Supplementary Materials for

Pb^{II}-Catalyzed Transformation of Aromatic Nitriles to Heptanitrogen Anion via Sodium Azide: A Combined Experimental and Theoretical Study

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1. Thermal decomposition behaviour of ***MOF-N$_7$*** *and* ***Pb-FBA***

To test the robustness of **MOF-N$_7$** and **Pb-FBA**, thermogravimetric analyses (TGA) were obtained via heating the crystalline samples in the temperature range of 20 to 800 ºC under a N_2 atmosphere (Figures 7 and S9). For **MOF-N$_7$**, the TGA results show that the **MOF-N$_7$** framework was stable up to approximately 369 ºC and then started to abruptly decompose. The first mass loss of the four guest water molecules and one hydronium ion per formula unit occurred in range of 20 to 369 ºC with a 3.5% mass loss (calc. 3.4%). The second major mass loss of the four $CHDA^{2-}$ ligands, one ox^{2-} ligand and two O^{2-} anions, occurred in range of 369 to 430 ºC with a 31.5% mass loss (calc. 30.1%). The third minor weight loss of the N_7^{3-} polynitrogen occurred with a 3.8% mass loss (calc. 3.7%). The percentage remaining was 61.0%, meaning that the final product was metallic lead (calc. 62.6%). In addition, the DSC curve presents three endothermic peaks at 381, 406 and 419 ºC in range of 369 to 430 ºC, which can be assigned to the removal of the four $CHDA^{2-}$ ligands, one ox^{2-} ligand and two O^{2-} anions, respectively. Interestingly, a larger exothermic peak was observed at 607 ºC in range of 430 to 800 ºC, accompanied an exothermic enthalpy change of 8.61 kJ/g，which was due to the decomposition of the N_7^{3-} polynitrogen. **Pb-FBA** lost two guest water molecules from 20 to 400 ºC, accompanied by a mass loss of 4.4% (calc.4.8%). After 400 ºC, **Pb-FBA** started to abruptly decompose, which corresponds to the decomposition of **FBA**$^-$ and O^{2-} anions. Up until 800 ºC, **Pb-FBA** did not decompose completely.

Table S1:

Selected bond lengths (Å) and angles (°) for **MOF-N_7**.

Pb(1)–O(1)	2.314(7)	Pb(1)–O(2)	2.592(10)
Pb(1)–O(1)#1	2.314(7)	Pb(1)–O(2)#2	2.592(10)
Pb(1)–O(4)	3.029(12)	Pb(1)–N(1)	2.600(2)
Pb(1)–O(4)#2	3.029(12)	Pb(2)–O(3)	2.642(12)
Pb(2)–O(5)#3	2.562(12)	Pb(2)–O(6)#3	2.934(12)
Pb(2)–O(3)#4	2.642(12)	Pb(2)–O(6)#5	2.588(12)
Pb(2)–O(5)#6	2.562(12)	Pb(2)–O(6)#6	2.934(12)
Pb(2)–O(6)#7	2.588(12)	Pb(3)–O(1)	2.278(7)
Pb(3)–O(2)	2.731(11)	Pb(3)–O(3)	2.638(12)
Pb(3)–O(4)#4	2.438(11)	Pb(3)–N(1)#4	2.910(8)
Pb(3)–O(5)#6	2.829(12)	Pb(3)–O(3)#4	2.913(11)
N(1)–N(2)	1.198(31)	N(3)–N(4)	1.191(30)
N(2)–N(3)	1.261(39)		
N(1)–N(2)–N(3)	165.2(3)	N(3)–N(4)–N(3)#8	180.0(2)
N(2)–N(3)–N(4)	165.9(3)		
O(1)–Pb(1)–O(2)	76.8(3)	O(1)–Pb(1)–O(4)	66.8(3)
O(1)–Pb(1)–O(1)#1	75.1(3)	O(1)–Pb(1)–O(2)#2	114.4(3)
O(2)–Pb(1)–O(4)	75.9(3)	O(2)–Pb(1)–N(1)	146.7(3)
O(2)–Pb(1)–O(2)#2	63.5(4)	O(2)–Pb(1)–O(4)#2	136.8(3)
O(4)–Pb(1)–O(1)#1	137.0(3)	O(4)–Pb(1)–O(2)#2	136.8(3)
N(1)–Pb(1)–O(1)#1	75.5(4)	N(1)–Pb(1)–O(2)#2	146.7(3)
O(1)#1–Pb(1)–O(2)#2	76.8(3)	O(1)#1–Pb(1)–O(4)#2	66.8(3)
O(3)–Pb(2)–O(5)#3	68.7(4)	O(3)–Pb(2)–O(6)#3	112.8(4)
O(3)–Pb(2)–O(6)#6	90.0(3)	O(3)–Pb(2)–O(3)#4	66.3(4)
O(3)–Pb(2)–O(6)#7	91.2(4)	O(5)#3–Pb(2)–O(6)#3	44.2(4)
O(5)#3–Pb(2)–O(6)#6	152.9(4)	O(5)#3–Pb(2)–O(3)#4	74.9(4)
O(5)#3–Pb(2)–O(6)#7	95.2(4)	O(6)#3–Pb(2)–O(5)#6	152.9(4)
O(6)#3–Pb(2)–O(3)#4	90.0(3)	O(6)#3–Pb(2)–O(6)#5	67.6(4)
O(5)#6–Pb(2)–O(6)#6	44.2(4)	O(5)#6–Pb(2)–O(3)#4	68.7(4)
O(5)#6–Pb(2)–O(6)#7	109.2(4)	O(6)#6–Pb(2)–O(3)#4	112.8(4)
O(6)#6–Pb(2)–O(6)#7	67.6(4)	O(3)#4–Pb(2)–O(6)#5	91.2(4)

O(6)#5–Pb(2)–O(6)#7	111.4(4)	O(1)–Pb(3)–O(2)	74.6(2)
O(1)–Pb(3)–O(5)#6	133.4(3)	O(1)–Pb(3)–O(3)#4	73.4(3)
O(1)–Pb(3)–N(1)#4	70.0(5)	O(2)–Pb(3)–O(3)#4	134.2(3)
O(2)–Pb(3)–O(5)#6	130.8(3)	O(3)–Pb(3)–O(4)#4	110.2(4)
O(2)–Pb(3)–N(1)#4	75.2(5)	O(5)#6–Pb(3)–O(3)#4	61.5(3)
O(3)–Pb(3)–O(3)#4	62.5(3)	O(5)#3–Pb(2)–O(6)#5	109.2(4)
O(5)#6–Pb(3)–N(1)#4	144.6(5)	O(6)#3–Pb(2)–O(6)#6	153.2(3)
O(3)#4–Pb(3)–N(1)#4	121.6(5)	O(6)#3–Pb(2)–O(6)#7	96.9(4)
O(1)–Pb(1)–N(1)	75.5(4)	O(5)#6–Pb(2)–O(6)#5	95.2(4)
O(1)–Pb(1)–O(4)#2	137.0(3)	O(6)#6–Pb(2)–O(6)#5	96.9(4)
O(2)–Pb(1)–O(1)#1	114.4(3)	O(3)#4–Pb(2)–O(6)#7	157.4(4)
O(4)–Pb(1)–N(1)	76.4(3)	O(1)–Pb(3)–O(3)	79.2(3)
O(4)–Pb(1)–O(4)#2	135.1(3)	O(1)–Pb(3)–O(4)#4	78.9(3)
N(1)–Pb(1)–O(4)#2	76.4(3)	O(2)–Pb(3)–O(3)	80.0(3)
O(2)#2–Pb(1)–O(4)#2	75.9(3)	O(2)–Pb(3)–O(4)#4	149.2(4)
O(3)–Pb(2)–O(5)#6	74.9(4)	O(3)–Pb(3)–O(5)#6	70.7(4)
O(3)–Pb(2)–O(6)#5	157.4(4)	O(3)–Pb(3)–N(1)#4	144.4(5)
O(5)#3–Pb(2)–O(5)#6	136.2(4)	O(5)#6–Pb(3)–O(4)#4	79.4(4)
O(4)#4–Pb(3)–N(1)#4	81.3(6)	O(3)#4–Pb(3)–O(4)#4	47.8(4)

Symmetry codes: #1 –x + 1, –y + 1, –z + 1; #2 x, –y + 1, z; #3 x + 1, y, z; #4 –x +1, y, –z + 1; #5 –x + 1/2, –y + 3/2, –z + 1; #6 –x, y, –z + 1; #7 x + 1/2, –y + 3/2, z; #8 –x +2, y, –z + 2.

Table S2:

Selected bond lengths (Å) and angles (°) for ***α*-Pb(N$_3$)$_2$**.

Pb(1)–N(4)	2.711(8)	Pb(1)–N(7)	2.632(7)
Pb(1)–N(6)#1	2.796(8)	Pb(1)–N(6)#2	2.695(8)
Pb(1)–N(10)	2.604(8)	Pb(1)–N(1)#1	2.896(4)
Pb(1)–N(7)#3	2.613(8)	Pb(1)–N(10)#3	2.753(8)
Pb(2)–N(3)	2.651(11)	Pb(2)–N(4)	2.578(8)
Pb(2)–N(9)#4	2.890(8)	Pb(2)–N(9)#2	2.890(8)
Pb(2)–N(1)#1	2.629(10)	Pb(2)–N(9)#5	2.833(8)
Pb(2)–N(9)#6	2.833(8)	Pb(2)–N(4)#7	2.578(8)
N(4)–Pb(1)–N(7)	78.3(2)	N(4)–Pb(1)–N(10)	78.5(2)
N(4)–Pb(1)–N(6)#1	120.2(2)	N(4)–Pb(1)–N(6)#2	84.3(2)
N(4)–Pb(1)–N(10)#3	134.5(2)	N(7)–Pb(1)–N(10)	68.7(3)
N(7)–Pb(1)–N(6)#1	135.1(2)	N(7)–Pb(1)–N(6)#2	74.7(2)
N(7)–Pb(1)–N(10)#3	126.9(2)	N(10)–Pb(1)–N(1)#1	79.5(3)
N(10)–Pb(1)–N(6)#2	141.9(2)	N(10)–Pb(1)–N(7)#3	99.3(2)
N(1)#1–Pb(1)–N(6)#1	85.7(2)	N(1)#1–Pb(1)–N(6)#2	124.4(3)
N(1)#1–Pb(1)–N(10)#3	69.8(3)	N(6)#1–Pb(1)–N(6)#2	67.9(2)
N(6)#1–Pb(1)–N(10)#3	71.5(2)	N(6)#2–Pb(1)–N(7)#3	83.2(2)
N(7)#3–Pb(1)–N(10)#3	66.7(2)	N(3)–Pb(2)–N(4)	73.6(2)
N(3)–Pb(2)–N(9)#5	136.65(18)	N(3)–Pb(2)–N(9)#4	68.8(2)
N(3)–Pb(2)–N(9)#6	136.65(18)	N(3)–Pb(2)–N(4)#7	73.6(2)
N(4)–Pb(2)–N(9)#5	78.9(2)	N(4)–Pb(2)–N(9)#4	141.5(2)
N(4)–Pb(2)–N(9)#6	144.6(2)	N(4)–Pb(2)–N(4)#7	99.1(3)
N(1)#1–Pb(2)–N(9)#4	138.44(17)	N(1)#1–Pb(2)–N(9)#2	138.44(17)
N(1)#1–Pb(2)–N(4)#7	73.9(2)	N(9)#5–Pb(2)–N(9)#4	124.8(2)
N(9)#5–Pb(2)–N(9)#6	82.9(2)	N(9)#5–Pb(2)–N(4)#7	144.6(2)
N(9)#4–Pb(2)–N(9)#6	73.2(2)	N(9)#4–Pb(2)–N(4)#7	78.2(2)
N(9)#2–Pb(2)–N(4)#7	141.5(2)	N(9)#6–Pb(2)–N(4)#7	78.9(2)
N(4)–Pb(1)–N(1)#1	67.7(3)	N(10)–Pb(1)–N(6)#1	149.4(2)
N(4)–Pb(1)–N(7)#3	156.1(2)	N(10)–Pb(1)–N(10)#3	78.3(3)
N(7)–Pb(1)–N(1)#1	137.3(2)	N(1)#1–Pb(1)–N(7)#3	135.8(2)
N(7)–Pb(1)–N(7)#3	78.7(2)	N(6)#1–Pb(1)–N(7)#3	73.2(2)

N(6)#2–Pb(1)–N(10)#3	134.8(2)	N(1)#1–Pb(2)– N(9)#5	71.7(2)
N(3)–Pb(2)–N(1)#1	128.9(3)	N(1)#1–Pb(2)–N(9)#6	71.7(2)
N(3)–Pb(2)–N(9)#2	68.8(2)	N(9)#5–Pb(2)–N(9)#2	73.2(2)
N(4)–Pb(2)–N(1)#1	73.9(2)	N(9)#4–Pb(2)–N(9)#2	80.9(2)
N(4)–Pb(2)–N(9)#2	78.2(2)	N(9)#2–Pb(2)–N(9)#6	124.8(2)

Symmetry codes: #1 x – 1, y, z; #2 –x + 1, –y + 1, –z + 1; #3 x – 1/2, y, –z + 3/2; #4 –x + 1, –y + 1/2, –z + 1; #5 –x + 1/2, –y + 1, z – 1/2; #6 –x + 1/2, y + 1/2, z – 1/2; #7 x, –y + 3/2, z.

Table S3:

Selected bond lengths (Å) and angles (°) for **Pb-FBA**.

Pb(1)–O(1)	2.293(3)	Pb(2)–O(3)#2	2.806(4)
Pb(1)–O(2)#1	2.554(5)	Pb(2)–O(1)	2.257(3)
Pb(1)–O(5)	2.435(5)	Pb(2)–O(1)#1	2.302(3)
Pb(1)–O(2)#3	2.800(4)	Pb(2)–O(3)	2.558(4)
Pb(1)–O(1)#1	2.307(3)	Pb(2)–O(4)	2.490(5)
O(1)–Pb(1)–O(5)	80.29(16)	O(1)–Pb(2)–O(3)#2	75.82(12)
O(1)–Pb(1)–O(2)#1	80.34(13)	O(3)–Pb(2)–O(3)#2	124.42(14)
O(5)–Pb(1)–O(2)#1	160.62(17)	O(4)–Pb(2)–O(1)#1	77.21(14)
O(1)#1–Pb(1)–O(2)#1	82.64(13)	O(1)–Pb(2)–O(3)	90.43(14)
O(1)–Pb(1)–O(2)#3	142.79(13)	O(1)–Pb(2)– O(1)#1	74.92(12)
O(5)–Pb(1)–O(2)#3	80.69(18)	O(3)–Pb(2)–O(1)#1	80.34(13)
O(2)#3–Pb(1)–O(1)#1	74.98(12)	O(3)#2–Pb(2)–O(1)#1	141.43(12)
O(1)–Pb(1)–O(1)#1	74.13(11)	O(1)– Pb(2)–O(4)	89.32(14)
O(5)–Pb(1)–O(1)#1	92.21(14)	O(3)–Pb(2)–O(4)	156.80(16)
O(2)#3–Pb(1)– O(2)#1	115.55(13)	O(4)–Pb(2)–O(3)#2	77.88(16)

Symmetry codes: #1 –x + 5/4, y – 3/4, z + 1/4; #2 x + 3/4, –y + 5/4, z – 1/4; #3 –x + 1/2, –y + 2, z + 1/2.

Table S4:

The calculated interaction energies corrected with BSSE and ZPE, ΔE_{int} for the associations **Pb···N_3** and **Pb···4-FBN** (kcal·mol^{-1}). Values listed in parentheses correspond to the values obtained based on the SMD solvation model.

Associations	ΔE_{int}
Pb···N_3	–316.48 (–305.37)
Pb···4-FBN	–106.18 (–94.64)

Table S5:

Topological parameters at bond critical points of the Pb-N and N-N bonds in **MOF-N_7′**

BCPs	ρ(r)	$\nabla^2\rho$(r)	G(r)	V(r)	H(r)	$\lvert V(r)\rvert/G(r)$
Pb(1)···N(1)	0.028552	0.024241	0.012277	–0.018494	–0.006217	1.506394
Pb(3)···N(1)	0.018723	0.026135	0.008237	–0.009940	–0.001703	1.206750
N(1)···N(2)	0.434017	–0.829389	0.371937	–0.951221	–0.579284	2.557479
N(2)···N(3)	0.370128	–0.454354	0.266194	–0.645976	–0.379782	2.426711
N(3)···N(4)	0.556798	–1.459952	0.484983	–1.334954	–0.849971	2.752579

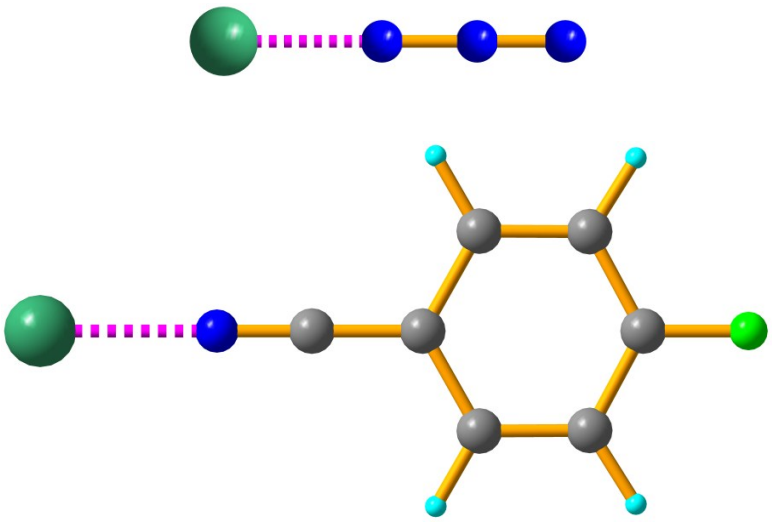

Figure S1. The calculated ground structures for the **Pb···N_3** and **Pb···4-FBN** associations.

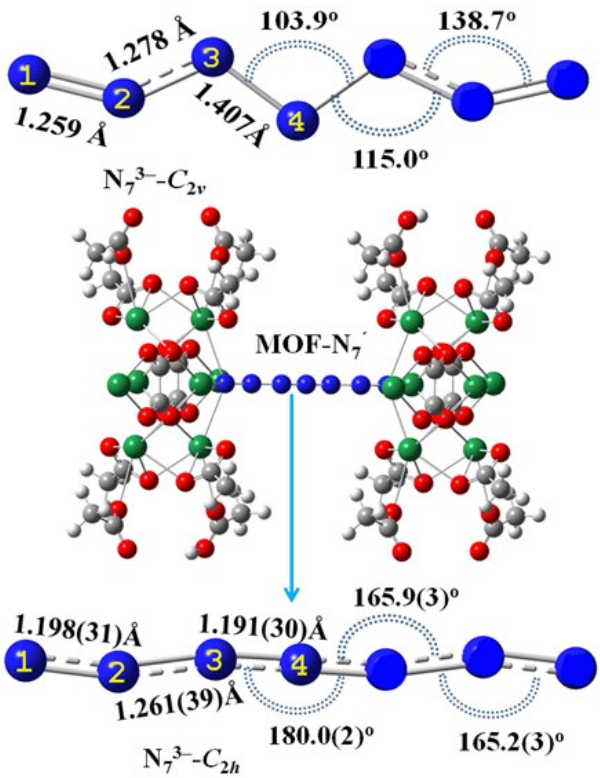

Figure S2. The structures of the representative fragments N_7^{3-}-C_{2h}, N_7^{3-}-C_{2v} and **MOF-N_7´**.

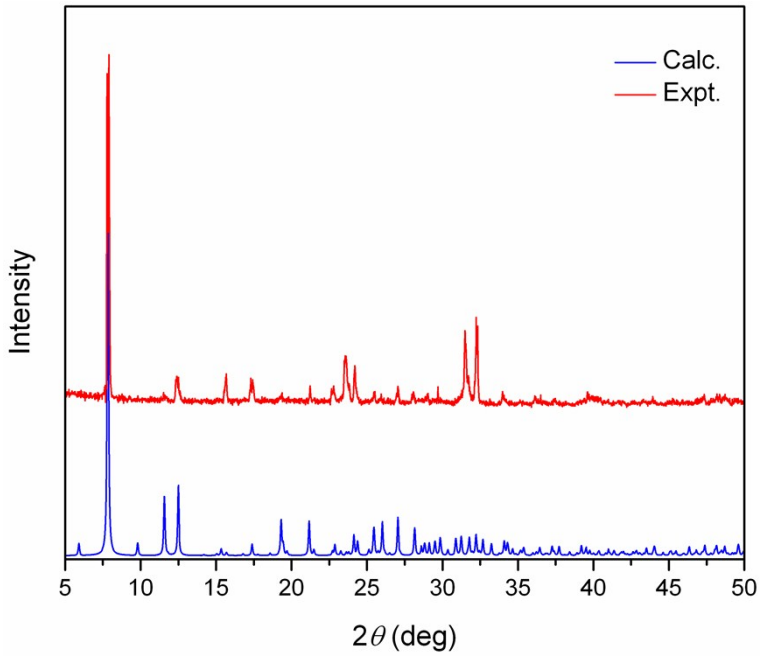

Figure S3. The XPRD patterns obtained for **MOF-N_7**.

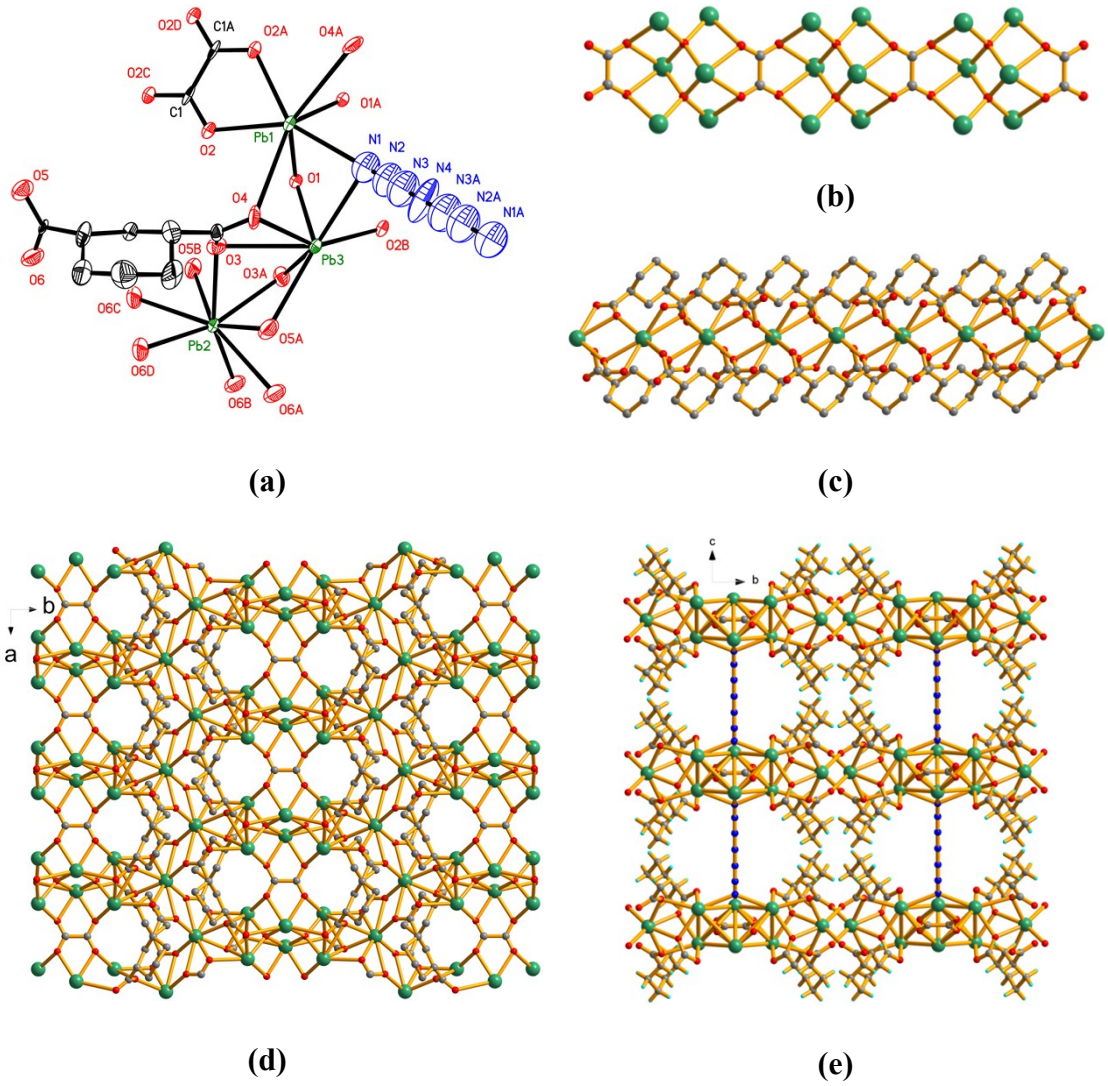

Figure S4. (a) The coordination environment of the Pb^{2+} ions in **MOF-N$_7$** with the ellipsoids drawn at the 30% probability level. Distorted water molecules and all hydrogen atoms were omitted for clarity. (b) The 1D chain constructed via the $C_2O_4^{2-}$ anions and $[Pb_6O_2]^{8+}$ cationic clusters along the *a*–axis. (c) The 1D chain constructed via the $CHDA^{2-}$ anions and Pb^{2+} ions along the *a*–axis. (d) The 2D metal-organic layer parallel to the *ab* plane in **MOF-N$_7$**. (e) The 3D open framework constructed from the 2D layers and N_7 anionic pillars of **MOF-N$_7$**.

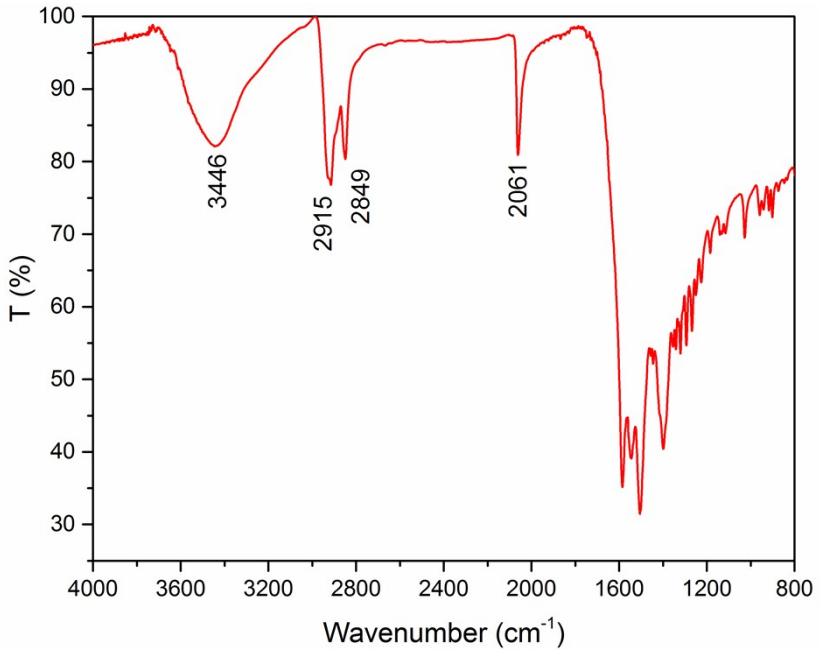

Figure S5. The FT–IR spectrum obtained of **MOF-N_7**.

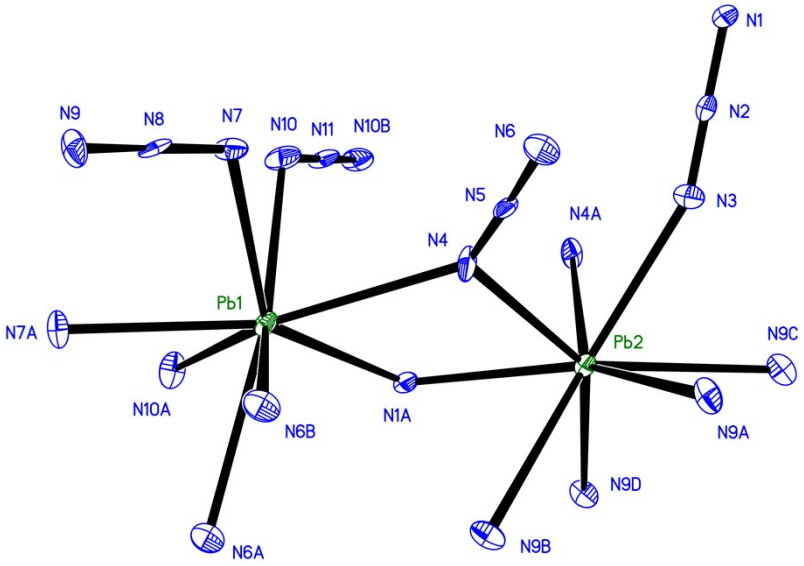

Figure S6. The coordination environment of the Pb^{2+} ions in ***α*-Pb$(N_3)_2$** with the ellipsoids drawn at the 30% probability level.

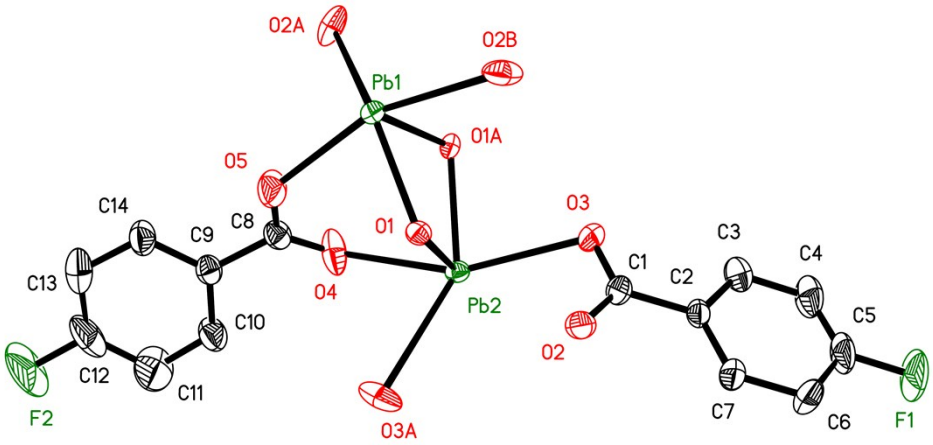

Figure S7. The coordination environment of the Pb^{2+} ion in **Pb-FBA** with the ellipsoids drawn at the 30% probability level. Distorted water molecules and all hydrogen atoms were omitted for clarity.

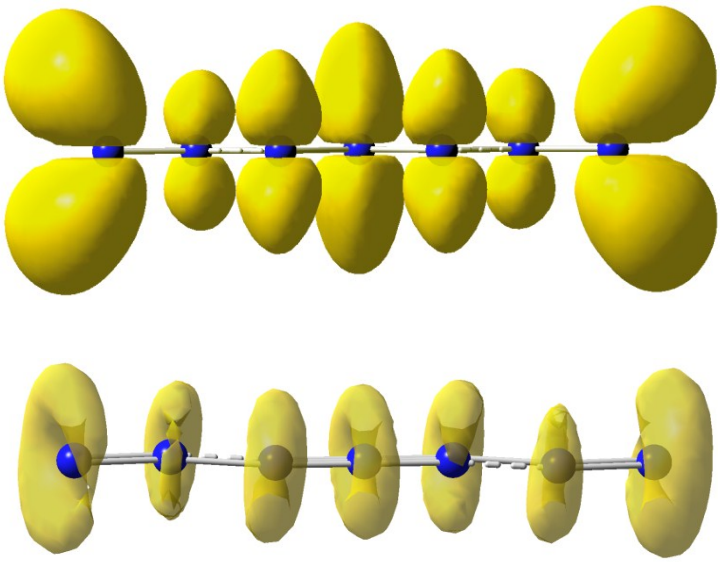

Figure S8. The ELF-π isosurfaces (value = 0.70) of $\mathbf{N_7^{3-}}$-$\boldsymbol{C_{2v}}$ (top) and the N_7^{3-} polynitrogen fragment in **MOF-N$_7$′** (bottom).

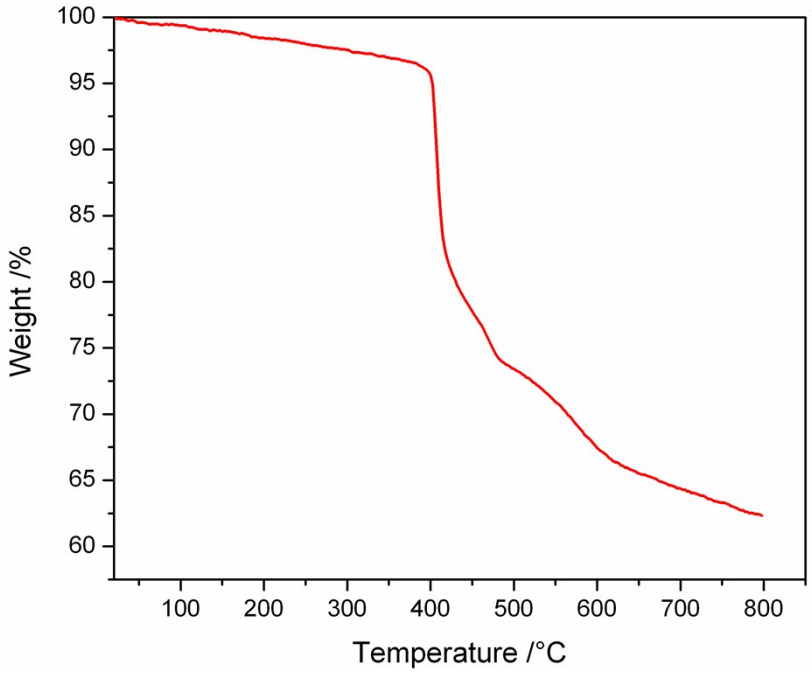

Figure S9. The TGA plot obtained for **Pb-FBA** at a heating rate of $10^{o}C \cdot min^{-1}$ under a flow of N_2.