Reversible Dynamic Isomerism Change in Solid State, from Bi_4I_{16} Cluster to BiI_4 1D Chain in L-cystin Based Hybrids: Templating Effect of Cations in Iodobismuthate Network Formation

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Supporting Information

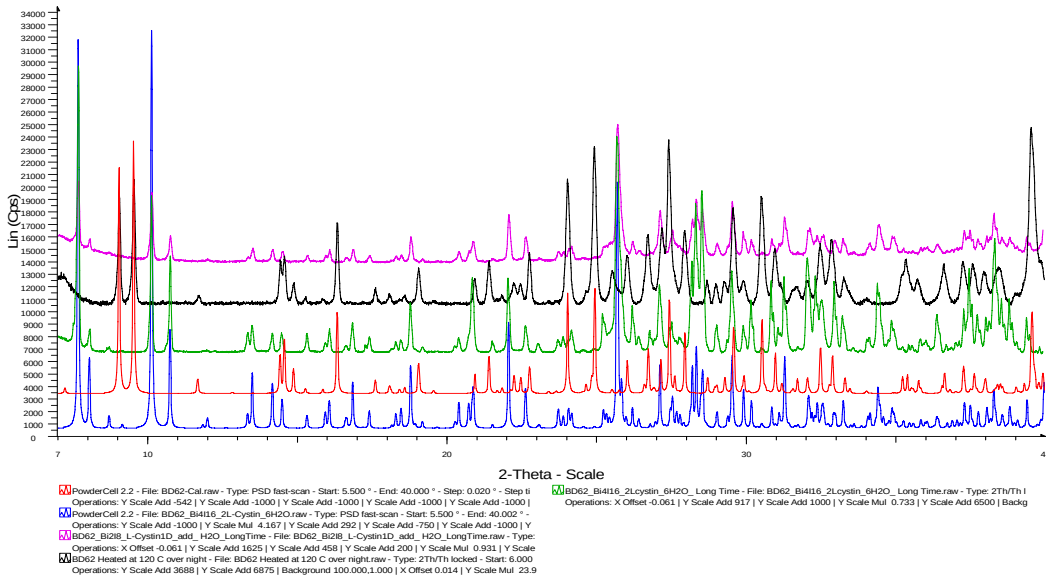

Fig S1. The X-ray Powder Diffraction of **1** and **2** (7-40° 2θ range)

From bottom to top: The calculated pattern of compound 1 (Blue, Bi_4I_{16}_2Lcystin_$6H_2O$) ; The calculated pattern of compound 2 (Red, Bi_2I_8_Lcystin) ; The experimental pattern of compound 1 (Green); The experimental pattern of compound 2 (Black, Heat 1 at 120°C for 2 hours); The experimental pattern of the recovered phase of 1 (Purple, Compound in the vapor of H_2O for 5 days).

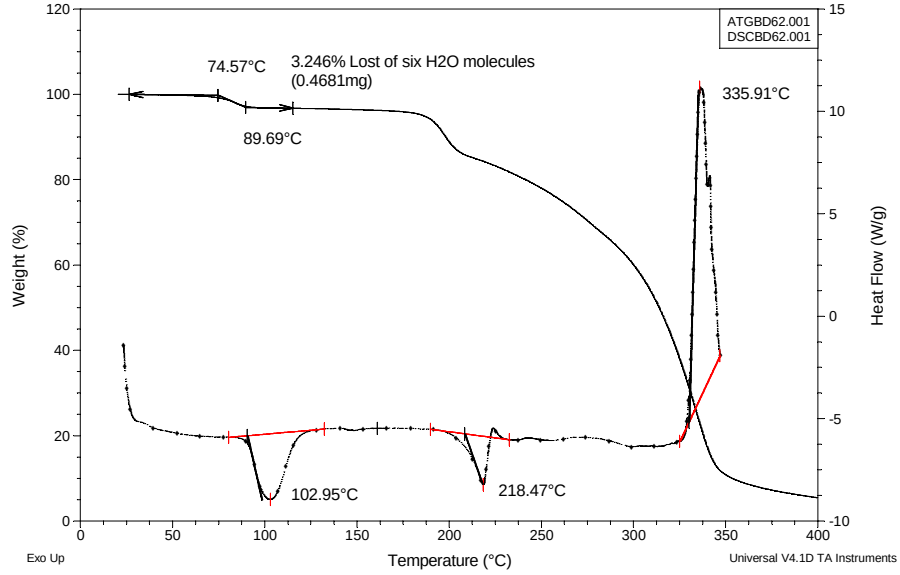

Fig S2. The TGA and DSC of Compound **2**.

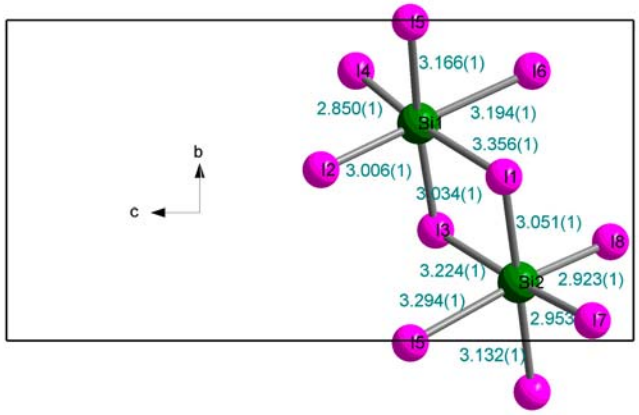

Fig S3. The $[Bi_1I_4]_n$ chain in compound 1.

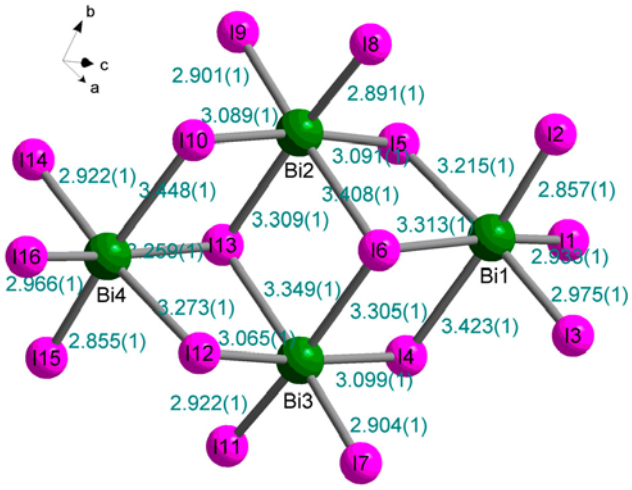

Fig S4. Bi_4I_{16} cluster in compound 2.

Crystallographic experiments

1- Summary of cristallographic data and refinements

‡**Crystal data for 1**: $C_6H_{14}O_4N_2S_2Bi_2I_8$, M = 1675.47, monoclinic, a = 12.317(3) Å, b = 7.763(2) Å, c = 15.223(3) Å, β = 93.07(3)° V = 1453.6(6) Å^3, space group $P2_1$, Z = 2, crystal size (mm3): 0.26 × 0.08 × 0.06; **Crystal data for 2**: $C_{12}H_{40}Bi_4I_{16}N_4O_{14}S_4$, M = 3459.08, monoclinic, a = 11.280(2) Å, b = 20.396(4) Å, c = 14.375(3) Å, β = 101.79(3)° V = 3237.4(11) Å^3, $P2_1$, Z = 2, crystal size (mm3): 0.16 × 0.08 × 0.02.
Data of both 1 and 2 are collected at T = 296(2) K, on a Bruker nonius KappaCCD diffractometer, graphite-monochromated MoKa radiation (λ = 0.71073 Å). The structures were refined by full-matrix least-squares routines against F^2 using the SHELXL97 package. No non-crystallographic inversion center was detected by the ADDSYM routine. The hydrogen atoms were treated with a riding model. In **2**, H atoms of water could not be located in difference Fourier map. The refinements of positions and anisotropic thermal motion parameters of the non-H atoms, converge to $R_{(F)}$ = 0.044 (8773 reflections (48600 collected (R(int)= 0.044)), 222 parameters), $wR2_{(F2)}$ = 0.082 (all data), GOF on F^2 is 1.068, $\Delta\rho_{max}$ = 1.46 e Å^{-3} for **1**; and to $R_{(F)}$ = 0.038 (15908 reflections (93175 collected (R(int)= 0.055)) , 496 parameters), $wR2_{(F2)}$ = 0.054 (all data), GOF on F^2 is 1.059, $\Delta\rho_{max}$ = 1.34 e Å^{-3} for **2**. CCDC 695943 (**1**) and 695944 (**2**).

2- Table S1. Crystal data and structure refinement for (1): Bi2I8-Lcystin.

Empirical formula	$C_6H_{14}Bi_2I_8N_2O_4S_2$
Formula weight	1675.47
Temperature	296(2) K
Wavelength	0.71073 A
Crystal system, space group	monoclinic, P2(1)
Unit cell dimensions	a = 12.317(3) A alpha = 90 deg.
	b = 7.763(2) A beta = 93.07(3) deg.
	c = 15.223(3) A gamma = 90 deg.
Volume	1453.6(5) A^3
Z, Calculated density	2, 3.828 Mg/m^3
Absorption coefficient	20.741 mm^-1
F(000)	1436
Crystal size	0.26 x 0.08 x 0.06 mm
Theta range for data collection	3.07 to 30.50 deg.
Limiting indices	-16<=h<=17, -11<=k<=11, -21<=l<=21
Reflections collected / unique	48600 / 8773 [R(int) = 0.0445]
Completeness to theta = 30.50	99.6 %
Max. and min. transmission	0.369 and 0.075
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8773 / 1 / 222
Goodness-of-fit on F^2	1.068
Final R indices [I>2sigma(I)]	R1 = 0.044, wR2 = 0.072
R indices (all data)	R1 = 0.077, wR2 = 0.082
Absolute structure parameter	-0.022(5)
Extinction coefficient	0.00026(3)
Largest diff. peak and hole	1.46 and -1.33 e.A^-3

3- Table S2. Crystal data and structure refinement for (2):

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Bi4I16_L-cystin_6H2O.

Empirical formula	$C_{12}H_{40}Bi_4I_{16}N_4O_{14}S_4$
Formula weight	3459.08
Temperature	296(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P 21
Unit cell dimensions	a = 11.280(2) A alpha = 90 deg.
	b = 20.396(4) A beta = 101.79(3) deg.
	c = 14.375(3) A gamma = 90 deg.
Volume	3237.4(11) A^3
Z, Calculated density	2, 3.549 Mg/m^3
Absorption coefficient	18.639 mm^-1
F(000)	2992
Crystal size	0.16 x 0.08 x 0.02 mm
Theta range for data collection	2.90 to 28.28 deg.
Limiting indices	-15<=h<=15, -27<=k<=27, -19<=l<=19
Reflections collected / unique	93175 / 15908 [R(int) = 0.0547]
Completeness to theta = 28.28	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.689 and 0.182
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	15908 / 1 / 496
Goodness-of-fit on F^2	1.059
Final R indices [I>2sigma(I)]	R1 = 0.038, wR2 = 0.046
R indices (all data)	R1 = 0.071, wR2 = 0.054
Absolute structure parameter	-0.026(3)
Extinction coefficient	0.000303(7)
Largest diff. peak and hole	1.34 and -1.18 e.A^-3