Electronic Supplementary Information

New nitrogen-rich heterocycle compounds to build 3D energetic metal complexes

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Table of contents

1. X-ray crystallography

Table S1 **Selected bond lengths (Å) and band angles** (°) **of compound 2**

Selected bond lengths (Å)		
O1-C2 1.389(2)	N2-C3 1.328(2)	N1-C1 1.327(2)
N1-N2 1.345(2)	C1-C1[1] 1.458(3)	N2-N3 1.328(2)
N2-C2 1.470(2)	N4-C3 1.320(2)	C1-N4 1.356(2)
N4-N3 1.320(2)		
Selected band angles (°)		
C1-N1-N2 101.55(14)	N1-N2-C2 122.75(14)	C3-N2-C2 125.13(15）
N3-N2-N1 112.11(14)	N3-N2-C2 125.13(15)	C3-N4-C1 104.22(14)
C3-N2-N1 112.11(14)	N4-C3-N2 108.28(115)	N4-N3-N2 108.28(15)
N1-C1-C1 122.9(2)	N4-C1-C1 123.25(19)	N3-N4-C1 104.22(14)
O1-C2-N2 111.27(14)	N1-C1-N4 113.83(15)	

Table S2 **Selected bond lengths (Å) and band angles** (°) **of compound 3**

Selected bond lengths (Å)		
Na1-O1 2.428(2)	Na1-O2 2.400(2)	Na1-O2 2.414(2)
Na1-O3 2.438(2)	Na1-O4 2.352(3)	Na1-N5 2.584(2)
Na1-O4A 2.489(6)		
Selected band angles (°)		
O1-Na1-O3 161.89(8)	O1-Na1-N5 102.61(8)	O1-Na1-O4A 103.92(16)
O2-Na1-O1 82.48(7)	O2-Na1-O1 86.28(8)	O2-Na1-O2 86.84(7)
O2-Na1-N5 174.91(8)	O2-Na1-N5 93.51(8)	O2-Na1-O4A 86.19(14)
O2-Na1-O4A 166.77(17)	O3-Na1-N5 94.87(8)	O3-Na1-O4 79.76(16)
O4-Na1-O1 86.31(9)	O4-Na1-O2 170.64(10)	O4-Na1-O2 97.84(9)
O4-Na1-O3 100.79(10)	O4-Na1-N5 182.55(9)	O4-Na1-O4A 22.58(15)

Table S3 **Selected bond lengths (Å) and band angles** (°) **of compound 4**

Selected bond lengths (Å)		
K1-O1 2.676(2)	K1-O1 2.840(2)	K1-N1 2.877(2)
K1-N7 2.882(2)	K1-N5 2.917(2)	K1-N7 3.021(2)
K1-N5 3.067(2)	K1-N4 3.236(3)	K1-N7 2.882(2)
O1-K1 2.676 (2)	O1-K1 2.676 (2)	
Selected band angles (°)		
O1-K1-O1 84.67(6)	O1-K1-N1 129.05(7)	O1-K1-N1 143.18(6)
O1-K1-N7 129.14(6)	O1-K1-N7 78.54(6)	N1-K1-N7 87.41(6)
O1-K1-N5 78.53(6)	O1-K1-N5 126.31(6)	N1-K1-N5 60.08(6)
N7-K1-N5 147.46(6)	O1-K1-N7 78.69(6)	O1-K1-N7 131.9(6)
N1-K1-N7 76.24(6)	N7-K1-N7 78.00(6)	N5-K1-N7 94.09(6)
O1-K1-N5 126.66(6)	O1-K1-N5 73.64(6)	N1-K1-N5 73.58(6)
N7-K1-N5 93.85(7)	N5-K1-N5 76.74(6)	N7-K1-N5 149.05(6)

Table S4 **Selected bond lengths (Å) and band angles** (°) **of compound 5**

Selected bond lengths (Å)		
Na1-O2 2.3246(14)	Na1-O1 2.3926(14)	Na1-N1 2.5403(17)
N1-N2 1.353(2)	Na1-N7 2.5870(17)	Na1-O1 2.4463(16)
N2-N3 1.315(2)	N3-N4 1.349(2)	O2-C3 1.3941(19)
N5-N6 1.3624(18)		
Selected band angles (°)		
C1-N4-N3 104.75(13)	C3-O2-Na1 135.71(10)	N6-N5-C3 121.44(13)
N2-N1-Na1 99.09(10)	C1-N1-Na1 147.46(12)	C2-N7-C4^{4} 102.08(13)
O1^{1}-Na1-N1 85.77(5)	N3-N2-N1 109.53(14)	C1-N1-N2 104.24(14)
O1^{1}-Na1-O1 80.02(5)	N2-N3-N4 109.46(13)	O1-Na1-N1-92.98(5)
O1^{1}-Na1-N7 91.89(5)	C2^{3}-N5-N6 109.38(13)	O1-Na1-N7 103.61(5)
C2-N7-Na1 107.97(11)	C4^{4}-N7-Na1 149.90(11)	O2-Na1-N1 100.67(5)
O2-Na1-O1 89.78(5)	O2-Na1-N7 84.82(5)	N4-C1-N1 112.01(14)
N1-C1-C4^{5} 124.56(15)	N7^{3}-C4-C1^{6} 124.58(15)	N4-C1-C4^{5} 123.39(15)
N6-C4-C1^{6} 120.94(15)	O2-C3-N5 111.17(14)	N5^{4}-C2-N7 111.22(14)
N1-Na1-N7 162.60(6)	N6-C4-N7^{3} 114.45(14)	

Table S5 **Selected bond lengths (Å) and band angles** (°) **of compound 6**

Selected bond lengths (Å)		
K1-N3^{1} 3.032(2)	K1-O1 2.7385(18)	K1-N1 3.374(3)
C3-N6 1.329(4)	K1-N6^{2} 3.360(3)	C3-N7 1.340(4)
N3-N1^{2} 1.347(3)	N2-N1 1.318(4)	K1-N3 2.851(2)
K1-N4 2.868(2)	C1-N54 1.338(3)	N2-N5^{3} 1.348(4)
K1-N6 -2.902(2)	C1-C2^{3} 1.455(3)	O1-C4 1.397(3)
N6-C2 1.369(3)	N3-C1 1.340(3)	N4-C2^{3} 1.326(3)
K1-N5 2.873(3)	N4-N7^{3} 1.364(3)	N7-C45 1.467(3)
Selected band angles (°)		
N4-k1-N3 69.06(7)	N5-K1-N6 82.11(7)	N7-N4-K1 140.25(16)
N3-N2-N1 109.1(2)	N1-N2-N5 110.3(2)	N1-N3-K1 92.66(16)
K1-N3-K1 85.42(7)	C1-N3-K1 110.74 (16)	N1-N3-K1 132.86(15)
C2-N4-K1 113.69(16)	N2-N5-K1 122.54(18)	C3-N5-K1 117.28(17)
C2-N6-K1 104.02(16)	C2-N6-K1 118.50(16)	C3-N6-K1 148.56(18)
C3-N6-K1 103.33(17)	K1-N6-K1 78.84(6)	C4-O1-K1 117.27(15)

2. The distances of hydrogen bonds of compounds 2~6

Table S6 The distances of hydrogen bonds of compounds **2~6**

(2-hydroxymethyl-tetrazole-5-yl)-triazole (2)				
O1--H1⋯N4	0.8400	1.9500	2.7847	173.00
[Na(Htztr)(H_2O)$_4$]n (3)				
O1--H1A⋯N7	0.8400	1.9800	2.8229	175.00
O1--H1B⋯O4	0.8400	1.9400	2.7726	169.00
N2--H2⋯N6	0.8400	1.9300	2.7613	171.00

O2--H2A···N1	0.8400	2.0500	2.8725	165.00
O2--H2B···N3	0.8400	2.1400	2.9291	157.00
O3--H3A···N4	0.8400	2.0000	2.8262	167.00
O3--H3B···O1	0.8400	2.0400	2.8446	159.00
O4--H4A···O3	0.8400	2.1100	2.8901	155.00
O4—H4B···N3	0.8400	2.1100	2.9185	160.00
[K(Htztr)(H_2O)]n (4)				
O1--H1A···N2	0.9900	2.0600	2.8889	141.00
O1--H1B···N4	0.9900	2.3100	2.8765	116.00
N6--H6···N3	0.8000	2.0100	2.8003	171.00
C3--H3···N1	0.9500	2.5300	3.2872	137.00
[Na(hmtztr)H_2O]n (5)				
O1--H1A···N3	0.8400	2.0400	2.8607	164.00
O1--H1B···N3	0.8400	1.9800	2.8114	171.00
O2--H2···N4	0.8400	1.8800	2.7162	176.00
C2--H2A···O1	0.9500	2.5400	3.2832	135.00
[K(hmtztr)]n (6)				
O1--H1···N2	0.8400	1.9000	2.741	179.00
C4--H4B···N1	0.9900	2.5500	3.400	144.00

3. The DSC curves of 3, 4, 5 and 6

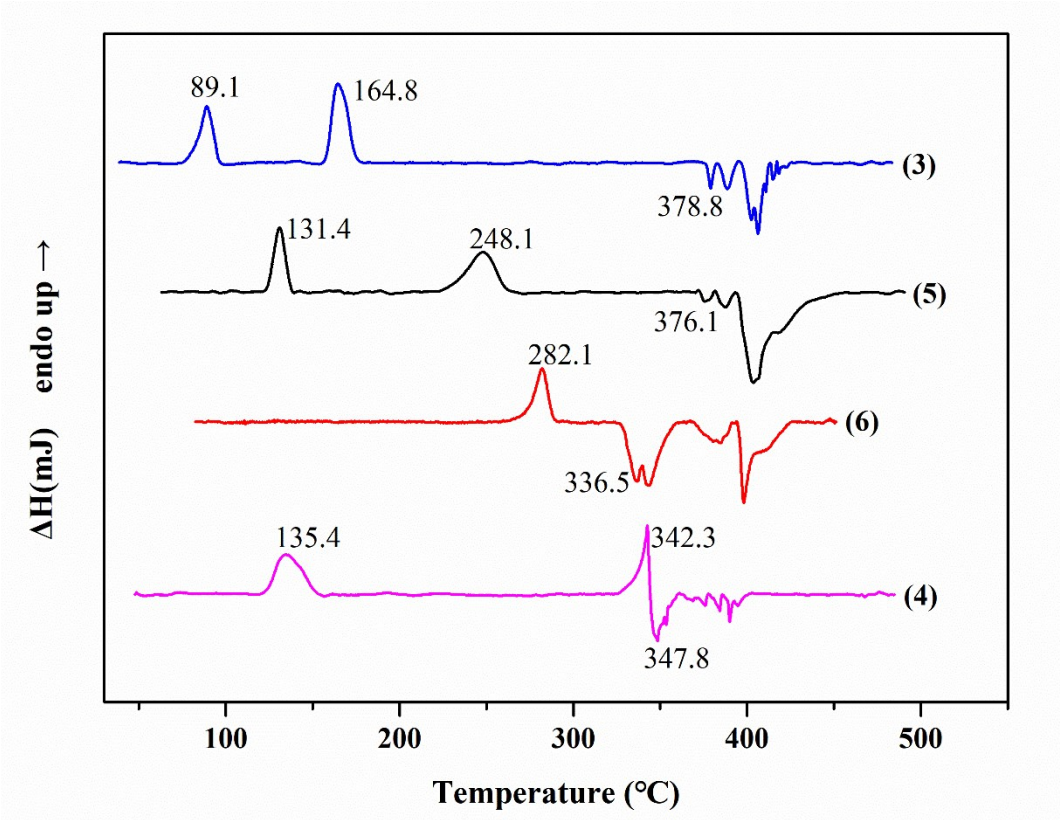

Figure S1 The DSC curves of **2**, **3**, **4**, **5** and **6** with a heating rate of 5 ℃ min^{-1}.

4. The first exothermic decomposition peak temperature with four heating rates

Table S7 The first exothermic decomposition peak temperature Tp with four heating rates (β=5, 10, 15, 20 K min^{-1})

β (K min^{-1})				
compound	5	10	15	20
5	649.35	652.95	654.55	658.75
6	609.75	616.95	626.65	627.55

5. Non-isothermal kinetics analysis

The peak temperatures of first decomposition processes were used to calculated kinetics parameters (apparent activation energies (*E*a) and the pre-exponential factor (A)), by Kissinger's method[3] (Eq. (1)) and Ozawa-Doyle's method[4] (Eq. (2)).

$$ln\frac{\beta}{T_p^2} = \ln\left(\frac{AR}{E_a}\right) - \frac{E_a}{RT_p} \quad (1)$$

$$ln\beta + 0.4567\frac{E_a}{RT_p} = C \quad (2)$$

Where Tp is the peak temperature (K) of first reaction process (see in Table S8), A is the pre-exponential factor (s^{-1}), Ea is the apparent activation energy (kJ mol^{-1}), R is the gas constant (J mol^{-1} K^{-1}), β is the heating rate (K min^{-1}) and C is a constant. The results are listed in Table S11. The symbol "S" stands for the standard deviation. *E*a is equal to the average of E_k and E_o.

Table S8 Non-isothermal reaction kinetics parameters.

compound	Kissinger's method			Ozawa's method		E_a
	E_K	lgA_K	R_K	E_O	R_O	
5	519.1	39.9	-0.9644	504	-0.9658	511.5
6	210.8	15.85	-.09765	210.3	-0.9786	210.6

6. References

1. H. E. Kissinger, Anal Chem, 1957, 29, 1702-1706.
2. T. Ozawa, Bull.chem.soc.jpn, 1965, 38, 1881-1886.