

Bis(4-cyano-1-pyridino)pentane halobismuthates.

Light-harvesting material with an optical band gap of 1.59 eV

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Synthesis of bis(4-cyano-1-pyridino)pentane bromide.

Bis(4-cyano-1-pyridino)pentane bromide was synthesized from 4-pyridinecarbonitrile (Aldrich 98%) and 1,5-dibromopentane $C_5H_{10}Br_2$ (Aldrich 97%). The reaction mixture of 5 ml 1,5-dibromopentane, 10 ml acetonitrile and 20 g of 4-pyridinecarbonitrile was refluxed for 1 h. After the mixture had been cooled down to room temperature, 100 ml of 95% ethyl alcohol was added and the mixture was boiled for another 3-5 min. The hot solution was filtered under the vacuum. The supernatant solution was stored for another 24 h. The precipitate formed during this period was separated, washed with acetone, and then dried in air. **Bis(4-cyano-1-pyridino)pentane bromide** ($C_{17}H_{18}N_4$)Br₂ (**PyC₅Br₂**) was isolated as a light-yellow precipitate (67.8% yield, content of main component – 99%, NMR). ¹H NMR (300 MHz, D₂O): 9.13 (d, 4H), 8.45 (d, 4H), 4.71 (t, 4H), 2.10 (m, 4H), 1.47(p, 2H).

Synthesis of bis(4-cyano-1-pyridino)pentane bromobismuthate.

The solution of 2.05 g **PyC₅Br₂** and 11.9 g KBr in 25 ml of water was added to reaction mixture of 23.8 g KBr, 4.75 g Bi(NO₃)₃·5H₂O and 75 ml of water. The solution was filtered under vacuum immediately after mixing. The filtered milky-white precipitate (**bis(4-cyano-1-pyridino)pentane bromobismuthate, 1**) was washed with water and ethanol, and then dried at room temperature. The composition of precipitate **1**, ($C_{17}H_{18}N_4$)₂Bi₂Br₁₀ (4.01 g, 96.6%), was confirmed by NMR (Fig. S1 in ESI[†]), EDX (Fig. S5 in ESI[†]) and DTG (Fig. S3a in ESI[†]).

Synthesis of bis(4-cyano-1-pyridino)pentane iodobismuthate.

The solution of 2.02 g $C_{17}H_{18}N_4$ Br₂ and 16.6 g KI in 25 ml of water was added to reaction mixture of 33.2 g KI, 4.75 g Bi(NO₃)₃·5H₂O in 75 ml of water. Formed black precipitate (**bis(4-cyano-1-pyridino)pentane iodobismuthate, 2**) was filtered, washed with water and ethanol, and then dried at room temperature. The composition of precipitate **2**, ($C_{17}H_{18}N_4$)BiI₅ (4.25 g, 82.2 %), was confirmed by NMR (Fig. S2 in ESI[†]), EDX (Fig. S6 in ESI[†]) and DTG (Fig. S3b in ESI[†]).

Table S1 Selected bond lengths [Å] and angles [°] for **1**, **3**, **4**.**1**

Bi(1)-Br(2)	2.719(2)
Bi(1)-Br(2)#1	2.719(2)
Bi(1)-Br(3)	2.8738(18)
Bi(1)-Br(3)#1	2.8739(18)
Bi(1)-Br(1)#2	3.031(2)
Bi(1)-Br(1)	3.031(2)
Br(1)-Bi(1)#2	3.031(2)

Br(2)-Bi(1)-Br(2)#1	95.94(10)
Br(2)-Bi(1)-Br(3)	86.27(5)
Br(2)#1-Bi(1)-Br(3)	92.48(5)
Br(2)-Bi(1)-Br(3)#1	92.48(5)
Br(2)#1-Bi(1)-Br(3)#1	86.27(5)
Br(3)-Bi(1)-Br(3)#1	178.15(7)
Br(2)-Bi(1)-Br(1)#2	170.66(4)
Br(2)#1-Bi(1)-Br(1)#2	88.92(7)
Br(3)-Bi(1)-Br(1)#2	85.56(4)
Br(3)#1-Bi(1)-Br(1)#2	95.78(4)
Br(2)-Bi(1)-Br(1)	88.92(6)
Br(2)#1-Bi(1)-Br(1)	170.67(4)
Br(3)-Bi(1)-Br(1)	95.79(4)
Br(3)#1-Bi(1)-Br(1)	85.56(4)
Br(1)#2-Bi(1)-Br(1)	87.41(8)
Bi(1)-Br(1)-Bi(1)#2	92.59(8)

Symmetry transformations used to generate equivalent atoms:

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

I(1)-I(2)	2.9025(4)
I(2)-I(3)	2.9226(4)
I(1)-I(2)-I(3)	178.576(15)

4

Bi(1)-I(1)	3.0759(3)
Bi(1)-I(1)#1	3.0759(3)
Bi(1)-I(3)	3.0801(3)
Bi(1)-I(3)#1	3.0801(3)
Bi(1)-I(2)	3.0875(3)
Bi(1)-I(2)#1	3.0875(3)

I(1)-Bi(1)-I(1)#1	92.237(13)
I(1)-Bi(1)-I(3)	91.252(8)
I(1)#1-Bi(1)-I(3)	172.418(8)
I(1)-Bi(1)-I(3)#1	172.418(8)
I(1)#1-Bi(1)-I(3)#1	91.252(8)
I(3)-Bi(1)-I(3)#1	86.097(12)
I(1)-Bi(1)-I(2)	96.643(9)
I(1)#1-Bi(1)-I(2)	83.845(8)
I(3)-Bi(1)-I(2)	89.066(8)
I(3)#1-Bi(1)-I(2)	90.422(8)
I(1)-Bi(1)-I(2)#1	83.846(8)
I(1)#1-Bi(1)-I(2)#1	96.644(9)
I(3)-Bi(1)-I(2)#1	90.422(8)
I(3)#1-Bi(1)-I(2)#1	89.066(8)
I(2)-Bi(1)-I(2)#1	179.299(14)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,y,-z+1/2

Table S2 Selected torsion angles [°] for **1**, **3**, **4**.

1	
C(5)-N(1)-C(6)-C(7)	-115(2)
C(1)-N(1)-C(6)-C(7)	63(3)
N(1)-C(6)-C(7)-C(8)	178(2)
C(6)-C(7)-C(8)-C(7)#1	-70.0(19)

Symmetry transformations used to generate equivalent atoms:
#1 -x+3/4,-y+3/4,z

3	
C(1)-N(1)-C(6)-C(7)	-127.0(4)
C(5)-N(1)-C(6)-C(7)	56.8(6)
N(1)-C(6)-C(7)-C(8)	176.4(3)
C(6)-C(7)-C(8)-C(7)#1	176.6(4)

Symmetry transformations used to generate equivalent atoms:
#1 -x,y,-z+1/2

4	
C(1)-N(1)-C(6)-C(7)	81.2(5)
C(5)-N(1)-C(6)-C(7)	-100.3(5)
N(1)-C(6)-C(7)-C(8)	70.8(5)
C(6)-C(7)-C(8)-C(7)#1	-177.1(4)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,y,-z+1/2

¹H NMR spectra of bis(4-cyano-1-pyridino)pentane halobismuthates

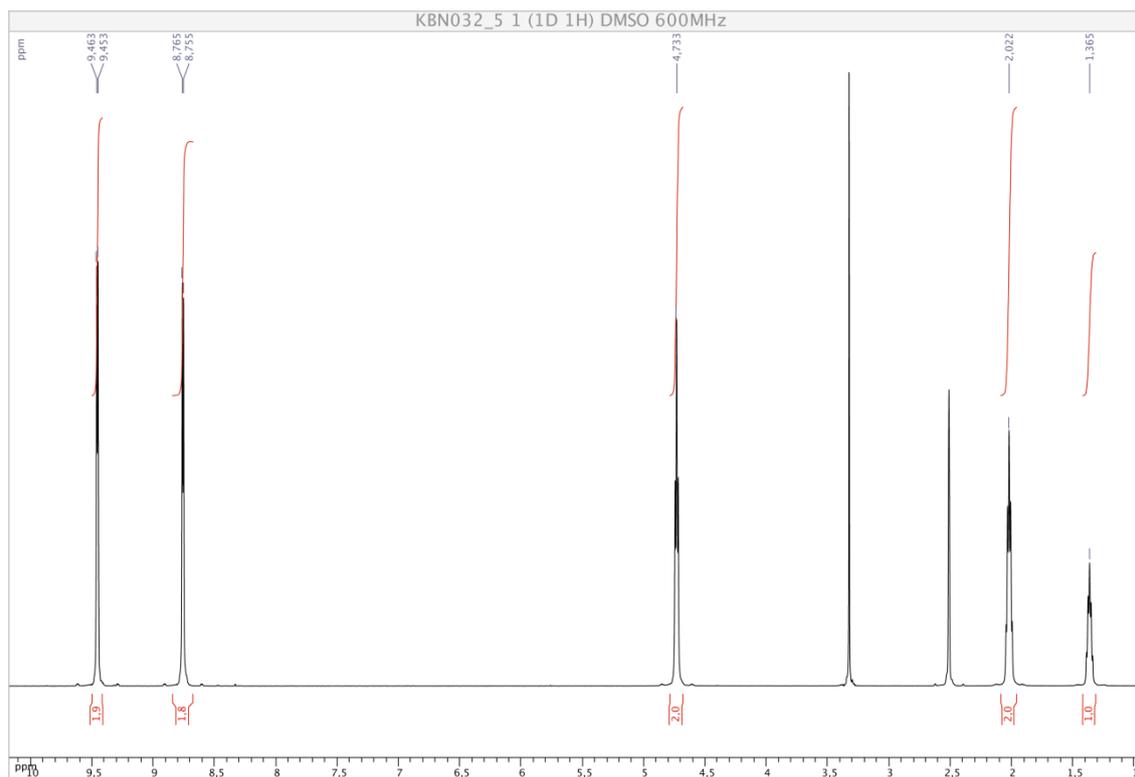


Figure S1 ¹H NMR spectrum of **1** in DMSO-d₆.

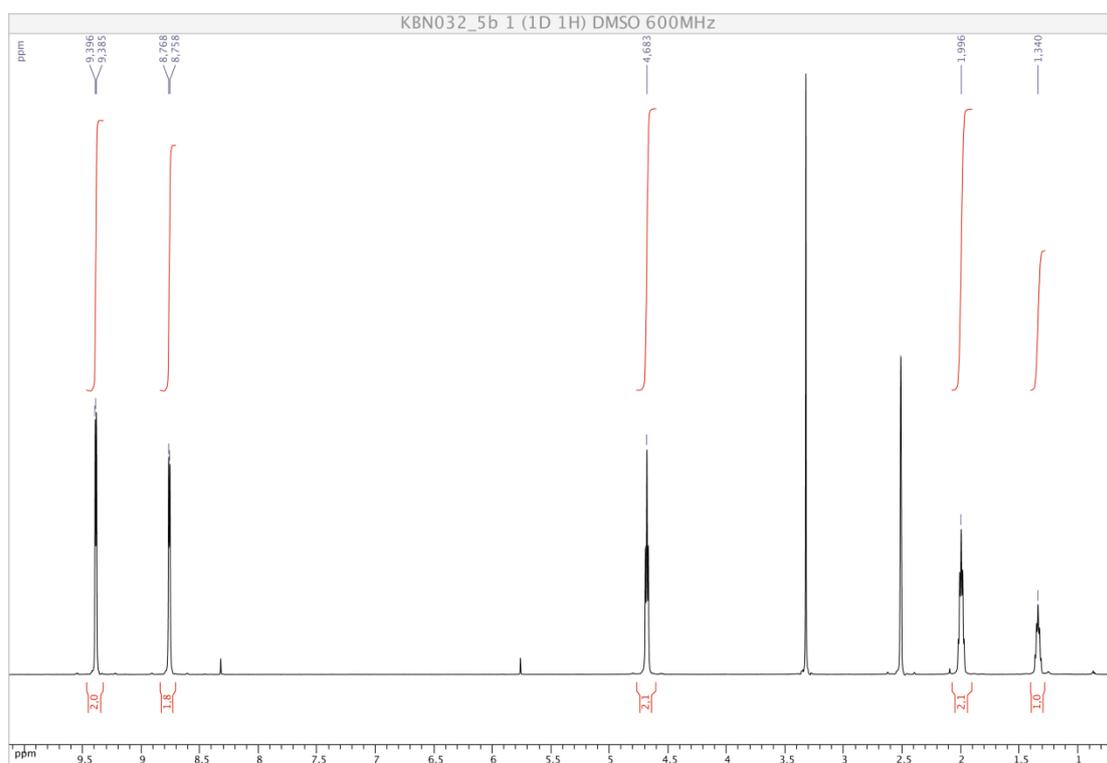
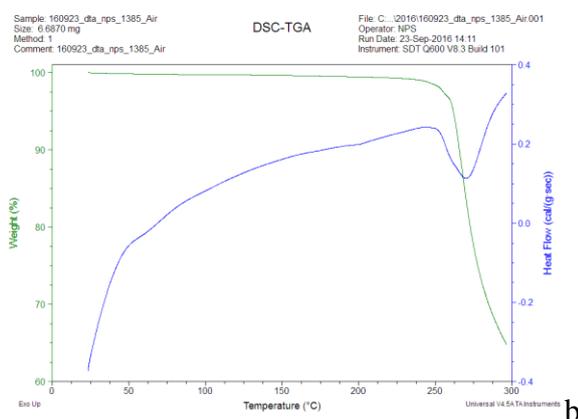
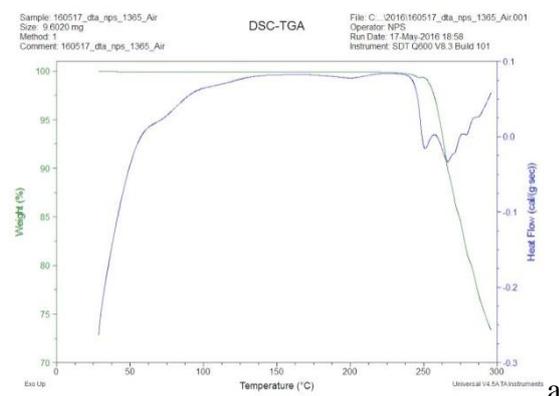


Figure S2 ¹H NMR spectrum of **2** in DMSO-d₆.

The thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were performed using an SDT Q600 V8.3 Build 101 Module DSC-TGA thermal analyzer instrument. The samples were heated from 25 to 300 °C at a rate of 10 K min⁻¹ in an atmosphere of Ar. X-ray powder diffraction patterns were recorded with a Bruker D8 Advance diffractometer with a horizontal goniometer axis using CuK α radiation in the 2θ range 3–120° at a 2θ step of 0.01–0.02° and a counting time of 0.3–0.5 s per step. Full-profile analysis of the XRD patterns of crystalline substances was performed using the TOPAS 4.2 software. Fourth-order Chebyshev polynomials were used to fit the background. The overall fitting was performed using a fundamental parameter approach. The compounds were analyzed by energy-dispersive X-ray spectroscopy (EDX) with a Carl Zeiss NVision 40 scanning electron microscope equipped with an Oxford Instruments X-Max detector at an accelerating voltage of 20 kV.

Thermal stability of bis(4-cyano-1-pyridino)pentane halobismuthates and bis(4-amido-1-pyridino)pentane dihydronium iodobismutate dihydrate



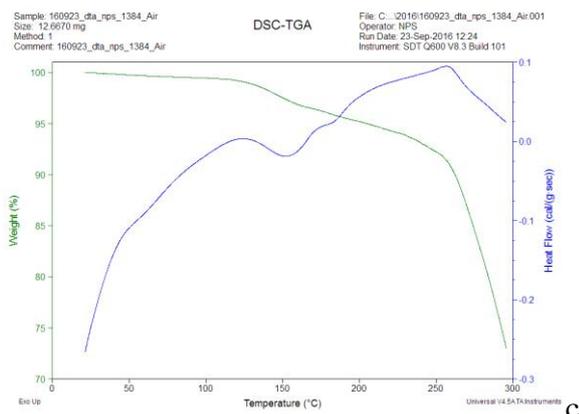


Figure S3 TGA and DTA curves of **1** (a), **2** (b), **4**(c).

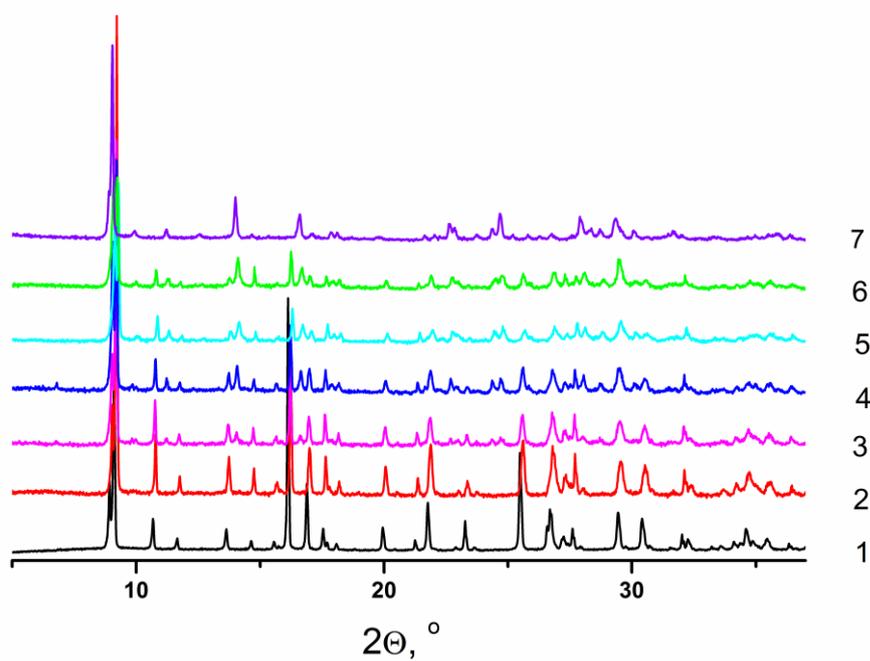
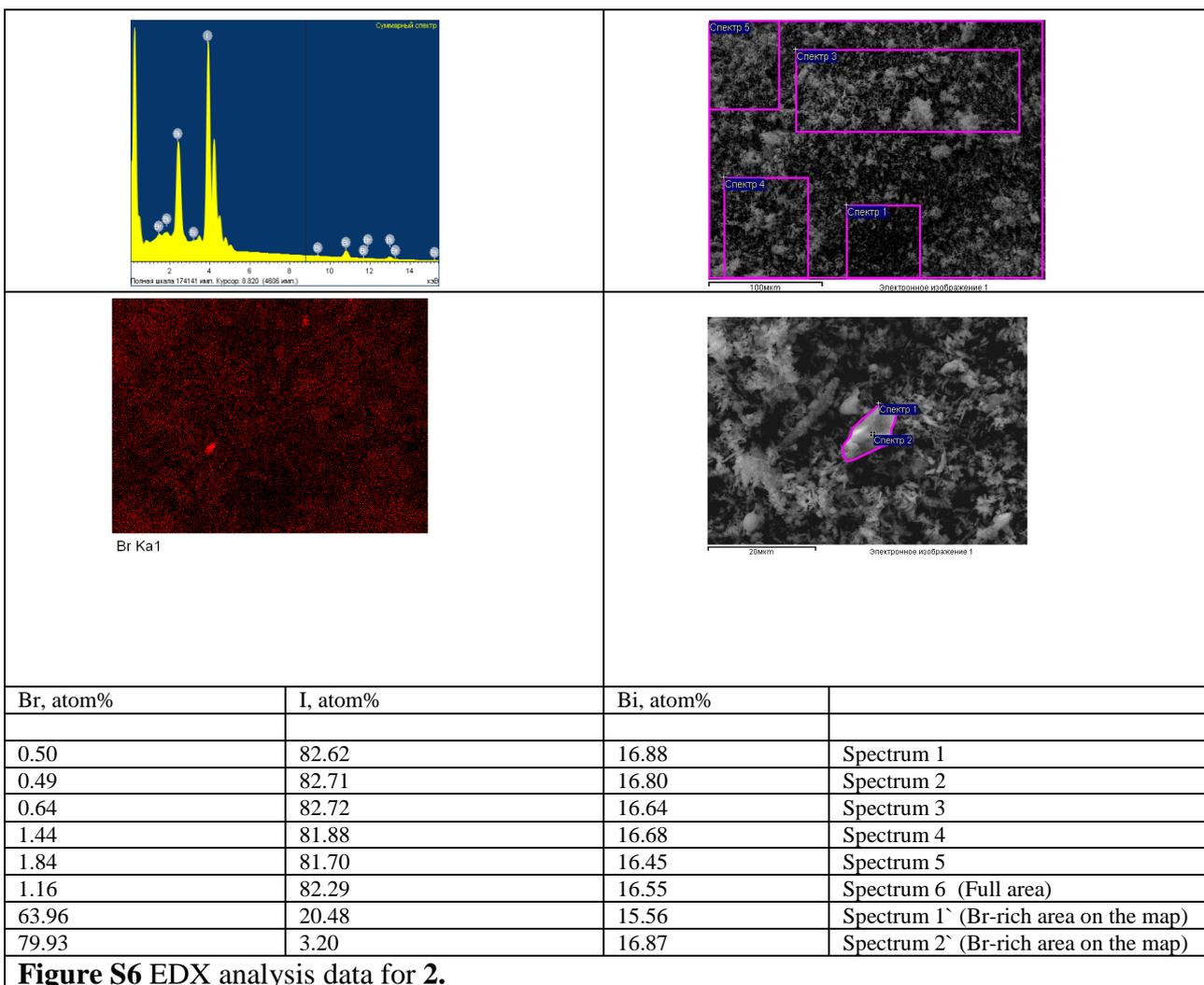
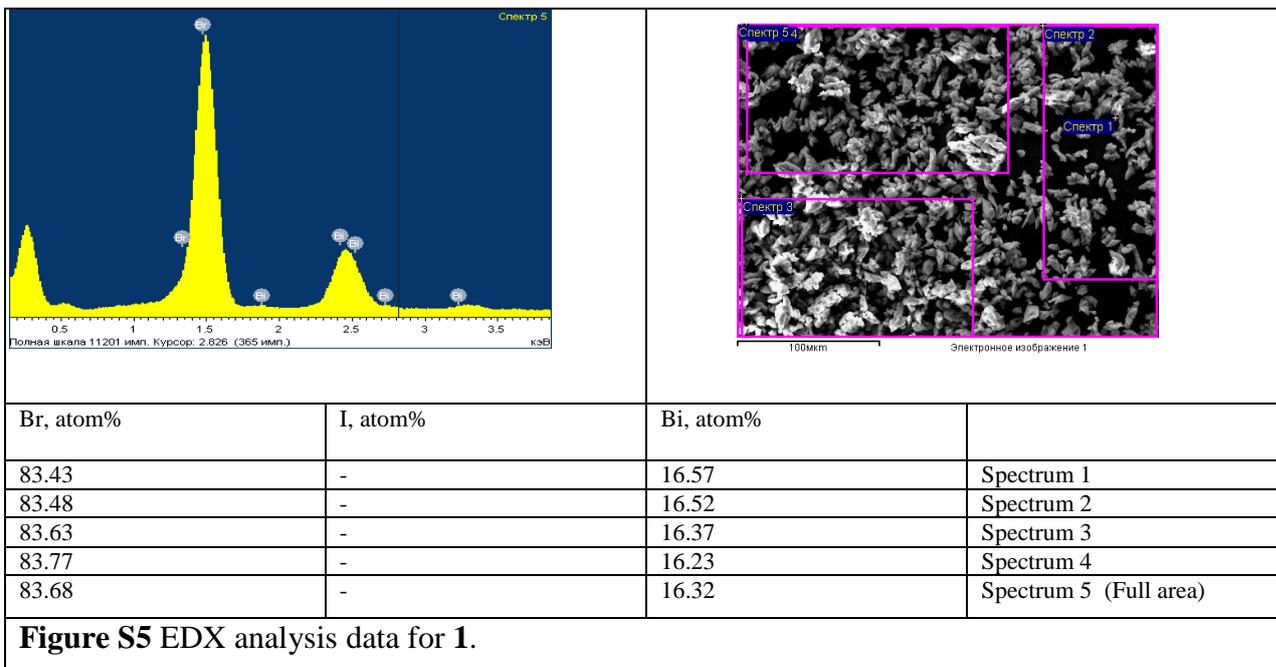


Figure S4 XRD patterns of **1** (1), **2a** (2), **2b** (3) **2c** (4), **2d** (5), **2e** (6), **2**(7). Samples **2a-2e** correspond to incomplete transition of **1** to **2**.



X-ray analysis of powders

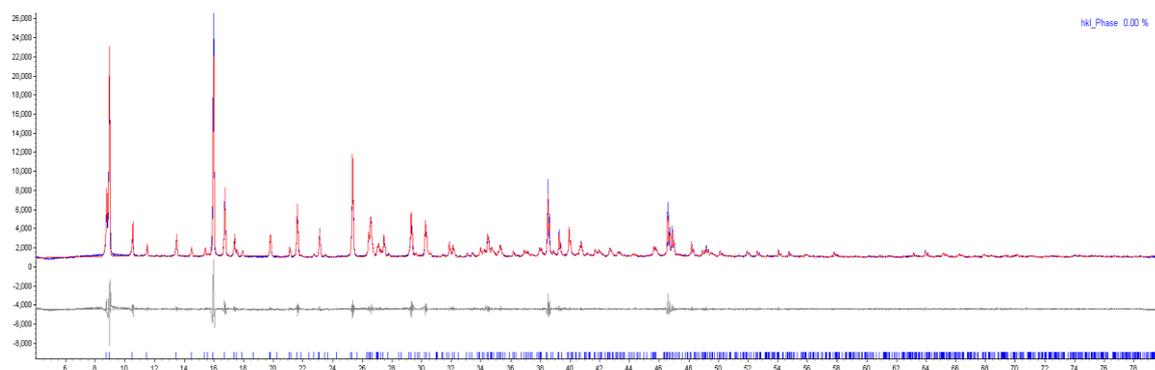


Figure S7 X-ray Rietveld refinement profiles for **1** recorded at room temperature. Red and blue lines correspond to the calculated profile and experimental pattern respectively. The bottom trace shows the difference curve. The vertical bars indicate the calculated positions of the Bragg peaks.

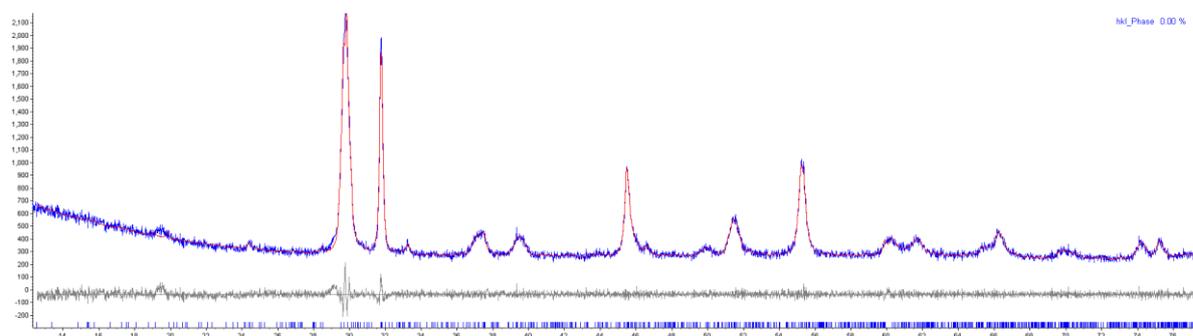


Figure S8 X-ray Rietveld refinement profiles for **4** recorded at room temperature. Red and blue lines correspond to the calculated profile and experimental pattern respectively. The bottom trace shows the difference curve. The vertical bars indicate the calculated positions of the Bragg peaks.