Supporting Information

Novel Metal–Organic Frameworks Assembled from the Combination of Polynitro-pyrazole and 5-Nitroamine-1,2,4-oxadiazol: Synthesis, Structure and Thermal Properties

Feng Yang, Yuangang Xu, Qiuhan Lin, Pengcheng Wang, Ming Lu*

School of Chemistry and Chemical Engineering, Nanjing University of Science and Technology, Xiaolingwei 200, Nanjing 210094, P. R. China.

Table of Contents

1.Experimental Section

General methods

All reagents used in this paper were purchased from energy chemical in analytical grade and without further purification. ^{1}H and ^{13}C spectra were recorded using a 500 MHz (AVANCE III500MHz) nuclear magnetic spectrometer operating at 500 MHz and 126 MHz, respectively, and the chemical shifts in ^{1}H and ^{13}C NMR spectra are reported relative to d_6-DMSO. The phase transition temperature and decomposition (onset) point were obtained by a different scanning calorimeter (Mettler Toledo DSC823e) at a heating rate of 5 °C min^{-1} in a closed Al crucibles with a nitrogen flow of 50 ml min^{-1}. IR spectra were recorded using KBr pellets for solids on a Thermo Nicolet iS10 spectrometer. Density was measured at 25 °C by using a gas pycnometer. The heats of formation were calculated by using Gaussian 09[1], and the detonation velocities (D) and pressures (P) were calculated with EXPLO5 v6.01[2]. Impact and friction sensitivity measurements were performed with a BAM Fallhammer and a BAM friction tester.

2.X-ray crystallographic study

Crystals **2**, **4** and **5** were performed on a Bruker Smart ApexII diffractometer at 296K. Integration and scaling of intensity data were accomplished using the SAINT program. Corrections for Lorentz and polarization effects and forabsorption (ψ scan) were applied. The structure was solved by directmethods using SHELXS-2014 and refined by full-matrix least-squares calculation on F^2 with SHELXL-2014. All non-hydrogen atoms were refined anisotropically. All hydrogen were placed in calculated positions and were assigned fixed isotropic thermal parameters at 1.2 times. Data were corrected for the effects of absorption using SADABS Relevant crystal data and refinement results are summarized in TableS1.

Table S1. Crystallographic data for **2** , **4** and **5**.

Chemical formula	$C_6H_5N_9O_7\cdot H_2O$	$(C_6H_4KN_9O_7\cdot H_2O)_n$	$(C_6H_2K_2N_{10}O_9\cdot H_2O)_n$
Formula mass	333.21	371.30	454.39
Crystal system	Monoclinic	Triclinic	Monoclinic
a/Å	7.8296(8)	7.1587(6)	10.3408(7)
b/Å	22.796(3)	8.4966(7)	18.3261(13)

c/Å	7.4593(7)	11.1631(10)	8.4021(5)
α/°	90	97.197(3)	90
β/°	108.117(3)	99.588(3)	101.452(2)
γ/°	90	90.474(3)	90
Volume/Å3	1265.4(2)	663.94(10)	1560.55(18)
Temperature/K	296(2)	296(2)	296(2)
Space group	$P2_1/c$	P-1	$P2_1/c$
Z	4	2	4
Radiation type	Mo-Ka	Mo-Ka	Mo-Ka
μ/mm^{-1}	0.161	0.470	0.690
Densitycalcd/g cm^{-3}	1.749	1.857	1.934
F(000)	680	376	912
2Θ range for data collection/°	2.737 to 27.465	2.417 to 27.522	2.223 to 27.580
Index ranges	-9/10; -25/29; -8/9	-9/9; -11/10; -14/14	-13/13; -23/20; -10/9
Reflections collected	12417	10026	15559
Independent reflections	2867	3035	3583
R_{int}	0.0749	0.0339	0.0365
Data/restraints/parameters	2867/0/246	3035/3/223	3583/0/253
R1 / wR2 [all data]	0.01695/ 0.1960	0.0778/0.1327	0.0498/0.0845
R1 / wR2 [I > 2σ(I)]	0.0689/ 0.1590	0.0527/0.1199	0.0350/0.0788
Goodness-of-fit on F^2	1.030	1.026	1.022
CCDC number	2089156	2045198	2005558

Table S2. Hydrogen bonds for compound **2** [Å and °].

D-H···A	D-H(Å)	H···A(Å)	D···A(Å)	D-H···A(°)
C(4)-H(4B)...N(5)#1	0.97	2.60	3.405(5)	140.5
N(4)-H(4)...O(8)	0.86	2.07	2.923(4)	172.5
N(9)-H(9A)...N(6)#2	0.86	2.70	3.403(5)	140.2

N(9)-H(9A)...O(6)#2	0.86	2.46	3.072(5)	128.5
N(9)-H(9A)...O(7)#2	0.86	2.34	3.117(5)	151.1
N(9)-H(9B)...O(4A^a)	0.86	2.39	2.895(14)	118.3
N(9)-H(9B)...O(4B^b)	0.86	2.25	2.76(2)	118.3
N(9)-H(9B)...O(1A^a)#3	0.86	2.41	3.188(18)	150.8
N(9)-H(9B)...O(1B^b)#3	0.86	2.66	3.27(2)	129.4
N(9)-H(9B)...O(1B^b)#4	0.86	2.64	3.340(14)	138.9
O(8)-H(8A)...O(7)#1	0.85	2.07	2.818(4)	145.7
O(8)-H(8B)...O(4A^a)#5	0.85	2.35	3.105(14)	148.0
O(8)-H(8B)...O(4B^b)#5	0.85	2.42	3.08(2)	134.4

Symmetry transformations used to generate equivalent atoms:

#1 x,y,z-1 #2 x-1,y,z-1 #3 x-1,y,z #4 x-1,-y+1/2,z-1/2

#5 x+1,-y+1/2,z+1/2

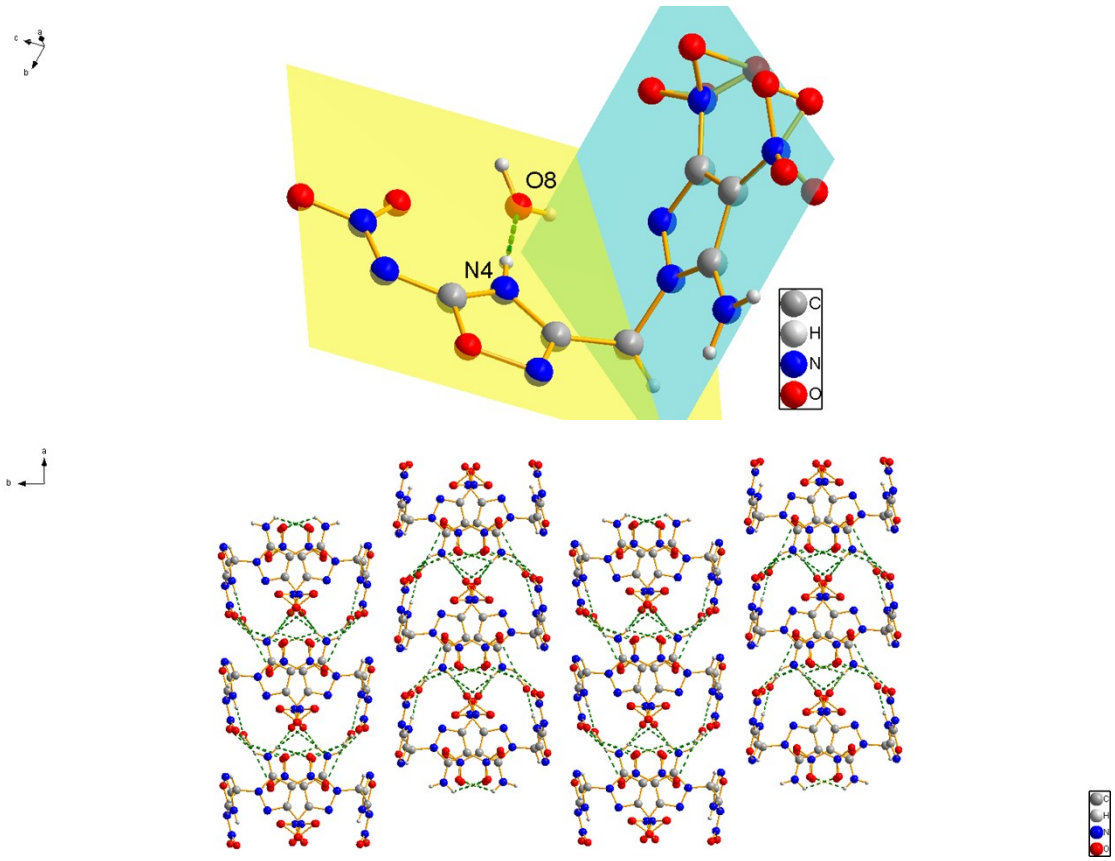

Fig. S1. Molecular structure and packing diagram of **2** (The green dotted line represents the hydrogen bond).

Table S3. Bond lengths [Å] and angles [°] for compound **2**.

Bond length		Bond angle	
C(1)-N(2)	1.305(5)	N(2)-C(1)-C(2)	113.4(3)
C(1)-C(2)	1.374(5)	N(2)-C(1)-N(7)	117.8(4)
C(1)-N(7)	1.452(6)	C(2)-C(1)-N(7)	128.8(4)
C(2)-C(3)	1.393(5)	C(1)-C(2)-C(3)	104.7(3)
C(2)-N(8)	1.397(6)	C(1)-C(2)-N(8)	130.2(4)
C(3)-N(9)	1.325(5)	C(3)-C(2)-N(8)	125.1(4)
C(3)-N(1)	1.350(5)	N(9)-C(3)-N(1)	123.7(4)
C(4)-N(1)	1.462(4)	N(9)-C(3)-C(2)	131.2(4)
C(4)-C(5)	1.491(5)	N(1)-C(3)-C(2)	105.1(3)
C(4)-H(4A)	0.9700	N(1)-C(4)-C(5)	110.1(3)
C(4)-H(4B)	0.9700	N(1)-C(4)-H(4A)	109.6
C(5)-N(3)	1.293(4)	C(5)-C(4)-H(4A)	109.6
C(5)-N(4)	1.363(4)	N(1)-C(4)-H(4B)	109.6
C(6)-N(4)	1.301(4)	C(5)-C(4)-H(4B)	109.6
C(6)-O(5)	1.347(4)	H(4A)-C(4)-H(4B)	108.1
C(6)-N(5)	1.351(4)	N(3)-C(5)-N(4)	115.2(3)
N(1)-N(2)	1.354(4)	N(3)-C(5)-C(4)	121.8(3)
N(3)-O(5)	1.415(4)	N(4)-C(5)-C(4)	123.0(3)
N(4)-H(4)	0.8600	N(4)-C(6)-O(5)	111.7(3)
N(5)-N(6)	1.319(4)	N(4)-C(6)-N(5)	137.6(3)
N(6)-O(6)	1.235(4)	O(5)-C(6)-N(5)	110.7(3)
N(6)-O(7)	1.254(4)	C(3)-N(1)-N(2)	112.8(3)
N(8)-O(3A)	1.174(12)	C(3)-N(1)-C(4)	127.3(3)
N(8)-O(4A)	1.215(14)	N(2)-N(1)-C(4)	119.2(3)
N(8)-O(3B)	1.26(2)	C(1)-N(2)-N(1)	103.9(3)
N(8)-O(4B)	1.29(3)	C(5)-N(3)-O(5)	102.7(3)
N(9)-H(9A)	0.8600	C(6)-N(4)-C(5)	103.5(3)
N(9)-H(9B)	0.8600	C(6)-N(4)-H(4)	128.3
O(8)-H(8A)	0.8500	C(5)-N(4)-H(4)	128.3
O(8)-H(8B)	0.8498	N(6)-N(5)-C(6)	116.2(3)
N(7)-O(1A)	1.086(13)	O(6)-N(6)-O(7)	118.8(3)
N(7)-O(2B)	1.156(9)	O(6)-N(6)-N(5)	125.1(3)
N(7)-O(2A)	1.279(10)	O(7)-N(6)-N(5)	116.0(3)
N(7)-O(1B)	1.333(17)	O(3A)-N(8)-O(4A)	118.9(9)
		O(3B)-N(8)-O(4B)	133.4(18)
		O(3A)-N(8)-C(2)	120.6(7)

	O(4A)-N(8)-C(2)	120.2(7)
	O(3B)-N(8)-C(2)	113.2(12)
	O(4B)-N(8)-C(2)	113.1(11)
	C(3)-N(9)-H(9A)	120.0
	C(3)-N(9)-H(9B)	120.0
	H(9A)-N(9)-H(9B)	120.0
	C(6)-O(5)-N(3)	106.9(2)
	H(8A)-O(8)-H(8B)	104.5
	O(1A)-N(7)-O(2A)	124.1(10)
	O(2B)-N(7)-O(1B)	117.2(9)
	O(1A)-N(7)-C(1)	121.8(11)
	O(2B)-N(7)-C(1)	121.0(7)
	O(2A)-N(7)-C(1)	113.6(6)
	O(1B)-N(7)-C(1)	114.9(7)

Table S4. Hydrogen bonds for compound **4** [Å and °].

D-H···A	D-H(Å)	H···A(Å)	D···A(Å)	D-H···A(°)
C(1)-H(1B)...O(6)#5	0.97	2.60	3.297(4)	128.6
N(9)-H(9A)...N(1)#6	0.86	2.16	2.965(3)	154.7
N(9)-H(9B)...O(7)	0.86	2.22	2.751(3)	120.1
N(9)-H(9B)...O(8)#7	0.86	2.28	3.047(4)	149.0
O(8)-H(8A)...O(3)#1	0.853(19)	2.28(3)	3.027(4)	146(5)
O(8)-H(8B)...O(2)#8	0.850(19)	2.62(3)	3.353(4)	145(4)
O(8)-H(8B)...O(3)#8	0.850(19)	2.19(3)	3.009(3)	161(4)

Symmetry transformations used to generate equivalent atoms:

#1 x+1,y,z #2 -x+1,-y+1,-z #3 -x+2,-y,-z

#4 x-1,y,z #5 x,y-1,z #6 -x+1,-y,-z+1 #7 -x+2,-y+1,-z+1
#8 -x+2,-y+1,-z

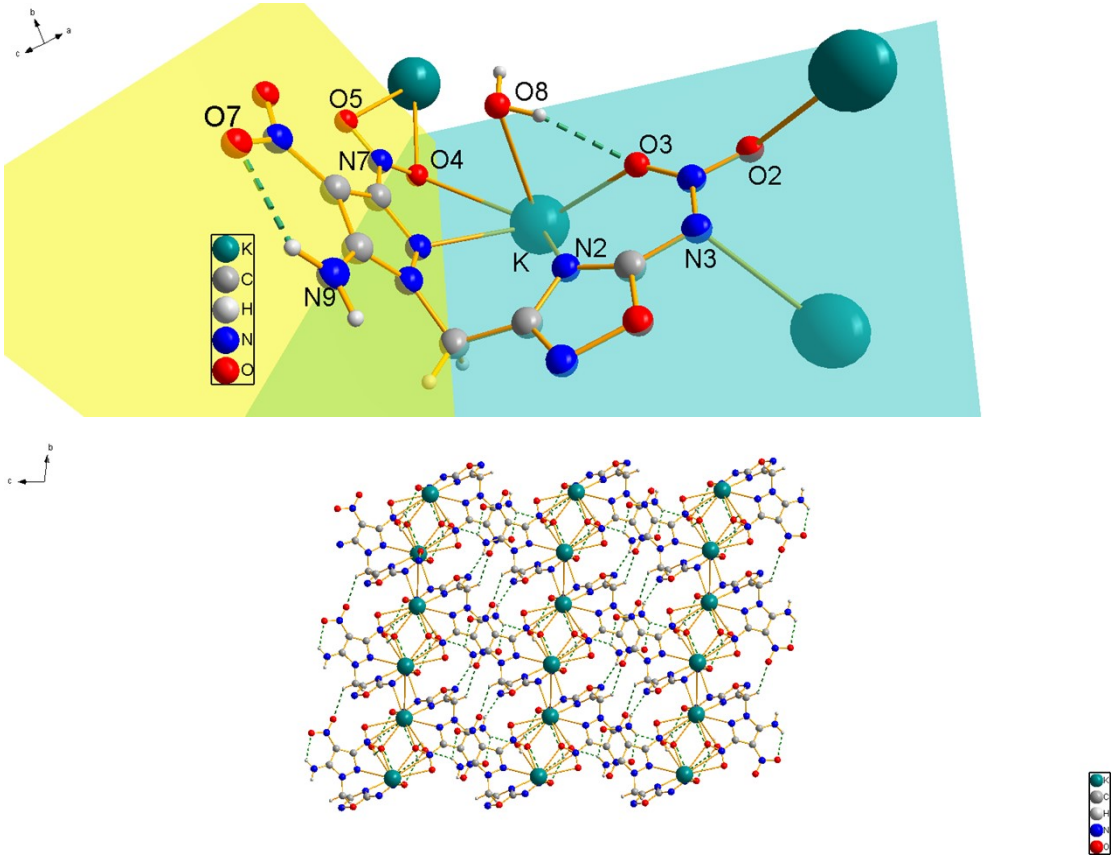

Fig. S2. Molecular structure and packing diagram of **4** (The green dotted line represents the hydrogen bond).

Table S5. Bond lengths [Å] and angles [°] for compound **4.**

Bond length		Bond angle	
K(1)-O(2)	2.694(3)	O(2)-K(1)-O(3)#1	156.20(8)
K(1)-O(3)#1	2.760(2)	O(2)-K(1)-N(2)#1	138.26(8)
K(1)-N(2)#1	2.831(2)	O(3)#1-K(1)-N(2)#1	57.44(7)
K(1)-O(4)#2	2.899(3)	O(2)-K(1)-O(4)#2	78.62(10)
K(1)-N(6)#1	2.908(2)	O(3)#1-K(1)-O(4)#2	92.79(9)
K(1)-N(3)#3	2.942(3)	N(2)#1-K(1)-O(4)#2	141.52(8)
K(1)-O(4)#1	3.046(3)	O(2)-K(1)-N(6)#1	92.18(7)
K(1)-O(5)#2	3.084(3)	O(3)#1-K(1)-N(6)#1	111.62(7)
K(1)-O(8)	3.302(3)	N(2)#1-K(1)-N(6)#1	67.71(6)
K(1)-N(7)#2	3.375(2)	O(4)#2-K(1)-N(6)#1	108.81(8)
K(1)-K(1)#3	4.5323(15)	O(2)-K(1)-N(3)#3	92.08(8)
C(1)-N(5)	1.457(3)	O(3)#1-K(1)-N(3)#3	74.43(7)
C(1)-C(2)	1.485(4)	N(2)#1-K(1)-N(3)#3	74.12(7)

C(1)-H(1A)	0.9700	O(4)#2-K(1)-N(3)#3	124.53(9)
C(1)-H(1B)	0.9700	N(6)#1-K(1)-N(3)#3	126.25(8)
C(2)-N(1)	1.294(3)	O(2)-K(1)-O(4)#1	69.02(8)
C(2)-N(2)	1.361(4)	O(3)#1-K(1)-O(4)#1	125.55(9)
C(3)-N(2)	1.307(3)	N(2)#1-K(1)-O(4)#1	115.39(7)
C(3)-O(1)	1.349(3)	O(4)#2-K(1)-O(4)#1	59.83(13)
C(3)-N(3)	1.358(4)	N(6)#1-K(1)-O(4)#1	51.40(7)
C(4)-N(6)	1.304(3)	N(3)#3-K(1)-O(4)#1	160.01(9)
C(4)-C(5)	1.408(4)	O(2)-K(1)-O(5)#2	65.73(12)
C(4)-N(7)	1.451(3)	O(3)#1-K(1)-O(5)#2	93.40(11)
C(5)-N(8)	1.406(3)	N(2)#1-K(1)-O(5)#2	147.99(10)
C(5)-C(6)	1.409(3)	O(4)#2-K(1)-O(5)#2	40.01(8)
C(6)-N(9)	1.323(3)	N(6)#1-K(1)-O(5)#2	142.58(8)
C(6)-N(5)	1.350(3)	N(3)#3-K(1)-O(5)#2	86.18(8)
N(1)-O(1)	1.412(4)	O(4)#1-K(1)-O(5)#2	91.56(8)
N(3)-N(4)	1.323(4)	O(2)-K(1)-O(8)	137.80(8)
N(4)-O(3)	1.240(3)	O(3)#1-K(1)-O(8)	59.10(7)
N(4)-O(2)	1.248(3)	N(2)#1-K(1)-O(8)	66.49(7)
N(5)-N(6)	1.359(3)	O(4)#2-K(1)-O(8)	77.61(8)
N(7)-O(5)	1.158(4)	N(6)#1-K(1)-O(8)	63.79(6)
N(7)-O(4)	1.198(4)	N(3)#3-K(1)-O(8)	130.10(7)
N(8)-O(6)	1.203(3)	O(4)#1-K(1)-O(8)	68.93(8)
N(8)-O(7)	1.227(3)	O(5)#2-K(1)-O(8)	112.12(10)
N(9)-H(9A)	0.8600	O(2)-K(1)-N(7)#2	68.91(8)
N(9)-H(9B)	0.8600	O(3)#1-K(1)-N(7)#2	95.59(7)
O(8)-H(8A)	0.853(19)	N(2)#1-K(1)-N(7)#2	152.47(7)
O(8)-H(8B)	0.850(19)	O(4)#2-K(1)-N(7)#2	20.25(7)
		N(6)#1-K(1)-N(7)#2	125.35(6)
		N(3)#3-K(1)-N(7)#2	105.95(7)
		O(4)#1-K(1)-N(7)#2	74.08(7)
		O(5)#2-K(1)-N(7)#2	20.01(7)
		O(8)-K(1)-N(7)#2	96.19(7)
		O(2)-K(1)-K(1)#3	52.59(7)
		O(3)#1-K(1)-K(1)#3	124.30(6)
		N(2)#1-K(1)-K(1)#3	90.05(5)
		O(4)#2-K(1)-K(1)#3	128.35(6)
		N(6)#1-K(1)-K(1)#3	90.79(5)
		N(3)#3-K(1)-K(1)#3	52.31(6)

	O(4)#1-K(1)-K(1)#3	108.56(7)
	O(5)#2-K(1)-K(1)#3	97.67(9)
	O(8)-K(1)-K(1)#3	150.05(5)
	N(7)#2-K(1)-K(1)#3	112.10(5)
	N(5)-C(1)-C(2)	110.9(2)
	N(5)-C(1)-H(1A)	109.5
	C(2)-C(1)-H(1A)	109.5
	N(5)-C(1)-H(1B)	109.5
	C(2)-C(1)-H(1B)	109.5
	H(1A)-C(1)-H(1B)	108.1
	N(1)-C(2)-N(2)	115.4(3)
	N(1)-C(2)-C(1)	121.7(3)
	N(2)-C(2)-C(1)	122.8(2)
	N(2)-C(3)-O(1)	112.7(3)
	N(2)-C(3)-N(3)	136.4(3)
	O(1)-C(3)-N(3)	110.8(2)
	N(6)-C(4)-C(5)	112.8(2)
	N(6)-C(4)-N(7)	115.5(2)
	C(5)-C(4)-N(7)	131.6(2)
	N(8)-C(5)-C(4)	132.6(2)
	N(8)-C(5)-C(6)	123.2(2)
	C(4)-C(5)-C(6)	104.2(2)
	N(9)-C(6)-N(5)	123.9(2)
	N(9)-C(6)-C(5)	131.1(2)
	N(5)-C(6)-C(5)	105.0(2)
	C(2)-N(1)-O(1)	103.5(2)
	C(3)-N(2)-C(2)	102.6(2)
	C(3)-N(2)-K(1)#4	129.11(18)
	C(2)-N(2)-K(1)#4	125.00(18)
	N(4)-N(3)-C(3)	116.8(2)
	N(4)-N(3)-K(1)#3	110.62(18)
	C(3)-N(3)-K(1)#3	113.02(19)
	O(3)-N(4)-O(2)	119.9(3)
	O(3)-N(4)-N(3)	124.4(3)
	O(2)-N(4)-N(3)	115.7(3)
	C(6)-N(5)-N(6)	113.5(2)
	C(6)-N(5)-C(1)	128.1(2)
	N(6)-N(5)-C(1)	118.3(2)

	C(4)-N(6)-N(5)	104.5(2)
	C(4)-N(6)-K(1)#4	116.99(16)
	N(5)-N(6)-K(1)#4	121.65(15)
	O(5)-N(7)-O(4)	121.3(3)
	O(5)-N(7)-C(4)	120.4(3)
	O(4)-N(7)-C(4)	118.3(2)
	O(5)-N(7)-K(1)#2	65.67(18)
	O(4)-N(7)-K(1)#2	56.89(16)
	C(4)-N(7)-K(1)#2	166.14(17)
	O(6)-N(8)-O(7)	122.6(3)
	O(6)-N(8)-C(5)	119.8(3)
	O(7)-N(8)-C(5)	117.5(2)
	C(6)-N(9)-H(9A)	120.0
	C(6)-N(9)-H(9B)	120.0
	H(9A)-N(9)-H(9B)	120.0
	C(3)-O(1)-N(1)	105.9(2)
	N(4)-O(2)-K(1)	116.4(2)
	N(4)-O(3)-K(1)#4	139.4(2)
	N(7)-O(4)-K(1)#2	102.86(19)
	N(7)-O(4)-K(1)#4	116.3(2)
	K(1)#2-O(4)-K(1)#4	120.17(13)
	N(7)-O(5)-K(1)#2	94.3(2)
	K(1)-O(8)-H(8A)	74(4)
	K(1)-O(8)-H(8B)	103(4)
	H(8A)-O(8)-H(8B)	108(3)

Table S6. Hydrogen bonds for **5** [Å and °].

D-H···A	D-H(Å)	H···A(Å)	D···A(Å)	D-H···A(°)
C(4)-H(4B)...O(3)#10	0.99	2.53	3.349(2)	140.1
C(4)-H(4A)...O(5)#11	1.00	2.59	3.476(2)	148.3
O(10)-H(10A)...O(1)#10	0.83	2.59	3.379(2)	159.1
O(10)-H(10A)...O(2)#10	0.83	2.43	3.173(2)	150.3

Symmetry transformations used to generate equivalent atoms:

#1 x-1,-y+1/2,z-1/2 #2 x-1,y,z #3 x-1,-y+1/2,z+1/2

#4 x,-y+1/2,z+1/2 #5 x,-y+1/2,z-1/2 #6 -x,-y+1,-z+1

#7 x+1,-y+1/2,z+1/2 #8 x+1,-y+1/2,z-1/2 #9 x+1,y,z

#10 x,y,z+1 #11 -x+1,-y+1,-z+1

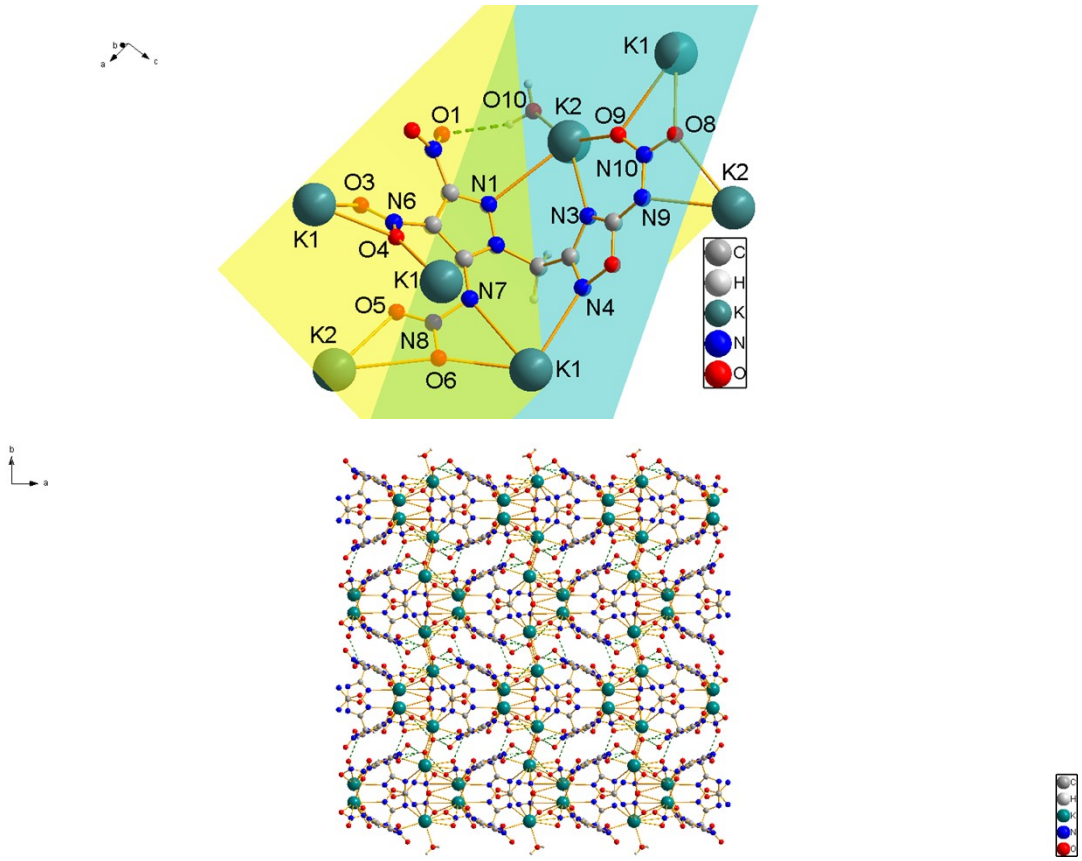

Fig. S3. Molecular structure and packing diagram of **5** (The green dotted line represents the hydrogen bond).

Table S7. Bond lengths [Å] and angles [°] for compound **5.**

Bond length		Bond angle	
C(1)-N(1)	1.310(2)	N(1)-C(1)-C(2)	112.95(14)
C(1)-C(2)	1.401(2)	N(1)-C(1)-N(5)	117.21(15)
C(1)-N(5)	1.452(2)	C(2)-C(1)-N(5)	129.58(15)
C(2)-C(3)	1.393(2)	C(3)-C(2)-C(1)	104.63(14)
C(2)-N(6)	1.424(2)	C(3)-C(2)-N(6)	126.59(15)
C(3)-N(2)	1.354(2)	C(1)-C(2)-N(6)	128.51(15)
C(3)-N(7)	1.368(2)	N(2)-C(3)-N(7)	117.53(15)
C(4)-N(2)	1.464(2)	N(2)-C(3)-C(2)	105.01(14)
C(4)-C(5)	1.492(2)	N(7)-C(3)-C(2)	137.40(16)
C(4)-H(4B)	0.9915	N(2)-C(4)-C(5)	110.57(13)
C(4)-H(4A)	0.9953	N(2)-C(4)-H(4B)	108.9
C(5)-N(4)	1.294(2)	C(5)-C(4)-H(4B)	110.3
C(5)-N(3)	1.362(2)	N(2)-C(4)-H(4A)	103.0

C(6)-N(3)	1.310(2)	C(5)-C(4)-H(4A)	113.6
C(6)-N(9)	1.351(2)	H(4B)-C(4)-H(4A)	110.1
C(6)-O(7)	1.356(2)	N(4)-C(5)-N(3)	116.37(15)
K(1)-O(8)	2.7412(16)	N(4)-C(5)-C(4)	121.30(15)
K(1)-O(6)#1	2.8188(16)	N(3)-C(5)-C(4)	122.32(15)
K(1)-O(4)#2	2.8625(15)	N(3)-C(6)-N(9)	136.76(16)
K(1)-O(4)#3	2.9424(14)	N(3)-C(6)-O(7)	112.25(14)
K(1)-N(7)#1	2.9660(15)	N(9)-C(6)-O(7)	110.93(14)
K(1)-N(4)#1	3.0090(15)	O(8)-K(1)-O(6)#1	83.62(6)
K(1)-O(9)	3.0116(15)	O(8)-K(1)-O(4)#2	138.37(5)
K(1)-O(3)#3	3.1864(15)	O(6)#1-K(1)-O(4)#2	88.49(5)
K(1)-N(8)#1	3.3528(16)	O(8)-K(1)-O(4)#3	77.81(5)
K(1)-N(6)#3	3.4438(15)	O(6)#1-K(1)-O(4)#3	149.40(5)
K(1)-K(1)#4	4.5707(4)	O(4)#2-K(1)-O(4)#3	121.39(4)
K(1)-K(1)#5	4.5707(4)	O(8)-K(1)-N(7)#1	119.33(5)
K(2)-O(10)#6	2.7829(16)	O(6)#1-K(1)-N(7)#1	44.13(4)
K(2)-O(9)	2.8262(15)	O(4)#2-K(1)-N(7)#1	78.90(4)
K(2)-N(3)	2.8356(14)	O(4)#3-K(1)-N(7)#1	129.40(4)
K(2)-O(5)#2	2.8504(13)	O(8)-K(1)-N(4)#1	149.56(5)
K(2)-O(8)#5	2.8803(17)	O(6)#1-K(1)-N(4)#1	113.89(4)
K(2)-N(9)#5	2.8927(16)	O(4)#2-K(1)-N(4)#1	69.61(4)
K(2)-O(10)	2.8966(16)	O(4)#3-K(1)-N(4)#1	75.13(4)
K(2)-N(1)	3.0930(14)	N(7)#1-K(1)-N(4)#1	70.21(4)
K(2)-O(6)#2	3.1677(15)	O(8)-K(1)-O(9)	43.62(4)
K(2)-N(10)#5	3.3247(17)	O(6)#1-K(1)-O(9)	73.07(4)
K(2)-N(8)#2	3.4061(16)	O(4)#2-K(1)-O(9)	95.03(4)
K(2)-K(2)#6	4.2141(9)	O(4)#3-K(1)-O(9)	107.55(4)
K(2)-H(10B)	2.9873	N(7)#1-K(1)-O(9)	116.70(4)
N(1)-N(2)	1.3563(19)	N(4)#1-K(1)-O(9)	162.28(4)
N(4)-O(7)	1.4143(19)	O(8)-K(1)-O(3)#3	85.53(4)
N(5)-O(1)	1.205(2)	O(6)#1-K(1)-O(3)#3	114.25(4)
N(5)-O(2)	1.208(2)	O(4)#2-K(1)-O(3)#3	134.14(4)
N(6)-O(3)	1.2187(19)	O(4)#3-K(1)-O(3)#3	40.75(4)
N(6)-O(4)	1.223(2)	N(7)#1-K(1)-O(3)#3	90.51(4)
N(7)-N(8)	1.324(2)	N(4)#1-K(1)-O(3)#3	64.84(4)
N(8)-O(5)	1.239(2)	O(9)-K(1)-O(3)#3	128.76(4)
N(8)-O(6)	1.254(2)	O(8)-K(1)-N(8)#1	99.47(5)
N(9)-N(10)	1.330(2)	O(6)#1-K(1)-N(8)#1	21.26(4)

N(10)-O(9)	1.230(2)	O(4)#2-K(1)-N(8)#1	86.03(4)
N(10)-O(8)	1.249(2)	O(4)#3-K(1)-N(8)#1	141.93(4)
O(10)-H(10A)	0.8287	N(7)#1-K(1)-N(8)#1	23.17(4)
O(10)-H(10B)	0.8939	N(4)#1-K(1)-N(8)#1	93.37(4)
		O(9)-K(1)-N(8)#1	94.33(4)
		O(3)#3-K(1)-N(8)#1	101.37(4)
		O(8)-K(1)-N(6)#3	82.81(4)
		O(6)#1-K(1)-N(6)#3	133.76(5)
		O(4)#2-K(1)-N(6)#3	128.73(4)
		O(4)#3-K(1)-N(6)#3	20.18(4)
		N(7)#1-K(1)-N(6)#3	109.81(4)
		N(4)#1-K(1)-N(6)#3	67.04(4)
		O(9)-K(1)-N(6)#3	121.00(4)
		O(3)#3-K(1)-N(6)#3	20.72(3)
		N(8)#1-K(1)-N(6)#3	122.09(4)
		O(8)-K(1)-K(1)#4	74.95(5)
		O(6)#1-K(1)-K(1)#4	154.47(3)
		O(4)#2-K(1)-K(1)#4	98.29(3)
		O(4)#3-K(1)-K(1)#4	37.45(3)
		N(7)#1-K(1)-K(1)#4	161.38(3)
		N(4)#1-K(1)-K(1)#4	91.47(3)
		O(9)-K(1)-K(1)#4	81.80(3)
		O(3)#3-K(1)-K(1)#4	78.19(2)
		N(8)#1-K(1)-K(1)#4	174.41(3)
		N(6)#3-K(1)-K(1)#4	57.60(3)
		O(8)-K(1)-K(1)#5	121.86(4)
		O(6)#1-K(1)-K(1)#5	49.91(4)
		O(4)#2-K(1)-K(1)#5	38.68(3)
		O(4)#3-K(1)-K(1)#5	158.59(3)
		N(7)#1-K(1)-K(1)#5	51.55(3)
		N(4)#1-K(1)-K(1)#5	87.31(3)
		O(9)-K(1)-K(1)#5	85.59(3)
		O(3)#3-K(1)-K(1)#5	139.87(3)
		N(8)#1-K(1)-K(1)#5	49.56(3)
		N(6)#3-K(1)-K(1)#5	153.40(3)
		K(1)#4-K(1)-K(1)#5	133.60(2)
		O(10)#6-K(2)-O(9)	155.33(4)
		O(10)#6-K(2)-N(3)	146.74(4)

	O(9)-K(2)-N(3)	57.58(4)
	O(10)#6-K(2)-O(5)#2	71.21(4)
	O(9)-K(2)-O(5)#2	88.83(4)
	N(3)-K(2)-O(5)#2	127.15(4)
	O(10)#6-K(2)-O(8)#5	83.33(5)
	O(9)-K(2)-O(8)#5	81.12(5)
	N(3)-K(2)-O(8)#5	121.42(4)
	O(5)#2-K(2)-O(8)#5	86.69(4)
	O(10)#6-K(2)-N(9)#5	111.23(5)
	O(9)-K(2)-N(9)#5	69.14(5)
	N(3)-K(2)-N(9)#5	80.82(4)
	O(5)#2-K(2)-N(9)#5	127.23(4)
	O(8)#5-K(2)-N(9)#5	44.13(4)
	O(10)#6-K(2)-O(10)	84.22(5)
	O(9)-K(2)-O(10)	104.64(5)
	N(3)-K(2)-O(10)	76.72(4)
	O(5)#2-K(2)-O(10)	74.20(4)
	O(8)#5-K(2)-O(10)	159.75(4)
	N(9)#5-K(2)-O(10)	156.09(4)
	O(10)#6-K(2)-N(1)	84.97(4)
	O(9)-K(2)-N(1)	116.33(4)
	N(3)-K(2)-N(1)	70.26(4)
	O(5)#2-K(2)-N(1)	154.71(4)
	O(8)#5-K(2)-N(1)	99.20(5)
	N(9)#5-K(2)-N(1)	68.91(4)
	O(10)-K(2)-N(1)	95.54(4)
	O(10)#6-K(2)-O(6)#2	107.72(4)
	O(9)-K(2)-O(6)#2	61.00(5)
	N(3)-K(2)-O(6)#2	85.31(4)
	O(5)#2-K(2)-O(6)#2	41.85(4)
	O(8)#5-K(2)-O(6)#2	110.63(5)
	N(9)#5-K(2)-O(6)#2	127.73(5)
	O(10)-K(2)-O(6)#2	58.62(5)
	N(1)-K(2)-O(6)#2	148.51(4)
	O(10)#6-K(2)-N(10)#5	100.77(4)
	O(9)-K(2)-N(10)#5	69.61(5)
	N(3)-K(2)-N(10)#5	100.14(4)
	O(5)#2-K(2)-N(10)#5	104.49(4)

	O(8)#5-K(2)-N(10)#5	21.74(4)
	N(9)#5-K(2)-N(10)#5	23.39(4)
	O(10)-K(2)-N(10)#5	174.21(5)
	N(1)-K(2)-N(10)#5	87.88(4)
	O(6)#2-K(2)-N(10)#5	116.57(5)
	O(10)#6-K(2)-N(8)#2	90.05(4)
	O(9)-K(2)-N(8)#2	73.03(4)
	N(3)-K(2)-N(8)#2	106.82(4)
	O(5)#2-K(2)-N(8)#2	20.48(4)
	O(8)#5-K(2)-N(8)#2	96.91(5)
	N(9)#5-K(2)-N(8)#2	128.39(4)
	O(10)-K(2)-N(8)#2	67.18(4)
	N(1)-K(2)-N(8)#2	162.45(4)
	O(6)#2-K(2)-N(8)#2	21.60(3)
	N(10)#5-K(2)-N(8)#2	109.61(4)
	O(10)#6-K(2)-K(2)#6	43.15(3)
	O(9)-K(2)-K(2)#6	140.70(4)
	N(3)-K(2)-K(2)#6	113.22(3)
	O(5)#2-K(2)-K(2)#6	66.43(3)
	O(8)#5-K(2)-K(2)#6	124.62(4)
	N(9)#5-K(2)-K(2)#6	150.17(4)
	O(10)-K(2)-K(2)#6	41.07(3)
	N(1)-K(2)-K(2)#6	90.48(3)
	O(6)#2-K(2)-K(2)#6	80.98(4)
	N(10)#5-K(2)-K(2)#6	143.83(3)
	N(8)#2-K(2)-K(2)#6	74.57(3)
	O(10)#6-K(2)-H(10B)	93.3
	O(9)-K(2)-H(10B)	90.3
	N(3)-K(2)-H(10B)	76.2
	O(5)#2-K(2)-H(10B)	63.4
	O(8)#5-K(2)-H(10B)	149.1
	N(9)#5-K(2)-H(10B)	155.1
	O(10)-K(2)-H(10B)	17.4
	N(1)-K(2)-H(10B)	111.1
	O(6)#2-K(2)-H(10B)	41.4
	N(10)#5-K(2)-H(10B)	157.4
	N(8)#2-K(2)-H(10B)	52.3
	K(2)#6-K(2)-H(10B)	51.9

	C(1)-N(1)-N(2)	103.77(13)
	C(1)-N(1)-K(2)	123.51(10)
	N(2)-N(1)-K(2)	115.29(9)
	C(3)-N(2)-N(1)	113.61(13)
	C(3)-N(2)-C(4)	126.93(14)
	N(1)-N(2)-C(4)	119.11(13)
	C(6)-N(3)-C(5)	102.31(14)
	C(6)-N(3)-K(2)	133.59(11)
	C(5)-N(3)-K(2)	124.10(11)
	C(5)-N(4)-O(7)	102.61(13)
	C(5)-N(4)-K(1)#7	125.59(11)
	O(7)-N(4)-K(1)#7	126.81(9)
	O(1)-N(5)-O(2)	124.52(17)
	O(1)-N(5)-C(1)	118.12(16)
	O(2)-N(5)-C(1)	117.36(16)
	O(3)-N(6)-O(4)	123.04(15)
	O(3)-N(6)-C(2)	118.95(15)
	O(4)-N(6)-C(2)	118.00(14)
	O(3)-N(6)-K(1)#8	67.66(9)
	O(4)-N(6)-K(1)#8	56.11(9)
	C(2)-N(6)-K(1)#8	168.49(11)
	N(8)-N(7)-C(3)	115.12(14)
	N(8)-N(7)-K(1)#7	95.04(10)
	C(3)-N(7)-K(1)#7	148.73(11)
	O(5)-N(8)-O(6)	120.96(15)
	O(5)-N(8)-N(7)	123.80(15)
	O(6)-N(8)-N(7)	115.22(15)
	O(5)-N(8)-K(1)#7	167.51(12)
	O(6)-N(8)-K(1)#7	54.62(9)
	N(7)-N(8)-K(1)#7	61.79(9)
	O(5)-N(8)-K(2)#9	53.58(8)
	O(6)-N(8)-K(2)#9	68.43(10)
	N(7)-N(8)-K(2)#9	170.29(12)
	K(1)#7-N(8)-K(2)#9	122.99(5)
	N(10)-N(9)-C(6)	116.83(15)
	N(10)-N(9)-K(2)#4	96.85(10)
	C(6)-N(9)-K(2)#4	135.10(12)
	O(9)-N(10)-O(8)	120.52(15)

	O(9)-N(10)-N(9)	124.97(15)
	O(8)-N(10)-N(9)	114.49(15)
	O(9)-N(10)-K(2)#4	161.94(14)
	O(8)-N(10)-K(2)#4	58.68(10)
	N(9)-N(10)-K(2)#4	59.75(9)
	N(6)-O(3)-K(1)#8	91.63(10)
	N(6)-O(4)-K(1)#9	152.19(11)
	N(6)-O(4)-K(1)#8	103.71(10)
	K(1)#9-O(4)-K(1)#8	103.87(4)
	N(8)-O(5)-K(2)#9	105.94(10)
	N(8)-O(6)-K(1)#7	104.11(11)
	N(8)-O(6)-K(2)#9	89.97(10)
	K(1)#7-O(6)-K(2)#9	165.62(5)
	C(6)-O(7)-N(4)	106.45(12)
	N(10)-O(8)-K(1)	103.71(11)
	N(10)-O(8)-K(2)#4	99.58(11)
	K(1)-O(8)-K(2)#4	139.47(8)
	N(10)-O(9)-K(2)	143.45(12)
	N(10)-O(9)-K(1)	90.89(10)
	K(2)-O(9)-K(1)	112.52(5)
	K(2)#6-O(10)-K(2)	95.78(5)
	K(2)#6-O(10)-H(10A)	112.7
	K(2)-O(10)-H(10A)	133.0
	K(2)#6-O(10)-H(10B)	121.4
	K(2)-O(10)-H(10B)	87.1
	H(10A)-O(10)-H(10B)	106.5

3. IR and NMR spectra

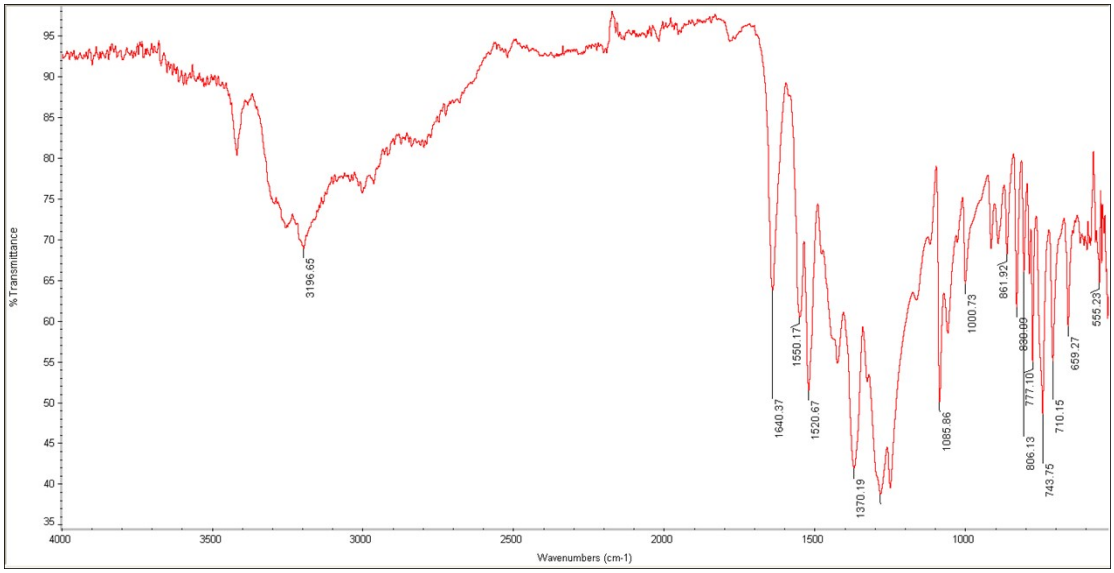

Fig. S4. IR spectra of compound **2**.

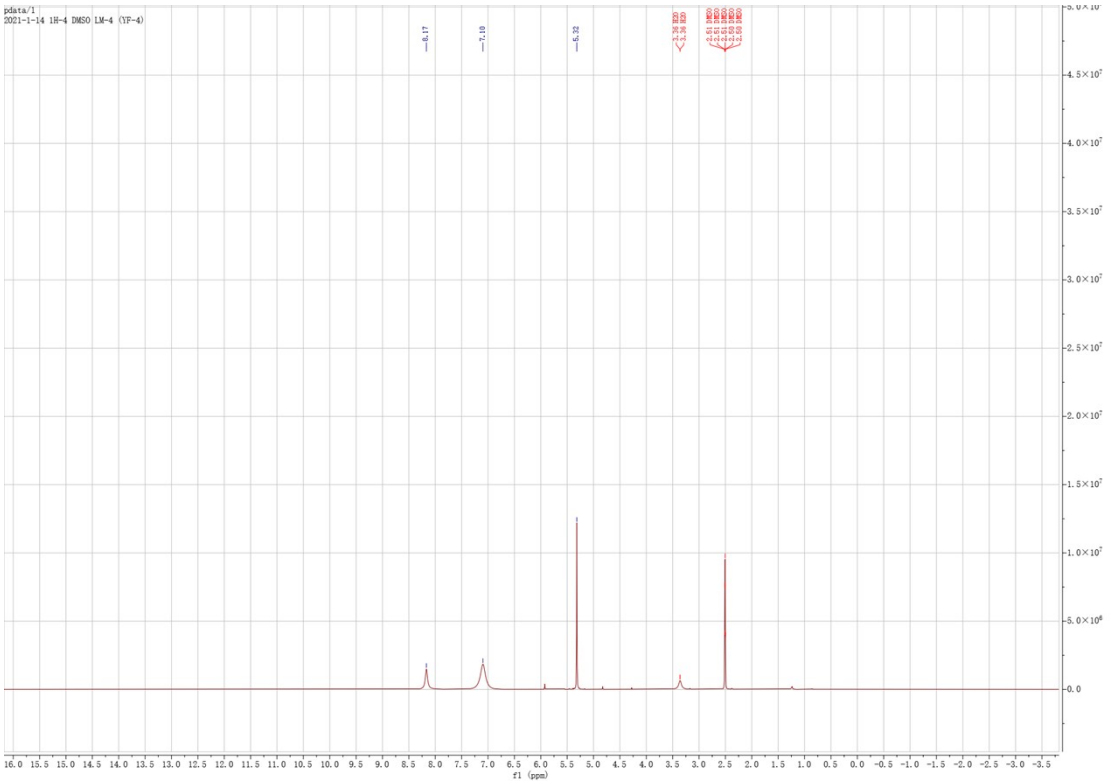

Fig. S5. ^{1}H NMR spectra of compound **2**.

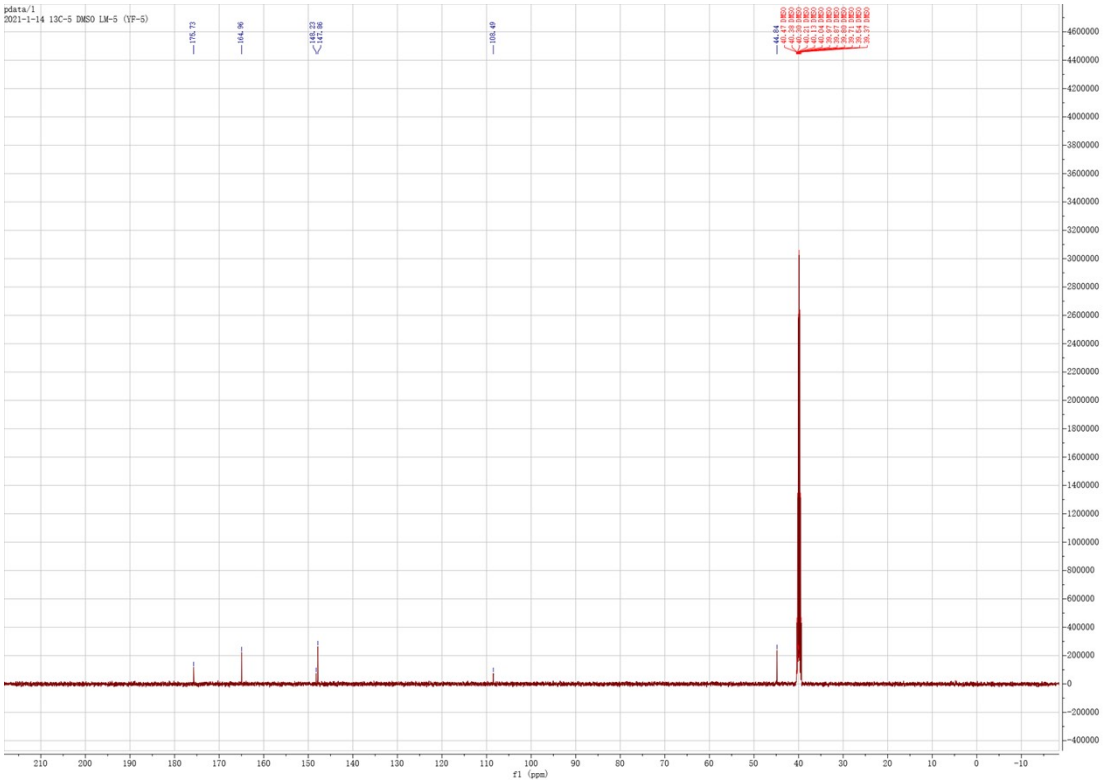

Fig. S6. ^{13}C NMR spectra of compound **2**.

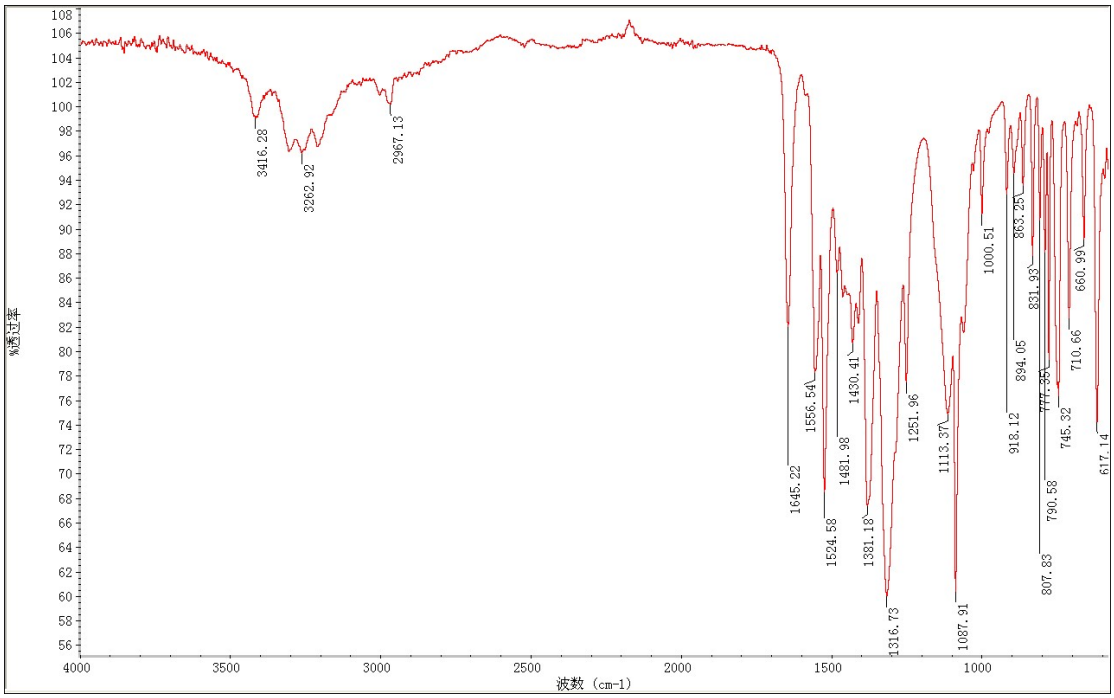

Fig. S7. IR spectra of compound **4**.

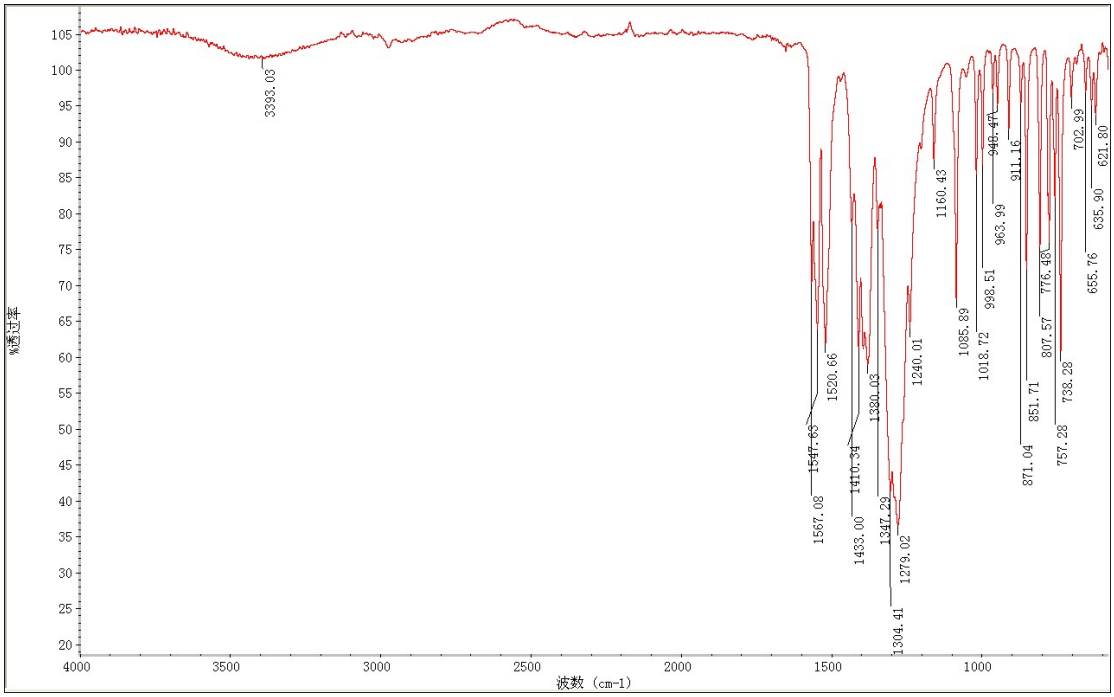

Fig. S8. IR spectra of compound **5**.

4. Computational Details

For the neutral compounds **2** all of the calculations were carried out using the Gaussian 09 suite of programs and using the B3LYP functional with the 6-31G(d) basis set. All of the optimized structures were characterized to be true local energy minima on the potential energy surface without imaginary frequencies. Total energy (E_0) and zero-point energy(ZPE) were calculated with vibration frequencies analysis.

The heat of formation in gas states is calculated based on follows:[3]

$R(NO_2)_n(NH_2)_n+2nCH_4 \rightarrow RH_4+nCH_3NO_2+nCH_3NH_2$ (1)

According to Hess' law of constant heat summation condensed-phase heats of formation can be determined.[4]

$\Delta H_{solid} = \Delta H_{gas} - \Delta H_{sub}$ (2)

The enthalpy of sublimation can be represented as eq (4) and on the basis of thepredicted electrostatic potential of a molecule.[5]

$$\Delta H_{sub} = a(SA)^2 + b\sqrt{\upsilon\sigma_{tot}^2} + c \quad (3)$$

Here SA is the surface area of the 0.001 electrons bohr^{-3} isosurface of the electronic density of the compounds, $\upsilon\sigma_{tot}^2$ is derived from the molecular electrostatic potential calculation, and a, b, c are

fitting parameters reported by Politzer et al.[5]

Table S8. Calculated total energy (E_0), zero-point energy (*ZPE*), thermal correction to enthalpy (H_T), and heats of formation (*HOF*) in gas state.

Compound	E_0 / a. u.	*ZPE* / kJ mol^{-1}	ΔH_T / a. u.	*HOF*/kJ mol^{-1}
2	-1250.5718518	441.005	0.186361	502.932
CH_4	-40.5240195	118.22	0.048836	-74.600
CH_3NO_2	-245.0133749	131.32	0.055294	-74.300
CH_3NH_2	-95.8532042	169.15	0.068745	-23.000

For EMOFs **4** and **5**, their enthalpy of formation is calculated from the constant volume combustion energies (Δ_cU). The constant-volume combustion energies of **4** and **5** were investigated by an oxygen-bomb calorimeter (Parr 6400, Parr Instrumentcompany, Moline Illinois, USA). Approximately 200 mg of the samples were pressed to form a tablet before the test. And benzoic acid (NIST Thermo chemicalStandard 39j) with a certified massic energy of combustion, under bomb conditions of -(26434 ± 3) J g^{-1},[6] was used for calibration of the bomb. The Δ_cU of the EMOFs **4** and **5** were experimentally determined to be -9489.088 J g^{-1}, and -8427.718 J g^{-1}, respectively. Based on the constant volume combustion energies and the formula (4) to (7) can be used to the calsulation of enthalpy of formation of EMOFs **4** and **5**, (ngis the total molaramount of gases in the products or reactants, R= 8.314 J mol^{-1}K^{-1}, and T= 298.15 K)

$$\Delta cHm^{\theta} = \Delta cUm^{\theta} + \Delta \mathbf{n}RT \quad (4)$$

$$C_6H_4N_9O_7K(s) + 3.75O_2(g) = 0.5K_2O(s) + 2H_2O(l) + 6CO_2(g) + 4.5N_2(g) \quad (5)$$

$$C_6H_2N_{10}O_9K_2(s) + 2.5O_2(g) = K_2O(s) + H_2O(l) + 6CO_2(g) + 5N_2(g) \quad (6)$$

$$\Delta_f H_m^{\theta} = \left[x\Delta_f H_m^{\theta}(\text{metal oxide}, s) + y\Delta_f H_m^{\theta}(CO_2, g) + z\Delta_f H_m^{\theta}(H_2O, l)\right] - \Delta_c H_m^{\theta} \quad (7)$$

In the above equation n is the total molar amount of gases in the products or reactants, R = 8.314 J mol^{-1} K^{-1}, T = 298.15 K, $\Delta_cH_m^{\theta}$ is standard molar enthalpies of combustion, x, y, and z represents the coefficient in the combustion equation. The enthalpies of combustion ($\Delta_cH_m^{\theta}$) calculated to be -3366.380 kJ mol^{-1} and -3695.555 kJ mol^{-1} for **4** and **5**. Furthermore, the calculated enthalpies of formation of **4** and **5** are 252.119 kJ mol^{-1} and 685.547 kJ mol^{-1}respectively.

For complex **4** and **5** the explosion equations that satisfy the largest exothermic principle (H_2O-CO_2) can be expressed as equation 8 and 9.

$$C_6H_4N_9O_7K = 0.5K_2O(s) + 2H_2O(g) + 2.25CO_2(g) + 4.5N_2(g) + 3.75C(s) \quad (8)$$

$$C_6H_2N_{10}O_9K_2 = K_2O(s) + H_2O(g) + 3.5CO_2(g) + 5N_2(g) + 2.5C(s) \quad (9)$$

Reference

(1) M. J. Frisch, Gaussian 09. Revision a. 02, Gaussian, Inc., Wallingford CT, 2009.

(2) M. Suceska, EXPLO5 Program. Croatia, Zagreb, 2011.

(3) J. Zhang, H. Du, F. Wang, X. Gong and Y. Huang, *J. Phys. Chem. A* 2011, **115**, 6617.

(4) P. W. Atkins, Physical Chemistry. Oxford University Press, Oxford, U. K., 1982.

(5) a) P. J. Politzer, S. Murray, T. Brinck and P. Lane, Immunoanalysis of agrochemicals. ACS Sympsium Series 586, American Chemical Society, Washington, DC, 1994; b) J. S. Murray and P. Politzer, In quantitative treatment of solute / solvent interactions. theoretical and computational chemistry. Elsevier, Amsterdam, 1994.

(6) A. V. Ribeiro da Silva and A. F. L. O. M. Santos, *J. Therm.Anal. Calorim.*, 2007, **88**,7.