_5(N_5)_5(H_2O)_2$ $[SO_2(CH_3)_2]\cdot SO(CH_3)_2$
Formula weight	673.49
Temperature/K	296.15
Crystal system	Orthorhombic
Space group	$C222_1$
a/Å	9.3283(9)
b/Å	30.151(3)
c/Å	9.6156(9)
α/°	90.00
β/°	90.00
γ/°	90.00
Volume/Å^3	2704.4(5)
Z	4
ρ_{calc}g/cm^3	1.654
μ/mm^{-1}	0.348
F(000)	1368.0
Crystal size/mm^3	0.24 × 0.16 × 0.15
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.7 to 52.74
Index ranges	-11≤h≤11, -37≤k≤37, -11≤l≤11
Reflections collected	6989
Independent reflections	2605 [R_{int} = 0.0505, R_{sigma} = 0.0661]
Data/restraints/parameters	2605/0/199
Goodness-of-fit on F^2	1.05
Final R indexes [I>=2σ (I)]	R_1 = 0.0407, wR_2 = 0.0874
Final R indexes [all data]	R_1 = 0.0502, wR_2 = 0.0940
Largest diff. peak/hole / e Å^{-3}	0.43/-0.28
Flack parameter	0.00(14)
CCDC	**2008732**

Table S2. Bond lengths for **MPF-2**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	O2	1.449(2)	N2	N3	1.321(4)
S1	O2[1]	1.449(2)	N3	Na3[10]	2.570(3)
S1	C3[1]	1.739(3)	N3	N3[9]	1.302(5)
S1	C3	1.739(3)	N4	N4[2]	1.309(6)
Na1	Na1[2]	3.640(2)	N4	N5	1.320(3)
Na1	Na1[1]	3.388(2)	N5	Na3[10]	2.567(3)
Na1	O1	2.372(3)	N5	N6	1.315(3)
Na1	O1[1]	2.396(2)	N6	N5[2]	1.315(3)
Na1	O2	2.423(3)	N7	N8[2]	1.324(3)
Na1	O2[2]	2.462(3)	N7	N8	1.324(3)
Na1	N2	2.463(3)	N8	Na3[4]	2.771(3)
Na1	N4	2.439(3)	N8	N9	1.313(4)
Na2	N6	2.464(4)	N9	N9[2]	1.316(6)
Na2	N7	2.459(4)	N10	N11	1.331(4)
Na2	N10	2.458(3)	N10	N14	1.305(4)
Na2	N10[2]	2.458(3)	N11	Na3[3]	2.497(3)
Na2	N12[3]	2.451(3)	N11	N12	1.331(4)
Na2	N12[4]	2.451(3)	N12	Na2[6]	2.451(3)
Na3	N3[5]	2.570(3)	N12	N13	1.319(4)
Na3	N5[5]	2.567(3)	N13	N14	1.337(4)
Na3	N8[6]	2.771(3)	N14	Na3[8]	2.543(3)
Na3	N11[7]	2.497(3)	S2	S2[11]	1.412(4)
Na3	N13	2.502(3)	S2	C4[11]	1.839(6)
Na3	N14[8]	2.543(3)	S2	C4	1.656(6)
O1	Na1[1]	2.396(2)	S2	O0AA	1.574(4)
O2	Na1[2]	2.462(3)	C4	S2[11]	1.839(6)
N1	N2[9]	1.319(3)	O0AA	S2[11]	1.574(4)
N1	N2	1.319(3)			

Symmetry code: [1]+X,-1-Y,-1-Z; [2]-1-X,+Y,-3/2-Z; [3]-1/2+X,-3/2-Y,-1-Z; [4]-1/2-X,-3/2-Y,-1/2+Z; [5]1+X,+Y,+Z; [6]-1/2-X,-3/2-Y,1/2+Z; [7]1/2+X,-3/2-Y,-1-Z; [8]-X,+Y,-3/2-Z; [9]-2-X,+Y,-3/2-Z; [10]-1+X,+Y,+Z; [11]-1-X,+Y,-1/2-Z

Table S3. Bond angles for **MPF-2**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O2	S1	O2[1]	115.4(2)	N13	Na3	N3[5]	95.63(10)
O2	S1	C3	107.88(16)	N13	Na3	N5[5]	161.23(10)
O2	S1	C3[1]	109.53(16)	N13	Na3	N8[6]	80.29(9)
O2[1]	S1	C3[1]	107.88(16)	N13	Na3	N14[8]	80.76(10)
O2[1]	S1	C3	109.53(16)	N14[8]	Na3	N3[5]	91.67(10)
C3[1]	S1	C3	106.2(3)	N14[8]	Na3	N5[5]	80.51(10)
Na1[1]	Na1	Na1[2]	117.45(2)	N14[8]	Na3	N8[6]	161.04(10)
O1[1]	Na1	Na1[2]	104.04(7)	Na1	O1	Na1[1]	90.56(9)
O1[1]	Na1	Na1[1]	44.43(7)	S1	O2	Na1	130.83(14)
O1	Na1	Na1[1]	45.01(6)	S1	O2	Na1[2]	132.48(14)
O1	Na1	Na1[2]	135.36(9)	Na1	O2	Na1[2]	96.33(9)
O1	Na1	O1[1]	85.66(10)	N2[9]	N1	N2	107.2(3)
O1[1]	Na1	O2[2]	87.98(9)	N1	N2	Na1	121.48(19)
O1[1]	Na1	O2	85.45(9)	N1	N2	N3	108.3(3)
O1	Na1	O2	97.13(9)	N3	N2	Na1	126.9(2)
O1	Na1	O2[2]	171.47(9)	N2	N3	Na3[10]	126.8(2)
O1	Na1	N2	89.73(10)	N3[9]	N3	Na3[10]	123.27(10)
O1[1]	Na1	N2	101.31(10)	N3[9]	N3	N2	108.11(18)
O1[1]	Na1	N4	165.37(10)	N4[2]	N4	Na1	118.54(7)
O1	Na1	N4	103.33(10)	N4[2]	N4	N5	108.26(17)
O2	Na1	Na1[1]	77.55(6)	N5	N4	Na1	133.2(2)
O2	Na1	Na1[2]	42.24(6)	N4	N5	Na3[10]	125.0(2)
O2[2]	Na1	Na1[1]	126.99(8)	N6	N5	Na3[10]	124.80(18)
O2[2]	Na1	Na1[2]	41.43(6)	N6	N5	N4	107.4(3)
O2	Na1	O2[2]	76.67(9)	N5	N6	Na2	125.68(16)
O2	Na1	N2	170.74(10)	N5[2]	N6	Na2	125.68(16)
O2[2]	Na1	N2	97.09(10)	N5	N6	N5[2]	108.6(3)
O2	Na1	N4	82.01(9)	N8	N7	Na2	125.66(18)
N2	Na1	Na1[1]	111.70(7)	N8[2]	N7	Na2	125.66(18)
N2	Na1	Na1[2]	129.01(9)	N8[2]	N7	N8	108.7(4)
N4	Na1	Na1[1]	138.19(9)	N7	N8	Na3[4]	121.74(19)
N4	Na1	Na1[2]	61.45(7)	N9	N8	Na3[4]	128.6(2)
N4	Na1	O2[2]	81.82(9)	N9	N8	N7	107.1(3)
N4	Na1	N2	90.39(10)	N8	N9	N9[2]	108.55(18)
N7	Na2	N6	180.000(1)	N11	N10	Na2	124.3(2)
N10	Na2	N6	85.14(7)	N14	N10	Na2	123.7(2)

N10^{2}	Na2	N6	85.14(7)	N14	N10	N11	108.4(3)
N10	Na2	N7	94.86(7)	N10	N11	Na3^{3}	126.40(19)
N10^{2}	Na2	N7	94.86(7)	N12	N11	Na3^{3}	126.33(19)
N10^{2}	Na2	N10	170.28(14)	N12	N11	N10	107.2(2)
N12^{3}	Na2	N6	92.87(7)	N11	N12	Na2^{6}	125.5(2)
N12^{4}	Na2	N6	92.87(7)	N13	N12	Na2^{6}	124.5(2)
N12^{3}	Na2	N7	87.13(7)	N13	N12	N11	108.7(3)
N12^{4}	Na2	N7	87.13(7)	N12	N13	Na3	125.6(2)
N12^{4}	Na2	N10^{2}	90.00(9)	N12	N13	N14	107.1(2)
N12^{3}	Na2	N10	90.00(9)	N14	N13	Na3	125.4(2)
N12^{3}	Na2	N10^{2}	90.48(10)	N10	N14	Na3^{8}	125.8(2)
N12^{4}	Na2	N10	90.48(10)	N10	N14	N13	108.6(2)
N12^{4}	Na2	N12^{3}	174.26(14)	N13	N14	Na3^{8}	125.03(19)
N3^{5}	Na3	N8^{6}	89.55(9)	S2^{11}	S2	C4^{11}	59.5(2)
N5^{5}	Na3	N3^{5}	86.10(9)	S2^{11}	S2	C4	73.2(2)
N5^{5}	Na3	N8^{6}	118.45(10)	S2^{11}	S2	O0AA	63.35(10)
N11^{7}	Na3	N3^{5}	175.73(10)	C4	S2	C4^{11}	103.7(4)
N11^{7}	Na3	N5^{5}	90.08(9)	O0AA	S2	C4^{11}	99.8(2)
N11^{7}	Na3	N8^{6}	90.59(9)	O0AA	S2	C4	108.2(2)
N11^{7}	Na3	N13	88.60(9)	S2	C4	S2^{11}	47.30(19)
N11^{7}	Na3	N14^{8}	89.57(9)	S2^{11}	O0AA	S2	53.30(19)

4. Spectroscopic Analyses

The IR absorption peak of *cyclo*-N_5^- anion is at 1226 cm^{-1} (Figure S8).

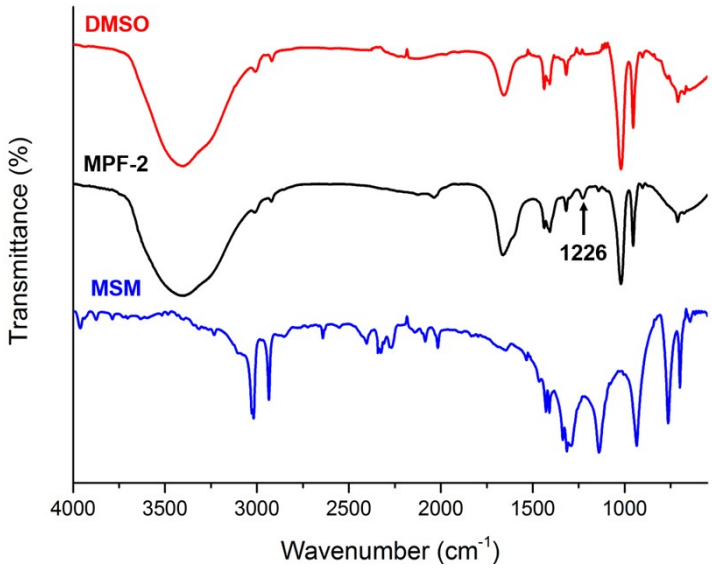


Figure S8. IR spectra of DMSO, **MPF-2**, MSM.

The characteristic peak of m/z=101.0031 and m/z=70.0178 are $[DMSO+Na]^+$ and *cyclo*-N_5^- anion, respectively (Figure S9). The responsive peaks of MSM cannot be effectively identified.

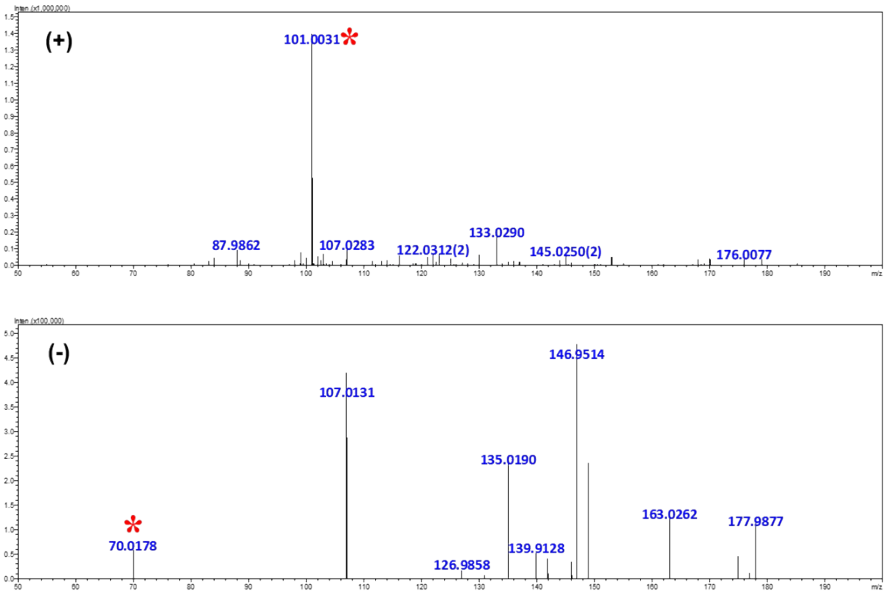


Figure S9. Mass spectrometry of **MPF-2**.

The characteristic UV-vis absorption of *cyclo*-N_5^- anion is approximately at 380 nm (Figure S10).

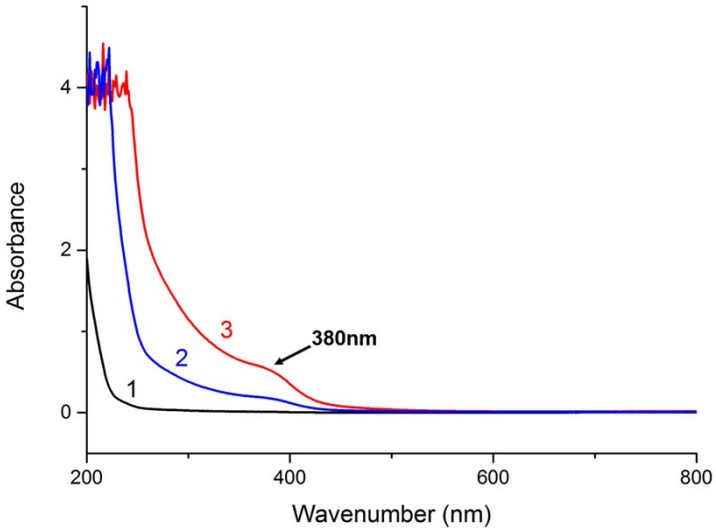


Figure S10. UV-visible spectra of **MPF-2**.

5. References

[1] C. Zhang, C. Sun, B. Hu and M. Lu, *J. Energ. Mater.*, 2016, **34**, 103.
[2] W. Zhang, K. Wang, J. Li, Z. Lin, S. Song, S. Huang, Y. Liu, F. Nie and Q. Zhang, *Angew. Chem. Int. Ed.*, 2018, **57**, 2592.