

Supporting Information

Improving properties of energetic coordination polymers through structural modulation from 1D to 3D without changes of ligands or metal nodes

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EXPERIMENTAL SECTION

Caution:

General caution: K_2AOT and complexes are potentially explosive. Therefore, only small amounts of complexes should be prepared and they should be handled with care. The instrument used for CHN analysis is the Vario EL III elemental analyzer

Materials and General Methods:

Synthesis of $Pb_2(AOT)_2 \cdot 7(H_2O)$ (1). Firstly, an aqueous solution (3 mL) of $Pb(NO_3)_2$ (0.50 mmol, 165.5mg) was added to an aqueous solution (5mL) of K_2AOT (0.50mmol, 137.0mg) at room temperature. Second, the resultant mixture was stirred for 5 min, filtered, and the filter cake was washed with water (5 mL*3) to obtain an orange solid product. Next, the product was dissolved in 10 mL of H_2O . The solution was added into a 25 mL beaker. Then the beaker was put into a 100 mL beaker with water inside. Finally, by the diffusion of water vapor after 5 days, crystals suitable for X-ray diffraction (XRD) measurement were obtained. Yield: 70.5mg (35%, based on K_2AOT). Elemental analysis (%) calcd for $Pb_2(AOT)_2 \cdot 7(H_2O)$: C 5.15, H 1.50, N 30.02; found: C 5.20, H 1.51, N 30.08. IR (KBr, cm^{-1}): 3360.20, 2162.42, 1763.07, 1601.60, 1472.76, 1428.39, 1374.08, 1259.47, 1224.33, 1139.38, 1065.87, 823.83, 780.53, 719.36, 592.02.

Synthesis of $Pb_2(AOT)O \cdot 3(H_2O)$ (2). An aqueous solution (3 mL) of $Pb(NO_3)_2$ (0.50 mmol, 165.5mg) and an aqueous solution (5mL) of K_2AOT (0.50mmol, 137.0mg) was mixed at room temperature. Then the resultant mixture was stirred for 5 min, filtered, and the filter cake was washed with water (5 mL*3) to obtain an orange solid product. The product taken in a screw-capped vial, were added 20 mL of water. Then the mixture was heated to 90 °C for 30 minutes and then filtered quickly. The filtrate was heated at 130°C for 1 day. Subsequently, the reaction mixture was allowed to cool to room temperature slowly for about 20 hours. Red crystals were collected by filtration, washed with water, and dried at room temperature. Elemental analysis (%) calcd for $Pb_2C_2N_{10}O_3 \cdot 3(H_2O)$: C 3.53, H 0.88, N 20.59; found: C 3.55, H 0.90, N 20.63. IR (KBr, cm^{-1}): 3316.40, 2162.10, 1621.72, 1471.45, 1427.26, 1262.53, 1221.36, 1137.85, 1062.95, 923.03, 779.49, 724.26, 592.49.

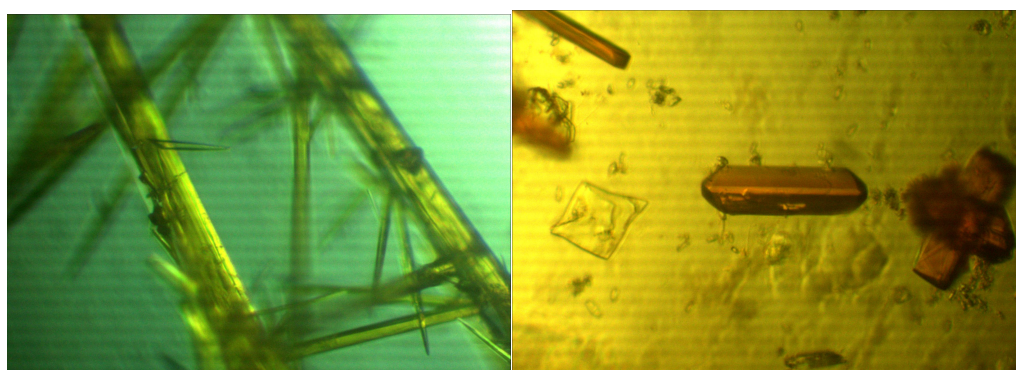


Figure S1. The image of the crystal for compound 1 and 2

X-ray crystallographic study

Two orange plate crystals 1 and 2 were performed on a Bruker Smart Apex II diffractometer at 173 K. Integration and scaling of intensity data were accomplished using the SAINT program². The structures were solved by intrinsic using SHELXT2014 and refinement was carried out by a fullmatrix least-squares technique using SHELXT2014³. The hydrogen atoms were refined isotropically, and the heavy atoms were refined anisotropically. Data were corrected for the effects of absorption using SADABS⁴ Relevant crystal data and refinement results are summarized in Table S1.

Table S1 summarizes the structure determination and crystallographic data of compounds 1,2

	1	2
CCDC	1883503	1845849
Empirical	C ₄ H ₁₄ Pb ₂ N ₂₀ O ₁₁	C ₂ H ₆ Pb ₂ N ₁₀ O ₆
Formula weight	932.73	680.55
Crystal system	triclinic	orthorhombic
Space group	P-1	Pccn
a	6.5991(6)	11.4741(12)
b	10.8137(10)	17.026(2)
c	15.2509(12)	5.9443(6)
α	84.753(3)	90
β	81.706(3)	90
γ	74.843(3)	90
V	1037.82(16)	1161.3(2)
Z	2	4
D _c (g·cm ⁻³)	2.985	3.893
T (K)	173	173
μ (mm ⁻¹)	16.304	29.008
F (000)	860.0	1200.0
GOF on F	1.030	1.059
R ₁ [$I > 2\sigma(I)$]	0.0543	0.0382
wR ₂ [$I > 2\sigma(I)$]	0.0853	0.0813
R ₁ (all data)	0.1061	0.0755
wR ₂ (all data)	0.0974	0.0923

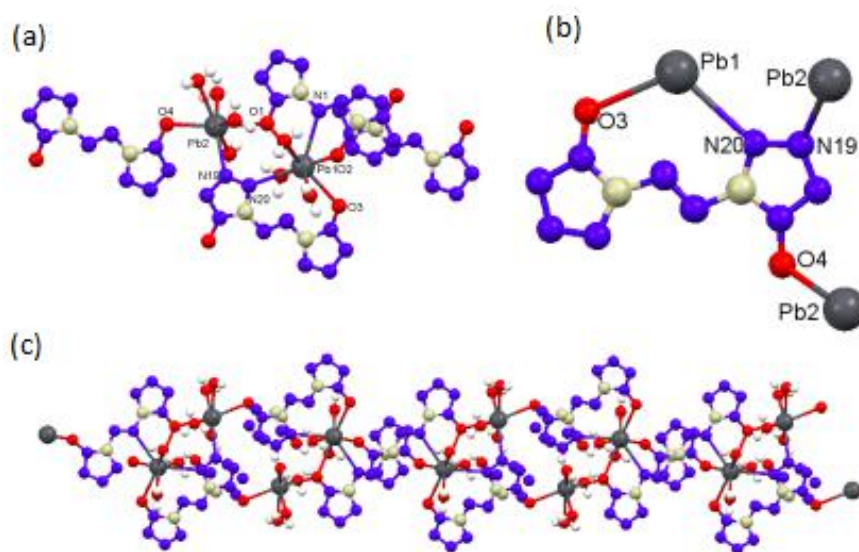


Figure S2. (a) Coordination environments of Pb in 1. (b) Coordination model of AOT in 1. (c) The chain structure of 1

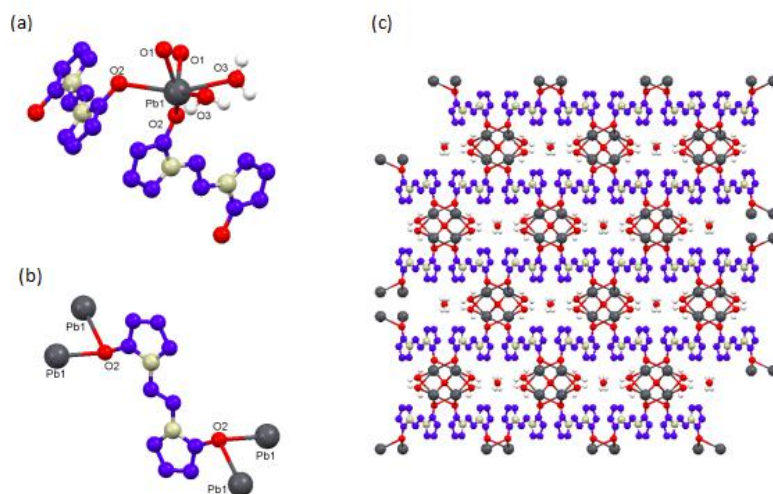


Figure S3. (a) Coordination environments of Pb in 2; (b) coordination model of AOT in 2; (c) 3D porous structure of 2.

Table S2 Bond lengths [\AA] and angles [$^\circ$] for compound 1

C1-N1	1.40(2)	N1-C1-N2	117(1)
C1-N2	1.34(2)	N1-C1-N5	133(1)
C1-N5	1.30(2)	N2-C1-N5	110(1)
N1-N1	1.28(2)	C1-N1-N1	111(1)
N2-N3	1.34(2)	C1-N2-N3	108(1)
N2-O2	1.33(1)	C1-N2-O2	129(1)
N3-N4	1.31(2)	N3-N2-O2	122(1)
N4-N5	1.35(2)	N2-N3-N4	105(1)
O1-Pb1	2.318	N3-N4-N5	111(1)
O2-Pb1	2.59(1)	C1-N5-N4	105(1)
O3-Pb1	2.63(1)	Pb1-O1-Pb1	100.8
O3-Pb1	2.92(1)	Pb1-O1-Pb1	117.7
		Pb1-O1-Pb1	110.7
		Pb1-O1-Pb1	100.1
		N2-O2-Pb1	123.7(8)
		N2-O2-Pb1	113.6(8)
		Pb1-O2-Pb1	88.9(3)
		H3A-O3-H3B	121
		H3A-O3-Pb1	118.5
		H3A-O3-Pb1	60.5
		H3B-O3-Pb1	120.7
		H3B-O3-Pb1	117.1
		Pb1-O3-Pb1	91.5(3)
		O1-Pb1-O2	72.6
		O1-Pb1-O3	96.3
		O1-Pb1-O1	79.5
		O1-Pb1-O2	142.4
		O1-Pb1-O3	70.2
		O2-Pb1-O3	157.2(3)
		O2-Pb1-O1	82.7
		O2-Pb1-O2	85.5(3)
		O2-Pb1-O3	122.2(3)
		O3-Pb1-O1	75.7
		O3-Pb1-O2	92.6(3)
		O3-Pb1-O3	69.4(3)
		O1-Pb1-O2	67.5
		O1-Pb1-O3	130.0
		O2-Pb1-O3	146.0(3)

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

C1-N1	1.37(2)	N1-C1-N3	119(2)
C1-N3	1.31(2)	N1-C1-N6	131(2)
C1-N6	1.36(2)	N3-C1-N6	109(2)
C2-N2	1.40(2)	N2-C2-N7	120(2)
C2-N7	1.32(2)	N2-C2-N10	129(2)
C2-N10	1.35(2)	N7-C2-N10	111(1)
C3-N13	1.36(2)	N13-C3-N16	109(1)
C3-N16	1.33(2)	N13-C3-N11	133(1)
C3-N11	1.38(2)	N16-C3-N11	111(1)
N1-N2	1.28(2)	C1-N1-N2	116(1)
N1-Pb1	2.91(1)	C1-N1-Pb1	117(1)
N3-N4	1.37(2)	N2-N1-Pb1	127(1)
N3-O1	1.31(2)	C2-N2-N1	112(1)
O1-Pb1	2.90(1)	C1-N3-N4	108(1)
O1-Pb2	2.57(1)	C1-N3-O1	131(1)
O2-Pb1	2.72(1)	N4-N3-O1	121(1)
O3-Pb1	2.77(1)	N3-N4-N5	106(1)
		N4-N5-N6	111(1)
		C1-N6-N5	105(1)
		C2-N7-N8	107(1)
		N7-N8-N9	105(1)
		N8-N9-N10	112(1)
		C2-N10-N9	104(1)
		C3-N13-N14	107(1)
		C3-N13-O3	126(1)
		N14-N13-O3	126(1)
		N13-N14-N15	106(1)
		N14-N15-N16	111(1)
		C3-N16-N15	107(1)
		N3-O1-Pb1	113.9(8)
		Pb1-O1-Pb2	124.0(4)
		N7-O2-Pb1	124(1)
		N13-O3-Pb1	120.1(9)
		H5A-O5-H5B	108

PXRD curves

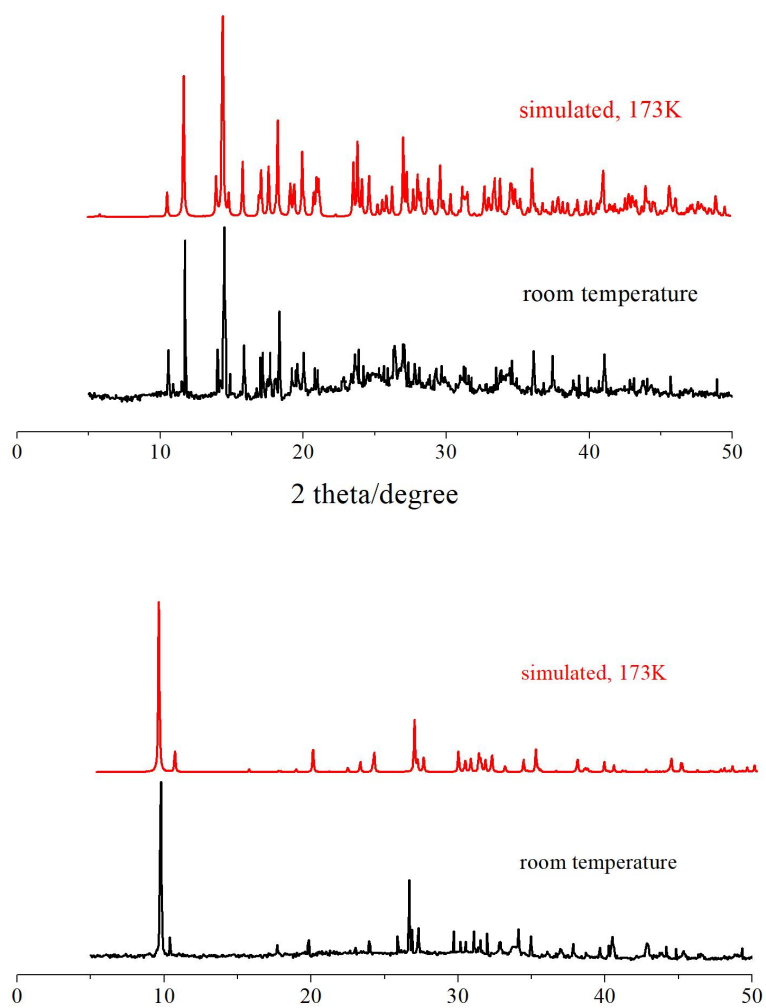


Figure S4. The PXRD curves for compound 1 and 2

Vibration spectroscopy

Infrared (IR) spectra were recorded on a Bruker FTTR instrument with KBr pellets (4000 - 400 cm^{-1})

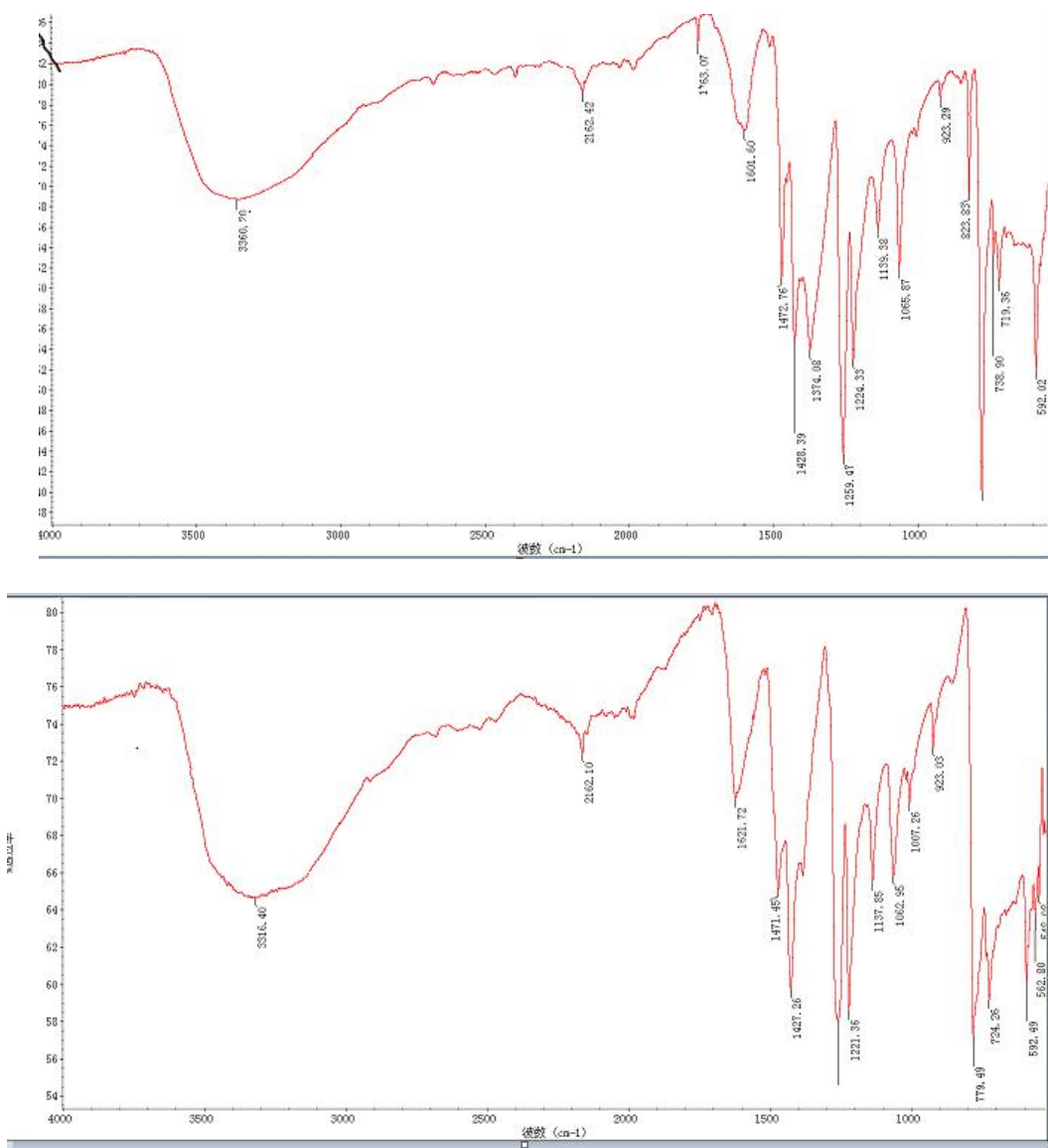


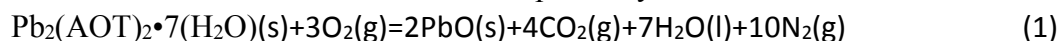
Figure S5 the IR curves of compound 1 and 2

Calculation of Detonation Properties

Oxygen bomb calorimetry and enthalpy of formation.

The constant-volume combustion energies ($\Delta_c U$) of compounds 1,2 were tested by an oxygen bomb calorimeter (Parr 6400, Parr Instrument Company, Moline Illinois, USA). Approximately 100-200 mg of the samples were pressed for the test. A well-define amount of benzoic acid (NIST Thermo chemical Standard 39j) was added to form a tablet which ensures better combustion. The standardization test is exactly the same as which was used for testing a EMOF sample. The average of five single measurements composed the recorded data.

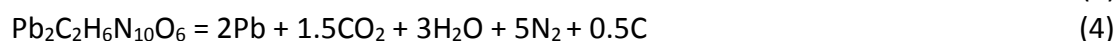
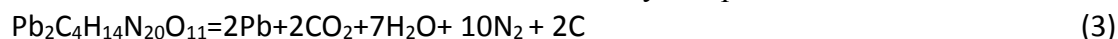
The $\Delta_c U$ values from experimental results is -2841.6 J g^{-1} and -2233.5 J g^{-1} respectively. According to the equation, $\Delta_c H_m^\theta = \Delta_c U_m^\theta + \Delta n RT$, $\Delta n = n_g(\text{products}) - n_g(\text{reactants})$ (n_g is the total molar amount of gases in the products or reactants, $R=8.314 \text{ J mol}^{-1} \text{ K}^{-1}$, and $T=298.15 \text{ K}$). The enthalpies of combustion $\Delta_c H_m$ can be calculated and the value are $-1311.6 \text{ KJ mol}^{-1}$ and $-1506.4 \text{ KJ mol}^{-1}$ respectively.



According to the enthalpies of combustion, the ideal combustion reactions and the enthalpies of formation of the combustion products¹ determined experimentally, $\text{PbO}(\text{s})$, $\Delta_c H_m^\theta(\text{PbO}, \text{s}) = (-219.50 \pm 0.27) \text{ kJ mol}^{-1}$, $\text{CO}_2(\text{g})$, $\Delta_c H_m^\theta(\text{CO}_2, \text{g}) = (-393.51 \pm 0.13) \text{ kJ mol}^{-1}$, $\text{H}_2\text{O}(\text{l})$, $\Delta_c H_m^\theta(\text{H}_2\text{O}, \text{l}) = (-285.830 \pm 0.04) \text{ kJ mol}^{-1}$, the standard enthalpies of formation $\Delta_f H$ of 1-2 are calculated to be $-1669.4 \text{ kJ mol}^{-1}$ and $-577.1 \text{ kJ mol}^{-1}$ on the basis of Hess's law, respectively.

Detonation properties

Detonation velocity (D) and detonation pressure (P) are the most important parameters to judge the performance of explosives. Professor Pang and coworkers has introduced a method for for calculating the detonation performance of metal-containing explosives like metal salts and E-CPs with the Kamlet–Jacobs (K–J) method and the Becker-Kistiakowsky-Wilson (BKW) equation.⁵ In this work ,this method is used to calculate the detonation velocity and pressure.



$$D = 1.01\phi^{1/2}(1 + 1.30\rho) \quad (5)$$

$$P = 1.558\phi\rho^2 \quad (6)$$

$$\Phi = 31.68N(\text{MQ})^{1/2} \quad (7)$$

$$Q = \frac{-(\Delta H_f(\text{detonation products}) - \Delta H_f(\text{explosive}))}{M_w} \quad (8)$$

where D is the detonation velocity, P is the detonation pressure, Q is the heat of detonation, N is the number of moles of the gas generated per gram, M is the average molecular weight of the gaseous product, and r is the crystal density.

As shown in Table 2, Q, D, P are calculated. 2 exhibits superior performance: D (8153 m s^{-1}), P (42Gpa) which is related to the particular structure. In addition, 1 exhibits rather good detonation properties: D (7362 m s), P (29Gpa).

REFERENCES

- S1 D. Fischer, T. M. Klapötke, D. G. Piercey, and J. Stierstorfer, *Chem. Eur. J.* 2013, 19, 4602–4613
- S2 SAINT v7.68A Bruker AXS inc.: Madison, WI (2009)
- S3 G. M. Sheldrick, SHELXL-2014/7, University of Gottingen, Germany (2014)
- S4 SADABS v2008/1 Bruker AXS Inc.: Madison, WI (2008)
- S5 M. J. Kamlet and S. T. Jacobs, *J. Chem. Phys.*, 1968, 48, 23-35