Supplementary Information

to

Bismuth sulphide/polymer nanocomposites from a highly soluble bismuth xanthate precursor

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Precursor Synthesis:

Potassium xanthate: Potassium O-3,3-dimethylbutan-2-yl dithiocarbonate

Potassium *tert*-butoxide (13.2 g, 117 mmol, 1.0 eqiv.) was dissolved in THF and cooled to 0 °C under an Argon flow. Afterwards 3,3-dimethyl-2-butanol (15.0 g, 129 mmol, 1.1 equiv.) was added slowly under stirring and after several minutes carbon disulphide was added drop wise. The reaction mixture was stirred for 5 hours before the solution was diluted with 1 L diethyl ether. The resulting solid was dried in vacuum before it was dissolved again in 150 mL refluxing acetone to remove insoluble side products. The acetone phase was concentrated to approx. 50 mL by rotary evaporation before the product was precipitated with diethyl ether (1 L). The yellowish-white powder was separated by filtration and dried in vacuum (yield: 18.3 g, 76 %).

^{1}H NMR (300 MHz, 20 °C, acetone-d_6, δ): 5.64-5.59 (m, 1H, CH-OK), 1.68-1.46 (m, 2H, CH_2), 0.93-0.89 (m, 12H, 4xCH_3) ppm, ^{13}C NMR (75 MHz, 20 °C, acetone-d_6, δ): 235.4 (CS_2O), 88.7 (CH), 36.2 ($\underline{C}(CH_3)$), 26.8 ($C(\underline{C}H_3)$), 24.1 (CH_2), 11.6 (CH_2-$\underline{C}H_3$) ppm.

IR (on Si wafer): 2964, 2872, 1457, 1393, 1382, 1365, 1231, 1205, 1140, 1109, 1070, 1042, 1021, 951 cm^{-1}.

Anal.calcd for $C_8H_{15}S_2OK$: C 41.70, H 6.56, S 27.83; found: C 42.70, H 6.59, S 26.38.

HRMS Investigations:

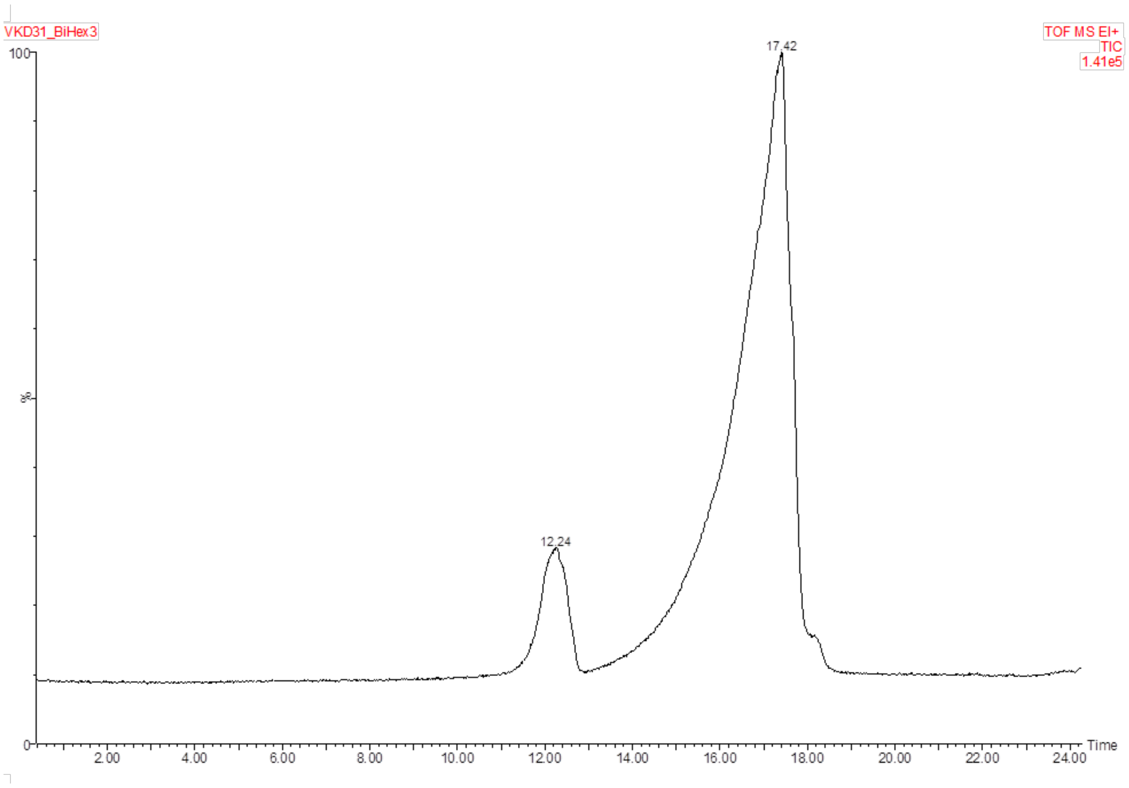

Fig. S1 Total ion current (TIC) of the HRMS investigations with DI-EI (temperature program of the DI: start at 40 °C, heating rate 10 °C/min), measurements were carried out under high vacuum.

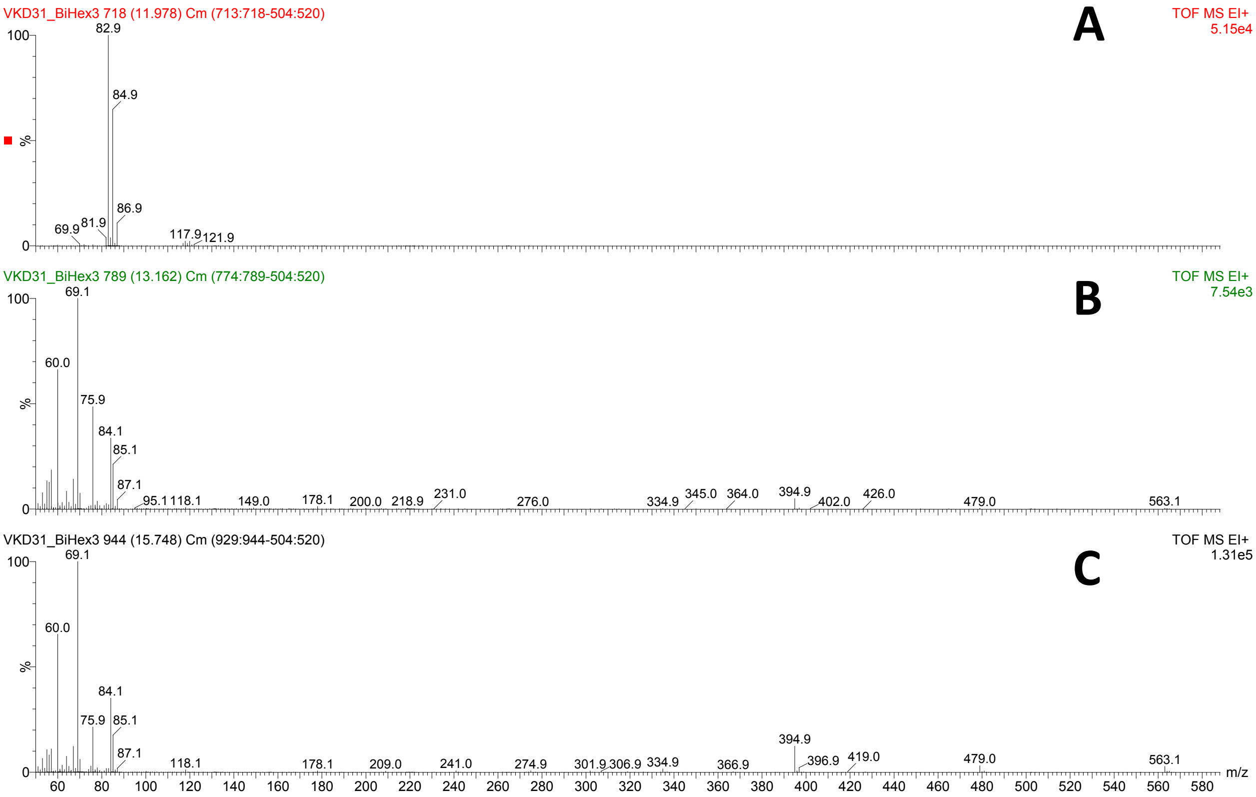

Fig. S2 EI mass spectra recorded at different temperatures of the direct insertion probe showing volatile species. Around 160 °C mainly chloroform was observed (A). At higher temperatures - 175 °C in (B) - the evolution of thermal decomposition products increases, e.g. COS at 60 Da, CS_2 at 75.9, and C_6H_{12} at m/z = 84 Da. Additionally, BiHexXan starts to evaporate due to the high vacuum conditions used during the measurement, what can be deduced from the Bi-containing fragment ion $C_2H_2O_2S_4Bi$ at 394.9 Da. Further increase of the temperature - 200 °C in (C) - favours the evaporation in comparison to the thermal decomposition, consequently the relative intensity of ions containing Bi increases (m/z = 394.9, 479.0, 563.1 Da). Exact masses and interpretations for these ions are shown in Fig. S3.

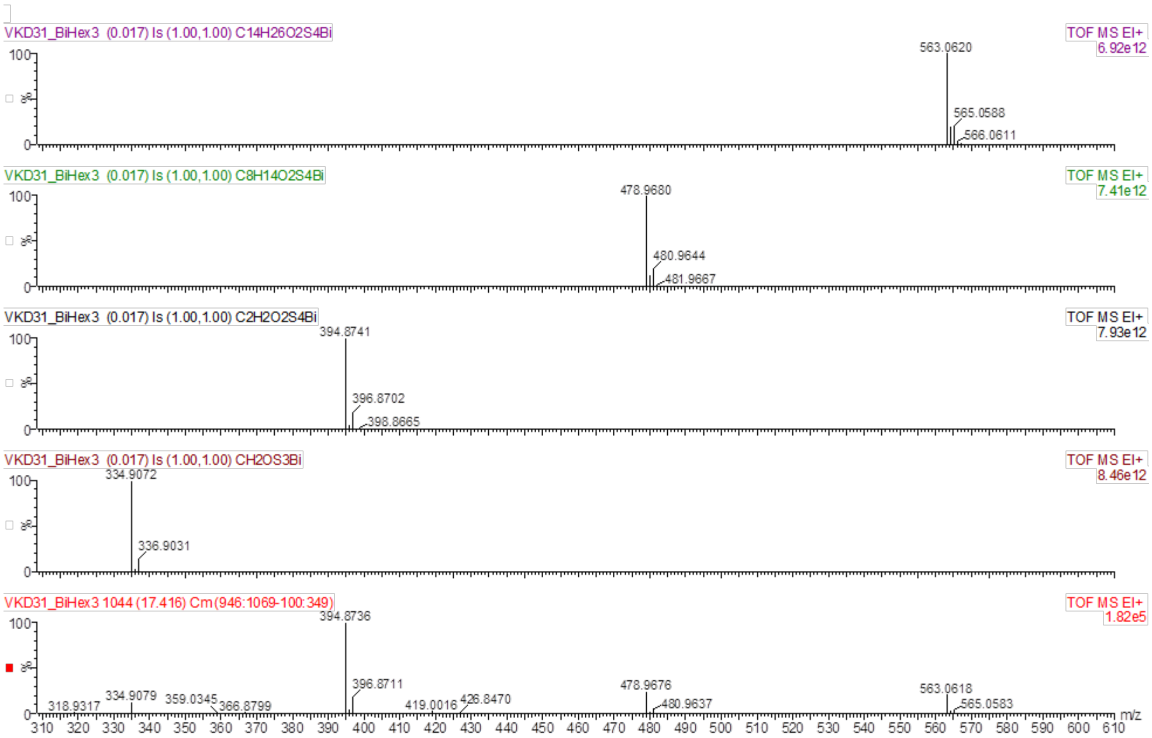

Fig. S3 Comparison of measured (bottom) and calculated masses (above) of ions containing Bi. No molecule ion was observed for BiHexXan, nevertheless these results are an additional proof of the structure.

Table S1 Assignment of the peaks of the Bi-xanthate precursor layer in the FT-IR spectra.[1,2]

IR frequency / cm^{-1}	Assignments
2963	$-CH_2-$ str. asym.
2871	$-CH_2-$ str. sym.
1475	alkane deformation
1450	
1369	sym. CH_3 bnding
1335	CH wagging
1238	asym. C-O-C str.
1203	
1115	sym. C-O-C str.
1047	C=S str.
1017	

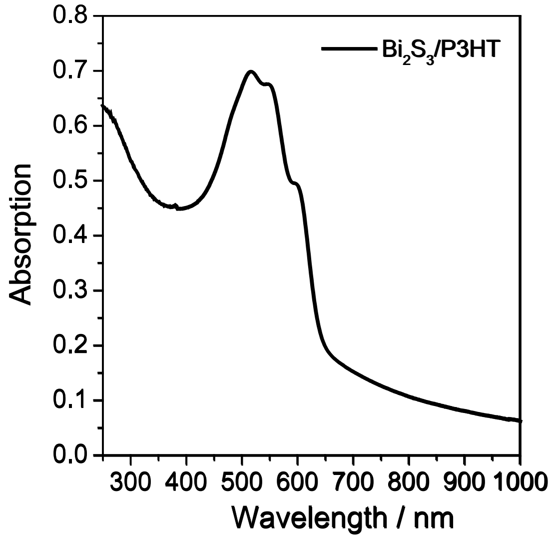

Fig. S4 Absorption spectrum of a Bi_2S_3/P3HT nanocomposite layer.

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[1] G. Socrates, Infrared Characteristic Group Frequences, Tables and Charts, Second Edition, Wiley, Chichester, **1994**.

[2] D. Barreca, A. Gasparotto, C. Maragno, R. Seraglia, E. Tondello, A. Venzo, V. Krishnan, H. Bertagnolli, *Appl. Organomet. Chem.* **2005**, *19*, 1002–1009.