

SUPPORTING INFORMATION

Covalently functionalized MoS₂ with dithiolenes

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Instrumentation

Tip sonication was performed with a Bandelin Sonoplus Ultrasonic Homogenizer HD 3200 equipped with a flat head probe (VS70T), running at 35% of the maximum power (250 W).

Mid-infrared spectra in the region 500-4500 cm^{-1} were acquired on a Fourier transform IR spectrometer (Equinox 55 from Bruker Optics) equipped with a single reflection diamond ATR accessory (DuraSamp1IR II by SensIR Technologies). A drop of the dispersion was placed on the diamond surface, followed by evaporation of the solvent, in a stream of nitrogen, before recording the spectrum. Typically, 100 scans were acquired at 2 cm^{-1} resolution.

Micro-Raman scattering measurements were performed at room temperature in the backscattering geometry using a RENISHAW inVia Raman spectrometer equipped with a CCD camera and a Leica microscope. A 1200 lines mm^{-1} grating was used for all measurements, providing a spectral resolution of $\pm 1 \text{ cm}^{-1}$. As an excitation source the Ar^+ laser 633 nm with less than 2.65 mW laser power was used. Measurements were taken with 10 seconds of exposure times at varying numbers of accumulations. The laser spot was focused on the sample surface using a long working distance 50x objective. Raman spectra were collected after map image acquisition was conducted on various (3-5) areas of the sample and recorded with Peltier cooled CCD camera. The intensity ratio $I_{\text{Alg}}/I_{\text{2LAM}}$ was obtained by taking the peak intensities following any baseline corrections. The data were collected and analyzed with Renishaw Wire and Origin software.

Thermogravimetric analysis was performed using a TGA Q500 V20.2 Build 27 instrument by TA in an inert atmosphere of nitrogen (purity >99.999%). In a typical experiment 2 mg of the material was placed in the platinum pan and the temperature was equilibrated at 40°C. Subsequently, the temperature was increased to 900°C with a rate of 10°C/min and the mass changes were recorded as a function of temperature.

Scanning transmission electron microscopy (STEM) analyses were performed in a probe aberration-corrected FEI Titan Low-Base microscope using high-angle annular dark field (HAADF) STEM imaging. The microscope was operated at 200 kV and spatially-resolved electron energy-loss spectroscopy (SR-EELS) was also developed in this microscope. EEL spectra were recorded using the spectrum-imaging (SPIM) in 2D or spectrum-line (SPLI) in 1D

mode in a Gatan GIF Tridiem ESR 865 spectrometer. The convergent semi-angle was of 25 mrad, the collection semi-angle was 80 rad and the energy resolution ~ 1.2 eV. No damage has been observed during the EELS and STEM acquisition.

Dynamic light scattering measurements were performed on an ALV/CGS-3 Compact Goniometer System (ALV GmbH, Germany), equipped with a JDS Uniphase 22 mW He-Ne laser, operating at 632.8 nm, interfaced with an ALV-5000/EPP multi-tau digital correlator with 288 channels and an ALV/LSE-5003 light scattering electronics unit for stepper motor-drive and limit-switch control. The scattering intensity and correlation functions were measured at 90°C. Correlation functions were collected ten times and were analyzed using the cumulant method and the CONTIN software, which provide the apparent hydrodynamic radii distributions by Laplace inversion of the correlation function and by aid of the Stokes-Einstein relationship.

Materials

All solvents and reagents were purchased from Aldrich and used without further purification.

Experimental

Exfoliated 1T-MoS₂ (1a). A modified previously reported procedure was followed. MoS₂ powder (1.5 g) was dried at 100°C overnight prior to use and then placed in a two-necked round bottom flask under argon with a dry vertical condenser attached. Subsequently, 15 mL of nBuLi (2.5 M) in hexanes was added at 0°C and the flask was placed in an oil bath, heated at 70°C and the suspension was allowed to stir under an inert atmosphere for 72 h. Reaction was then quenched with ~ 600 mL of distilled water at 0°C. After hydrogen evolution ceased, the resulting suspension was left overnight to precipitate. The next day about 500 mL of the supernatant were collected and filtrated through a PTFE filter (0.2 μ m pore size) and washed with ~ 200 mL of hexane, MeOH and chloroform to remove any organic impurities. The solid material (550 mg) was then collected, dried in vacuum and used for further functionalization.

Exfoliated 2H-MoS₂ (1b). Bulk MoS₂ (150 mg) was dispersed in chlorosulfonic acid (15 mL), sonicated for 2 hours and left under stirring at room temperature for 24 hours. Cold water (200 mL) was added dropwise (please note that the reaction is exothermic and releases gaseous hydrochloric acid) and the mixture was filtrated over a PTFE filter (0.2 μ m pore size) and washed with an excess of methanol and acetone. The solid material was added to 150 mL of N-methyl pyrrolidone and sonicated for 1 hour (tip sonication at 30-35% of amplitude 100% of

200W). The suspension was left to precipitate over a 3 day period and the supernatant was then collected and filtrated on PTFE filter (0.2 μm pore size), washed with a large amount of methanol, acetone and dichloromethane, dried in vacuum and used for further functionalization.

Synthesis of potassium (Z)-but-2-ene-2,3-bis(thiolate) (2). Compound (2) was synthesized in three steps according to previously reported procedures (Figure S1). All the spectroscopic NMR and IR data match with those reported in literature.

Synthesis of O-isopropyl S-3-oxobutan-2-yl dithiocarbonate. *O*-isopropylxanthate (3.48 g, 20 mmol) dissolved in 50 mL dry acetone was slowly added to a solution of 3- chlorobutane-2-one (2.7 mL, 2.02 g, 19.1 mmol) in 50 mL dry acetone. The mixture was stirred for 1 h at r.t. and then the solvent was removed on a rotary evaporator. The residue was dissolved in water and extracted twice with Et_2O . The organic phases were combined, dried over Na_2SO_4 and the solvent was removed in vacuum at 40°C affording *O*-isopropyl S-3-oxobutan-2-yl carbonodithioate as yellow oil. Yield: 3.52g (89%). ^1H NMR (600 MHz, CDCl_3) δ (ppm): 1.35 (d, $J=6.5$ Hz, 6H), 1.43 (d, $J=7.5$ Hz, 3H), 2.27 (s, 3H), 4.34 (q, $J=7.2$ Hz, 1H), 5.68 (spt, $J=5.8$ Hz, 1H).

Synthesis of 4,5-dimethyl-1,3-dithiol-2-one. *O*-isopropyl S-3-oxobutan-2-yl dithiocarbonate (3.5 g, 17 mmol) was slowly added to a solution of concentrated H_2SO_4 (90 mL) that had been pre-cooled at 0°C . The resulting solution was stirred for 30 min at 0°C and then allowed to heat to r.t. and stirred for a further 90 min. Next, the solution was cooled in an ice bath and slowly poured into ice-cooled H_2O (400 mL). After stirring for 15 min, the solution was extracted twice with CH_2Cl_2 , dried over Na_2SO_4 and concentrated on a rotary evaporator to produce crude, dark purple low melting point solid that was purified by column chromatography in Petr. Ether: EtOAc (95:5) to afford a pale-yellow oil. The freshly prepared pale yellow oil was dissolved in warm hexane followed by cooling at -20°C yielding white single crystals of 4,5-dimethyl-1,3-dithiol-2-one. Yield: 1.6g (65%). ^1H NMR (600 MHz, CDCl_3) δ (ppm): 2.13 (s, 4H).

Synthesis of potassium (Z)-but-2-ene-2,3-bis(thiolate) (2). A solution of 1.5 g (2.5 eq., 27.5 mmol) potassium hydroxide in 50mL methanol was added to 1.5 g (11 mmol) of 4,5-dimethyl-1,3-dithiol-2-one in a round bottom flask under nitrogen atmosphere. The solution was allowed to stir in r.t. and after ~1 hour period turned yellow indicating the deprotection of the ring. The yellow solution was left to stir for 1 more hour and then MeOH was evaporated in vacuum to give a brownish low melting point solid. ^1H NMR (600 MHz, CDCl_3) δ (ppm): 2.11 (s, 6H). ^{13}C

NMR (600 MHz, CDCl₃) δ (ppm): 161.8 158.2, 133.2, 125.0 and 13.8. **IR**: ν ~ 3404, 3251, 2976, 2925, 2825, 1710, 1568, 1442, 1373, 1311, 1176, 1136, 1089, 1043, 864, 702 cm⁻¹.

Functionalized MoS₂-based materials (3a, b). Exfoliated MoS₂ materials (**1a, b**) (10 mg) and potassium (Z)-but-2-ene-2,3-bis(thiolate) (**2**) (5 mg) in water (5 mL) were stirred at 80°C for 3 days after adequate sonication. The reaction mixture was then filtered through a PTFE membrane (0.2 μ m pore size) and the solid residue was successively collected, bath sonicated and filtrated with an excess of methanol, DMSO, water and dichloromethane, dried in vacuum and collected as a dark grey solid.

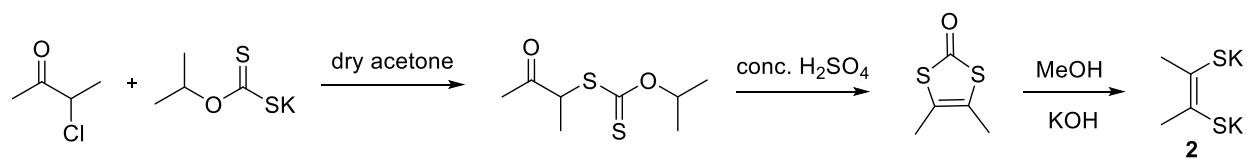


Figure S1. Three-step synthesis of bis(thiolate) salt (**2**).

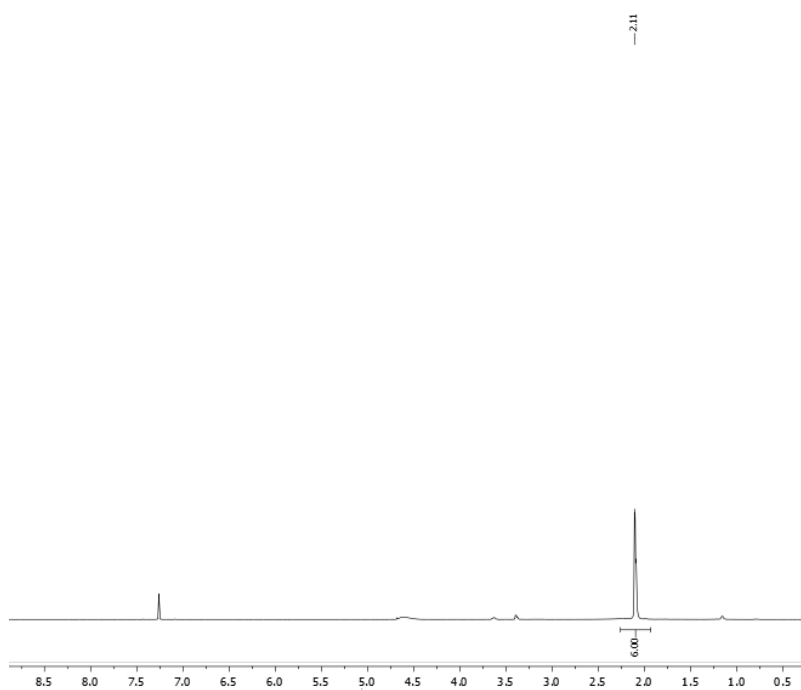


Figure S2. ^1H -NMR of (Z)-but-2-ene-2,3-bis(thiolate) potassium salt (**2**) in CDCl_3 .

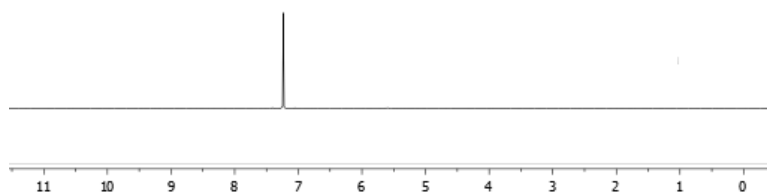


Figure S3. ^1H -NMR in CDCl_3 of the PTFE filtrate of (**3a**) after extensive washing.

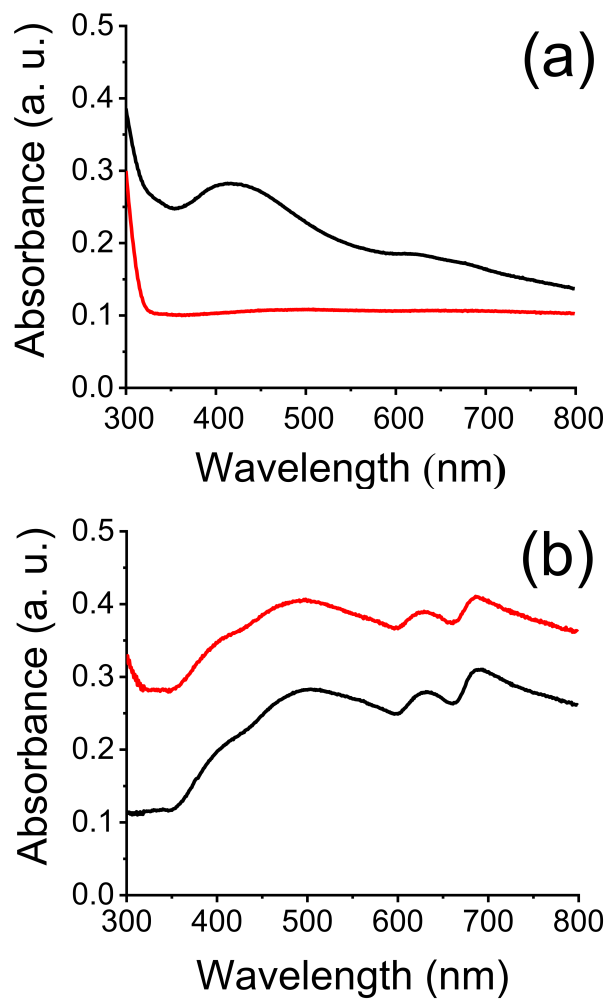


Figure S4. UV-Vis spectra in DMF of **a)** exfoliated $1T$ -MoS₂ (**1a**-black) and functionalized $1T$ -MoS₂ (**3a**-red) and **b)** exfoliated $2H$ -MoS₂ (**1b**-black) and functionalized $2H$ -MoS₂ (**3b**-red).

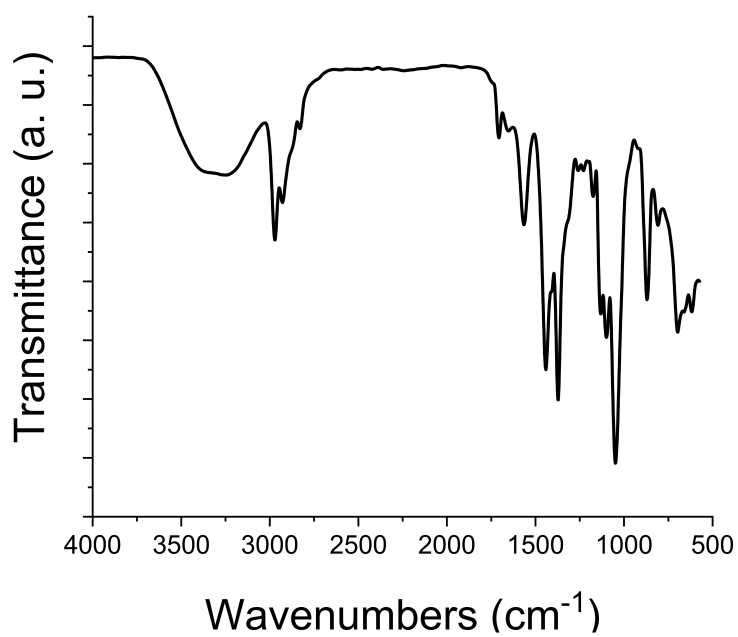


Figure S5. ATR-IR spectrum of (Z)-but-2-ene-2,3-bis(thiolate) potassium salt (**2**).

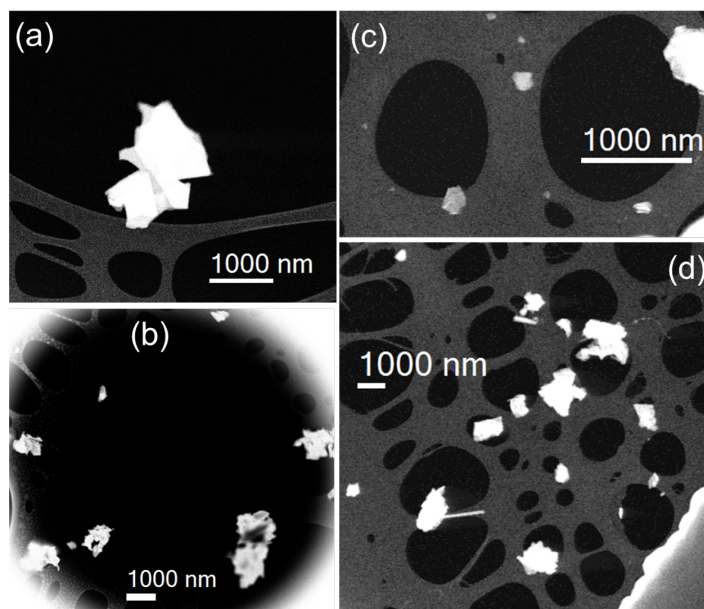


Figure S6. Low magnification STEM images of a) exfoliated *1T*-MoS₂ (**1a**), b) functionalized *1T*-MoS₂ (**3a**), c) exfoliated *2H*-MoS₂ (**1b**), and d) functionalized *2H*-MoS₂ (**3b**).