

Supplementary Information

Taking Bismuthinite to Bismuth Sulfide Nanorods in Two Easy Steps

Dimuthu C. Senevirathna, Victoria L. Blair, Melissa V. Werrett and Philip C. Andrews

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Experimental

General Considerations

All chemicals were purchased from Sigma Aldrich and used as received, unless otherwise stated. THF was dried prior to use by an M-Braun-SPS-800 solvent purification system and stored over molecular sieves (4Å). ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance III 400 spectrometer with a 9.4 Tesla magnet (400.13 MHz for ^1H) at room temperature. The spectra were recorded with a 5 mm broadband autotunable probe with Z-gradients and a BACS 60 tube autosampler. All spectra were internally referenced using the deuterated solvent signal. Infrared spectra were recorded on an Agilent Technologies Cary 630 FTIR spectrometer in the range of 4000-500 cm^{-1} . IR frequencies are reported in wavenumbers with the relative intensities indicated as strong (s), medium (m) or weak (w). Elemental microanalyses were performed by the Campbell Microanalytical Laboratory, Department of Chemistry, University of Otago, Dunedin, New Zealand. Melting points were measured (uncalibrated) on a Stuart Scientific SMP10 digital melting point apparatus but were confirmed by differential scanning calorimetry (DSC) measurements carried out using a TA Q100 DSC between 40 °C and 300 °C, with a temperature ramp rate of 10°C per minute. Mass spectrometry (ESI) was performed on a Micromass Platform QMS spectrometer with an electrospray source and a cone voltage of 35 eV. Samples were analysed in DMSO.

TEM, HRTEM and SAED observations were carried out using an FEI Tecnai G2 F20 S-Twin FEGTEM operating at 200 kV and incorporating a Bruker X-Flash silicon drift X-ray detector for EDS analysis. Samples were dispersed in either hexane or ethanol and a small amount was deposited on a holey-carbon coated copper grid.

p-Toluenemagnesium bromide was prepared from *p*-bromotoluene (0.05 mol) and magnesium turnings (0.055 mol) in THF (100 mL) at 0 °C.¹

4-Methylbenzodithioic acid and 4-methoxybenzodithioic acid were prepared according to previously published methods.^{2,3} Using standard Schlenck techniques, dry THF (50 mL) was added to the appropriate Grignard reagent (0.05 mol) and cooled in an ice bath. Carbon disulfide (0.09 mol) was slowly added to the Grignard reagent and stirred at 0 °C for one hour. The reaction mixture was then poured over ice (100 g) and concentrated HCl (50 mL). The resultant dark red solution was extracted with diethyl ether (4 x 50 mL). The organic phase was dried over anhydrous magnesium sulfate. Removal of the solvent *in vacuo* gave the corresponding aryldithioic acid as a dark red oil or dark red precipitate. The aryldithioic acids were used soon after synthesis due to their known instability.^{2,3}

Synthesis of the bismuth(III) benzodithioates

General procedure

Bi₂S₃ (0.25 mmol, 1 eq.) was added to a solution of the aryldithioic acid (1.5 mmol, 6 eq.) in toluene (15 mL) and the reaction was placed in a sonicator for 4-6 hours. The reaction was filtered and a dark red solid was collected and washed with acetone. The crude solid was dissolved in hot toluene and left for crystallisation by slow evaporation.

Bismuth tris(4-methylbenzodithioate) [Bi(S₂C(C₆H₄)-4-CH₃)₃] (1)

The general procedure was carried out using Bi₂S₃ (0.129g, 0.25 mmol) and 4-methylbenzodithioic acid (0.252 g, 1.5 mmol). After three days, dark red crystals were obtained. 0.221 g, 62% yield m.p. 218 °C (decomp). ¹H NMR (400 MHz, DMSO-d₆, 25 °C): δ = 8.06 (d, ³J = 9 Hz, 6H, *o*-CH), 7.27 (d, ³J = 9 Hz, 6H, *m*-CH), 2.33 (s, 9H, CH₃). ¹³C NMR (100 MHz, DMSO-d₆, 25 °C): δ = 146.8 (CCH₃), 144.5 (CCS₂), 128.4 (*m*-CH), 125.9 (*o*-CH), 21.1 (CH₃). ν_{max} FTIR (cm⁻¹): 2962 m, 2912 m, 2722 m, 2591 w, 2450 w, 2389 m, 2302 w, 2115 m, 2084 m, 1919 w, 1594 s, 1561 m, 1468 m, 1443 m, 1401 m, 1381 w, 1304 s, 1261 s, 1216 s, 1173 s, 1092 s, 1006 s, 969 m, 904 s, 816 s, 725 s, 684 s. MS (ESI)⁺ *m/z* 543 [Bi(S₂C(C₆H₄)-4-CH₃)₂]⁺. Elemental analysis for C₂₄H₂₁BiS₆: calculated: C 40.56, H 2.98; found: C 40.43, H 2.81.

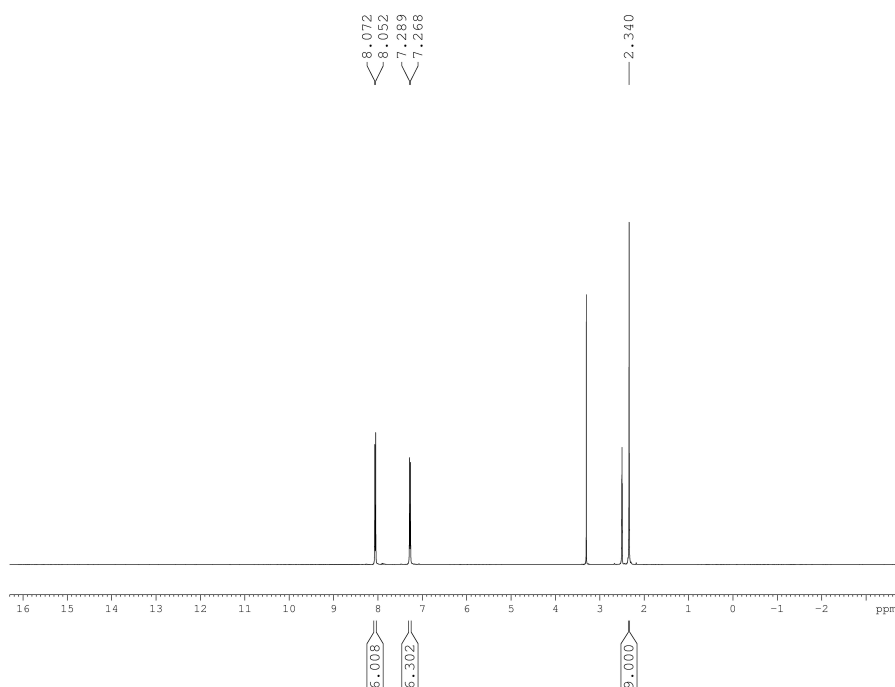


Figure S1: ^1H NMR of $[\text{Bi}(\text{S}_2\text{C}(\text{C}_6\text{H}_4)\text{-4-CH}_3)_3]$ (**1**).

Bismuth tris(4-methoxybenzodithioate) $[\text{Bi}(\text{S}_2\text{C}(\text{C}_6\text{H}_4)\text{-4-OCH}_3)_3]$ (2**)**

The general procedure was carried out using Bi_2S_3 (0.129g, 0.25 mmol) and 4-methoxybenzodithioic acid (0.276 g, 1.5 mmol). After three days, dark red crystals were obtained. 0.243 g, 64% yield m.p. 195 °C (decomp). ^1H NMR (400 MHz, DMSO-d_6 , 25 °C): δ = 8.18 (d, 3J = 9 Hz, 6H, *o*-CH), 7.02 (d, 3J = 9 Hz, 6H, *m*-CH), 3.84 (s, 9H, OCH_3). ^{13}C NMR (100 MHz, DMSO-d_6 , 25 °C): δ = 164.7 (COCH_3), 142.3 (CCS_2), 128.5 (*o*-CH), 113.1 (*m*-CH), 55.7 (OCH_3). ν_{max} FTIR (cm^{-1}): 3004 w, 2927 w, 2836 m, 2749 m, 2627 w, 2572 m, 2381 m, 2324 m, 2289 w, 2092 m, 1994 m, 1903 m, 1858 w, 1690 m, 1586 s, 1565 m, 1497 s, 1459s, 1449 m, 1418 m, 1311 s, 1262 s, 1228 s, 1156 s, 1020 s, 967 s, 905 s, 829 s, 806 m, 728 s, 693 s. MS (ESI) $^+$ m/z 1333.1 $[\text{Bi}_2(\text{S}_2\text{C}(\text{C}_6\text{H}_4)\text{-4-OCH}_3)_5]^+$, 574.9 $[\text{Bi}(\text{S}_2\text{C}(\text{C}_6\text{H}_4)\text{-4-OCH}_3)_2]^+$. Elemental analysis for $\text{C}_{24}\text{H}_{21}\text{BiO}_3\text{S}_6$: calculated: C 37.99, H 2.79; found: C 38.14; H 2.67.

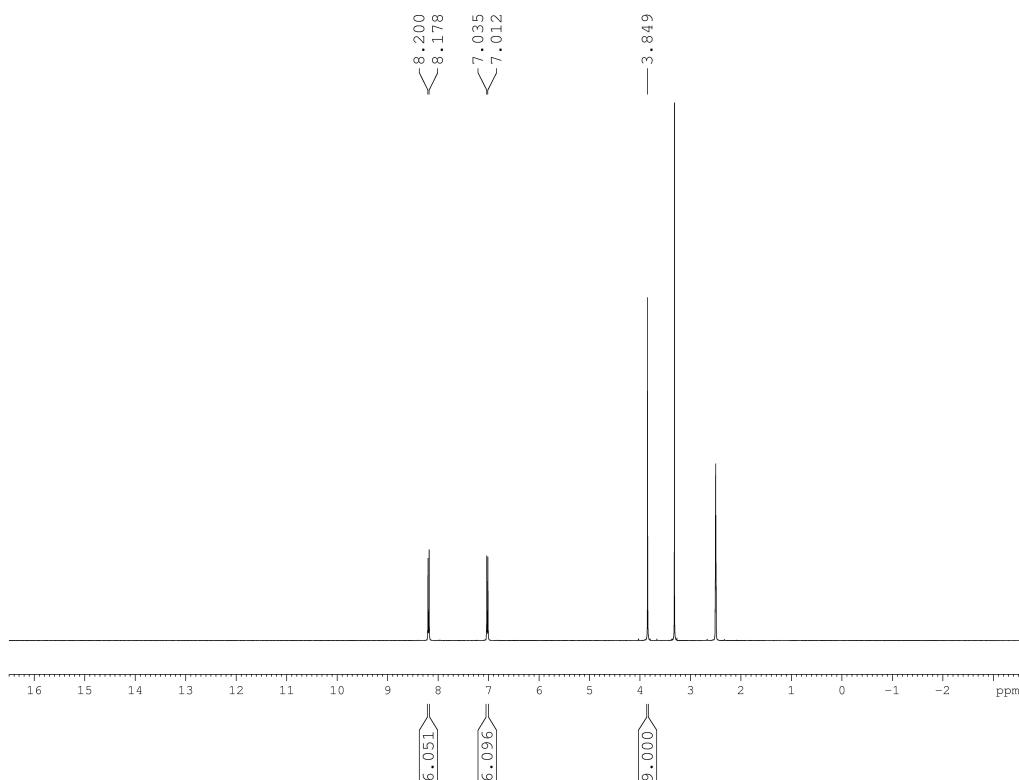


Figure S2: ^1H NMR of $[\text{Bi}(\text{S}_2\text{C}(\text{C}_6\text{H}_4)\text{-4-OCH}_3)_3]$ (**2**).

Synthesis of Bi_2S_3 nanorods: Two-Step Process

Note: This procedure will slowly generate toxic and flammable H_2S *in situ* and all necessary precautions should be taken.

Bi_2S_3 nanoparticles were synthesised via a solution decomposition method based on previously published procedures.^{4,5} The bismuth aryldithioate complex (100 mg of **1** or **2**) was suspended in mesitylene (20 mL) and 1-dodecanethiol (1 mL). The suspension was heated, with stirring, to 120 °C for 2-4 hours. Formation of Bi_2S_3 nanoparticles was observed as the colour of the reaction changed from bright orange to brown/black. The brown/black precipitate was washed several times with ethanol and collected by centrifugation. The Bi_2S_3 nanoparticles were suspended in either hexane or ethanol and deposited on a holey-carbon coated copper grid, ready for TEM analysis.

Synthesis of Bi₂S₃ nanorods: One-pot Reaction

Note: This procedure will slowly generate toxic and flammable H₂S *in situ* and all necessary precautions should be taken.

Bi₂S₃ (0.25 mmol, 1 eq.) was added to a solution of 4-methoxybenzodithioic acid (1.5 mmol, 6 eq.) in mesitylene (20 mL) and 1-dodecanethiol (1 ml). The reaction mixture was heated at 75 °C for 3-4 hours (or until the black colour of the Bi₂S₃ disappeared and a red solid was formed) and then heated at 120 °C for 2-4 hours. Formation of Bi₂S₃ nanoparticles was observed as the colour of the reaction changed from dark red to brown/black. The brown/black precipitate was washed several times with ethanol and collected by centrifugation. The Bi₂S₃ nanoparticles were suspended in acetone and deposited on a holey-carbon coated copper grid, ready for TEM analysis.

Crystallography Details

Crystallographic data for compound **1** was obtained on a Bruker X8 APEXII CCD diffractometer equipped with an OXFORD Cryosystems 700 Cryostream and cooled to 123(2) K. Data was collected with monochromatic (graphite) MoK α radiation ($\lambda = 0.71073$ Å) and processed using the Bruker Apex2 v2012.2.0 software; Lorentz, polarization and absorption corrections (multi-scan – SADABS⁶) were applied. The structure was solved by standard methods and refined by full matrix least squares using the SHELX-97 program.⁷ Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms attached to C were placed in calculated positions using a riding model with C-H distances of 0.99 Å and $U_{\text{iso}}(\text{H}) = 1.2 \times U_{\text{eq}}(\text{C})$. CCDC reference number 1436251 contains supplementary crystallographic data for this paper.

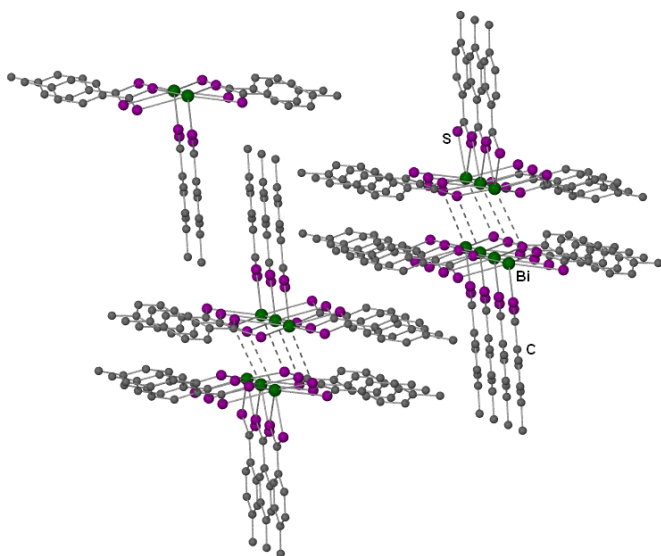


Figure S3: Extended packing arrangement of complex **1**.

SAED Pattern Analysis

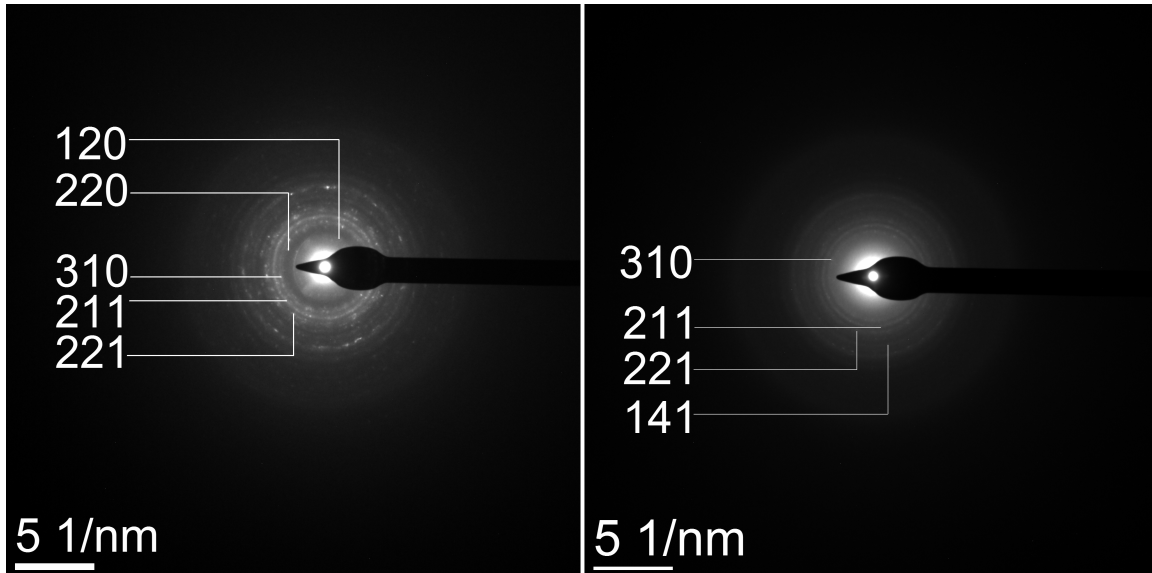


Figure S4: SAED pattern of Bi_2S_3 nanorods produced from **1** (left) and **2** (right).

EDS Analysis

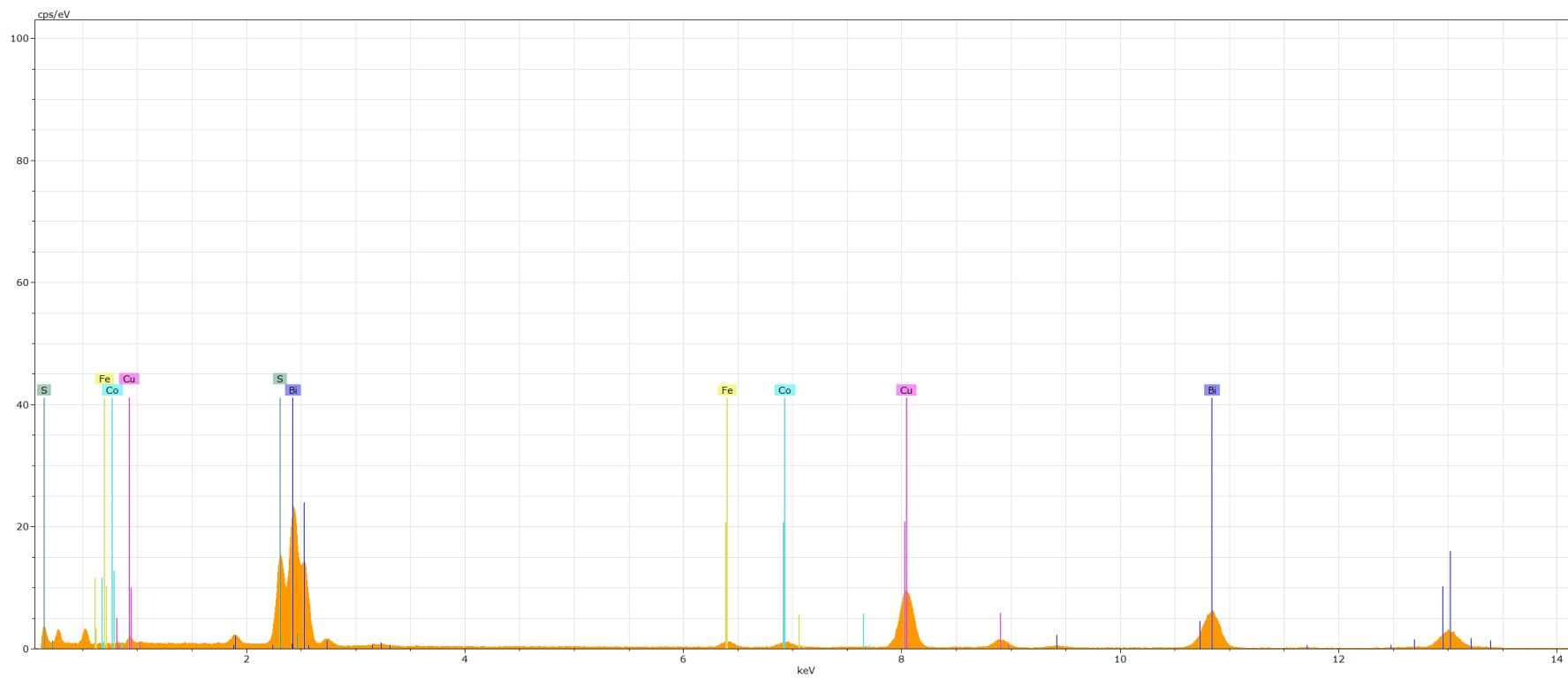


Figure S5: EDS spectrum of the Bi_2S_3 nanorods isolated from the solution decomposition of **1**.

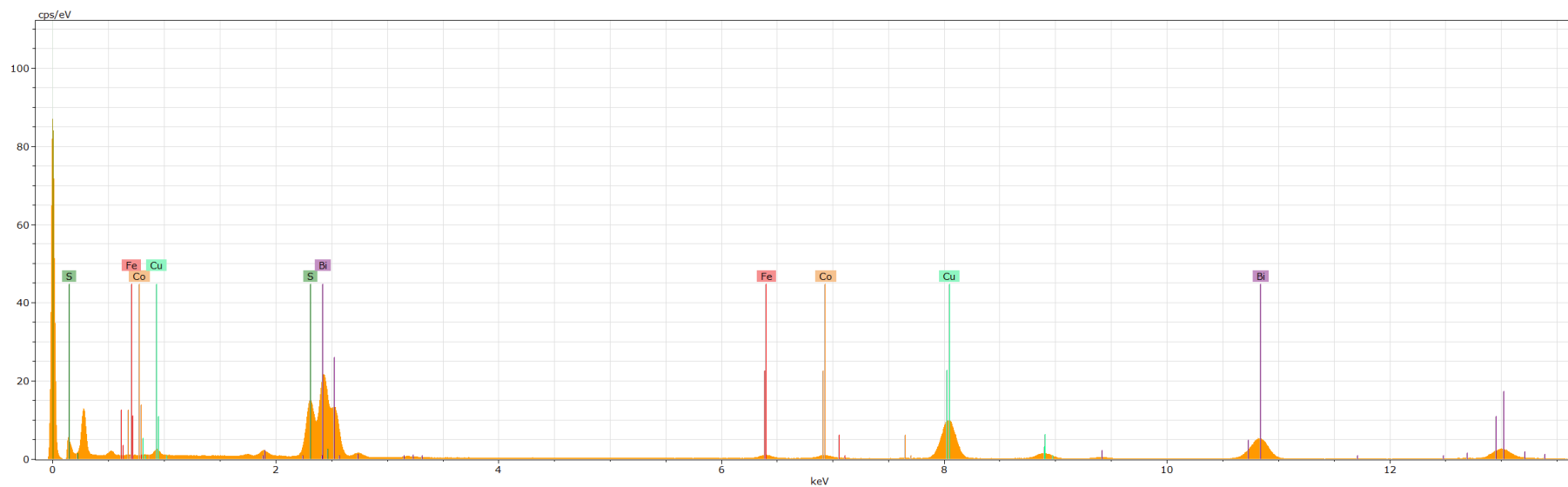


Figure S6: EDS spectrum of the Bi_2S_3 nanorods isolated from the solution decomposition of **2**.

Note: The signals seen for carbon and copper in Figures S5 and S6 are from the holey-carbon coated copper grid. The iron and cobalt arise from the objective lens pole piece.

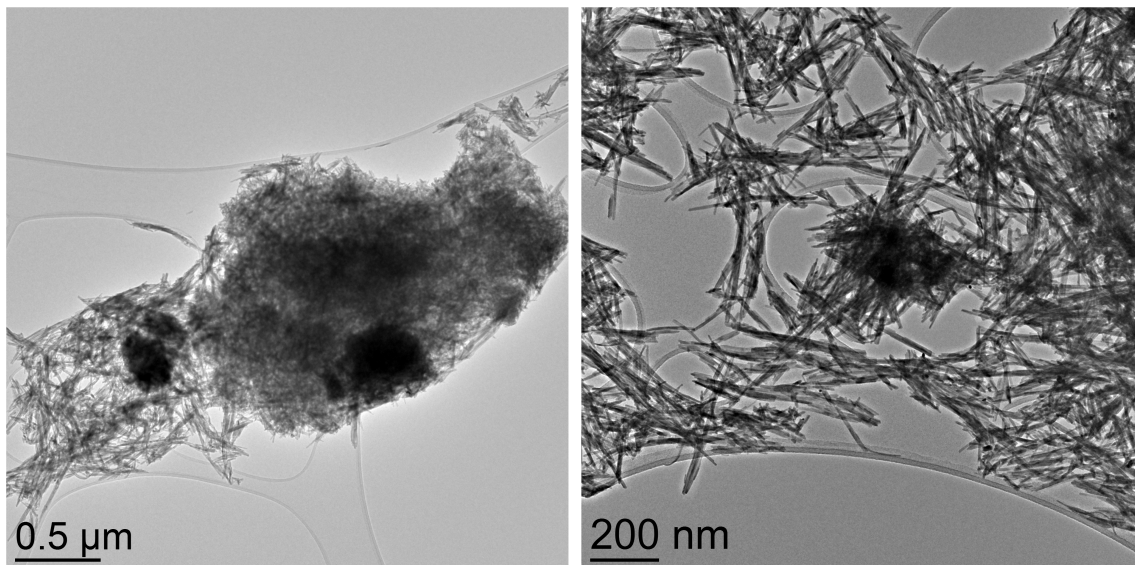


Figure S7: TEM images of the Bi_2S_3 nanorods isolated from a one-pot synthesis. This sample contains (many) larger aggregates of small nanorods.

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