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Hybrid halobismuthates: a coordinated $BrIBr^-$ anion

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Synthesis of Bis(1-pyridino)hexane bromide

Bis(1-pyridino)hexane bromide (**PyC_6Br_2**) was synthesized from pyridine (Aldrich 98%) and 1,6-dibromohexane $C_6H_{12}Br_2$ (Aldrich 96%). The reaction mixture of 5 ml 1,6-dibromohexane and 20 ml of pyridine was stirred for one day. The filtered precipitate was washed with acetonitrile and ethanol and then dried at room temperature (overall yield: 10.91 g, 83.5%).

Synthesis of bis(1-pyridino)hexane bromobismuthate (1)

The solution of PyC_6Br_2 (0.603 g) in 3 ml of concentrated HBr was added to 10 ml of 0.1 M $BiBr_3$ solution in concentrated HBr and kept in air at room temperature for 3 days. The lemon-yellow crystals of **1** were decanted, washed with acetonitrile and ethanol and then dried at room temperature (overall yield: 0.932 g, 88.6%).

Synthesis of bis(1-pyridino)hexane bromobismuthate (2)

The solution of PyC_6Br_2 (2.00 g) and KBr (11.9 g) in 25 ml of water was added to the mixture of KBr (23.8 g) and $Bi(NO_3)_3 \cdot 5H_2O$ (4.75 g) in 75 ml of water. The solution was filtered under vacuum. The lemon-yellow precipitate **2** was washed with acetonitrile and ethanol and then dried at room temperature (yield: 4.22 g).

The reaction between 1 and concentrated HBr in the presence of HI vapor and the products of HI oxidation on air

The solution of **2** (1.00 g) in 10 ml of concentrated HBr was kept in air at room temperature for one week. The solutions of organic cation iodides in concentrated HBr were kept in air near our reaction vessel. The single crystals of byproduct **3** were found in a mixture with crystals of **1** when they were decanted, washed with acetonitrile and ethanol and then dried at room temperature.

The reflectance spectra were measured with a Cary 5000 spectrophotometer in a range of 200-1000 nm at room temperature. The thermo gravimetric analysis (TGA) and differential thermal analysis (DTA) were carried out using an SDT Q600 V8.3 Build 101 Module DSC-TGA thermal analyzer instrument. The samples were heated from 25 to 300ºC at a rate of 10 K/min in air in an open alumina pan. X-ray powder diffraction patterns were recorded with a Bruker D8 Advance diffractometer with a horizontal goniometer axis (CuK_α, Ni-filter, LYNXEYE detector, reflection geometry) in a 2θ range of 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 X-ray diffraction patterns of crystalline substances was performed using the TOPAS 4.2 software.[1] Fourth-order Chebyshev polynomials were used to fit the background. The overall fitting was performed using the fundamental parameter approach. Chemical composition of powder was analyzed by energy-dispersive X-ray spectroscopy (EDX) with a Jeol JSM 6610LV scanning electron microscope (SEM) equipped with an Oxford Instruments Inca X-max20 detector at a 20 kV accelerating voltage in low vacuum mode (P = 50Pa). Polypropylene tablets were used as a support during EDX measurements.

Thermal stability of bis(1-pyridino)hexane bromobismuthates

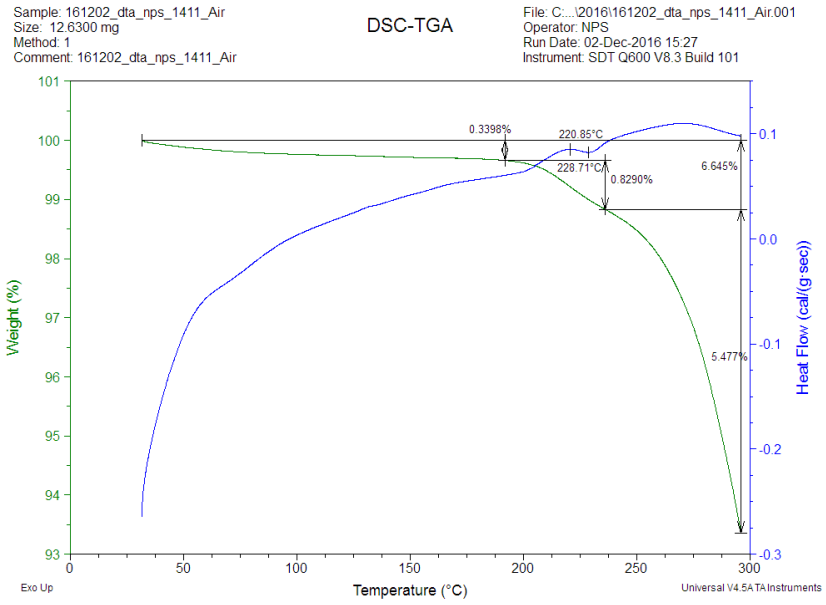

Figure S1 TGA and DTA curves of **2**.

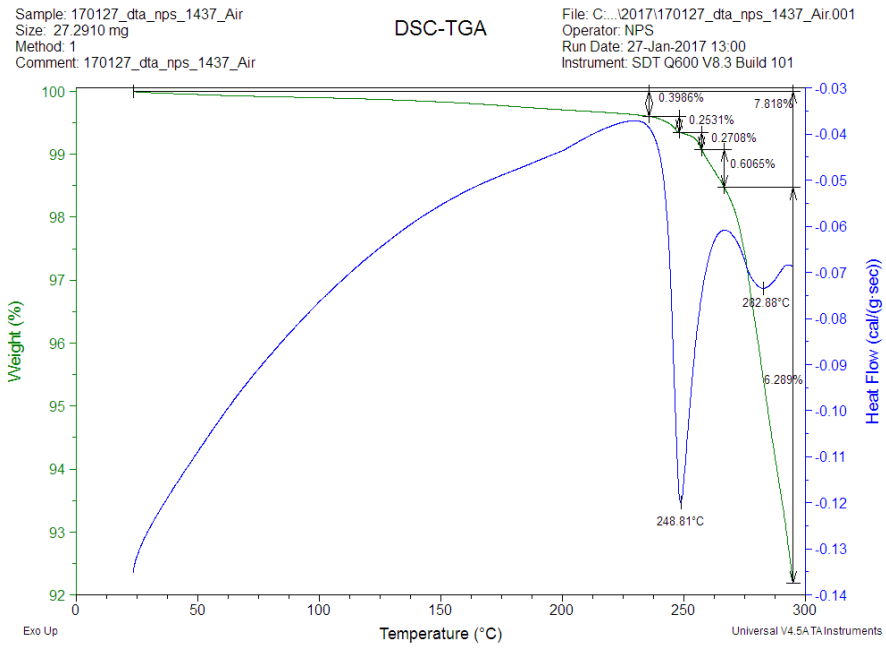

Figure S2 TGA and DTA curves of **1 .**

EDX analysis data

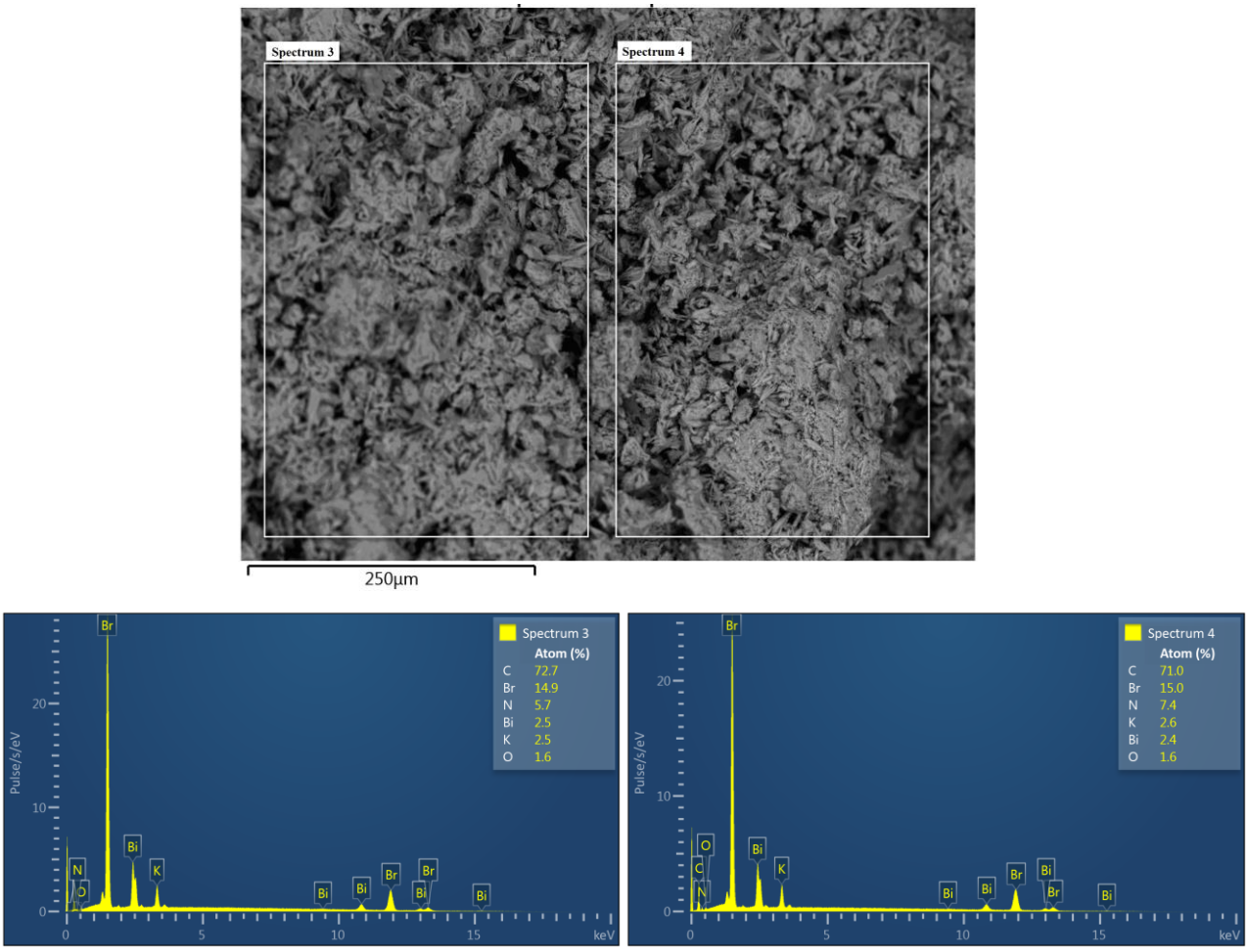

Figure S3 EDX analysis data for **2.**

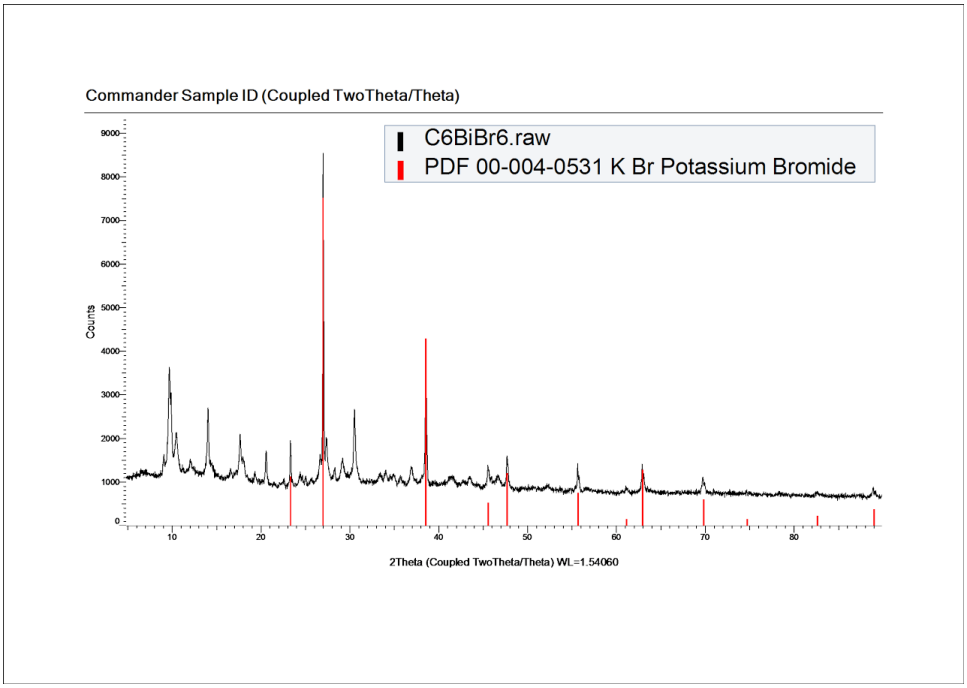

Figure S4 XRD data for product **2.** Red lines correspond to KBr.

Reflectance spectra

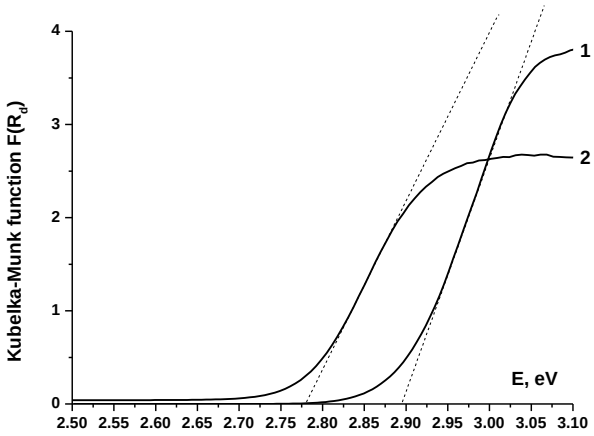

Figure S5 Reflectance spectra of **1**(1) and **2** (2). The Kubelka-Munk function is defined by[2] $F(R_d) = \frac{(1-R_d)^2}{2R_d}$, where R_d is absolute reflectance of the sample layer.

References

1 A. A. Coelho, *TOPAS, Version 4.2 (Computer Software)*, Coelho Software, Brisbane, Australia, 2009.

2 P. Kubelka and F. Munk, *Z. Tech. Phys.*, 1931, **12**, 593.