

Supramolecular electrostatic functionalization of 1T-MoS₂ based on alkylammonium salts.

Giuseppe Misia,^a Michele Cesco,^b Maurizio Prato*^{a, b, c} and Alessandro Silvestri *^d

- a. Department of Chemical and Pharmaceutical Sciences, INSTM UdR Trieste, Università Degli Studi di Trieste Trieste, 34127, Italy
- b. Center for Cooperative Research in Biomaterials (CIC BiomaGUNE) Basque Research and Technology Alliance (BRTA) Paseo de Miramon 194, 20014, Donostia-San Sebastián, Spain
- c. Ikerbasque Basque Foundation for Science Bilbao, 48009, Spain
- d. Department of Molecular Sciences and Nanosystems Ca' Foscari University of Venice Venezia, 30170, Italy

Supporting information

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1. Characterization of 1T-MoS₂

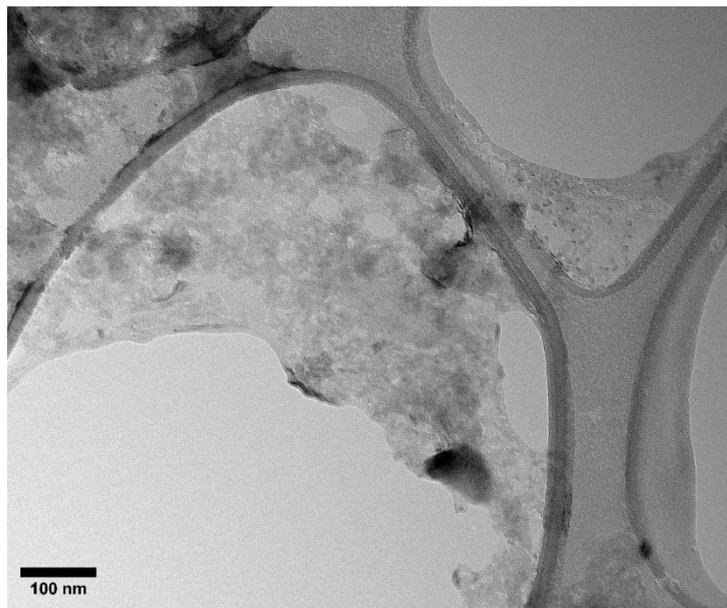


Figure S1 TEM micrograph of 1T-MoS₂.

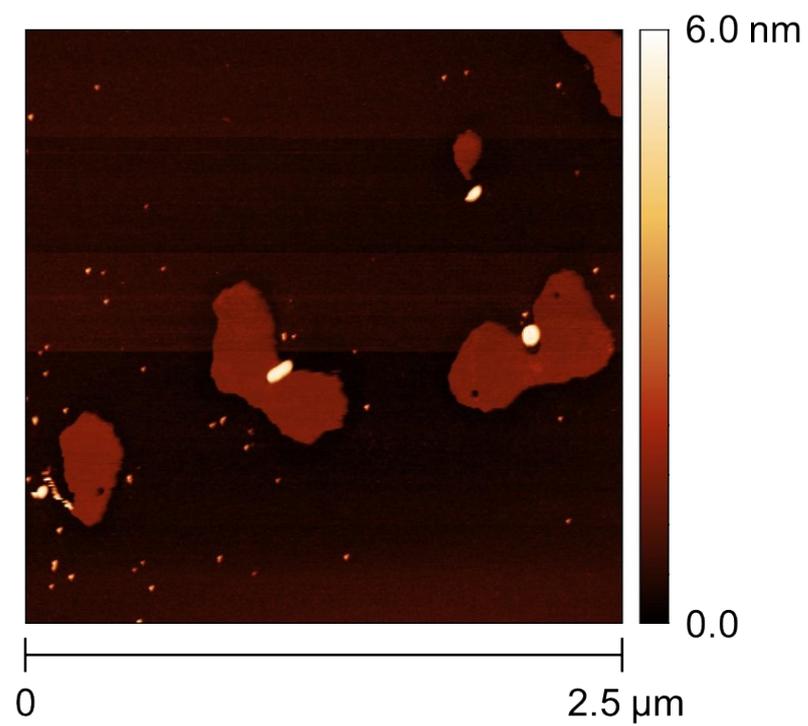


Figure S2 AFM micrograph of 1T-MoS₂.

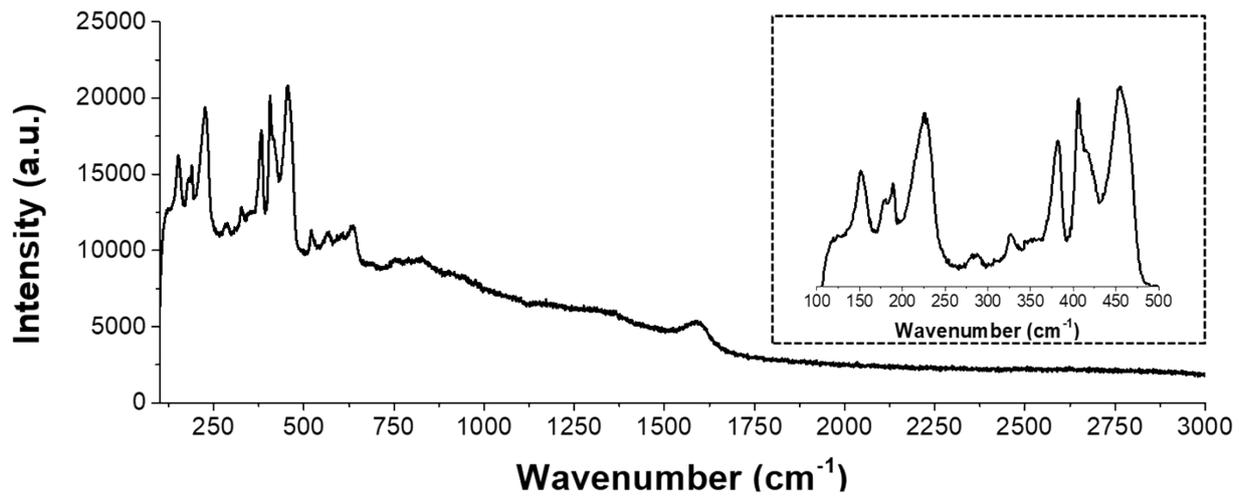


Figure S3 Raman spectrum of 1T-MoS₂; the inset shows the magnification of the region from 100 to 500 cm⁻¹.

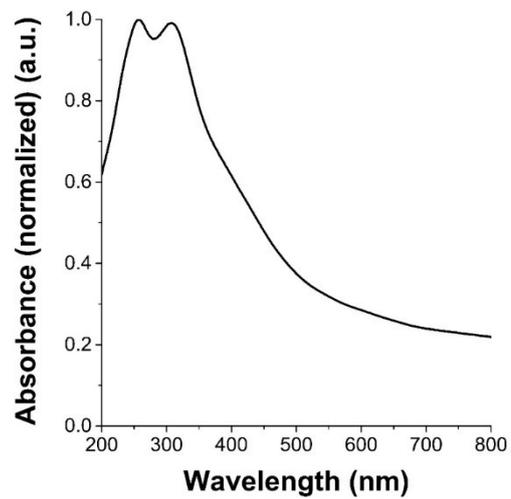


Figure S4 UV-vis spectrum of 1T-MoS₂.

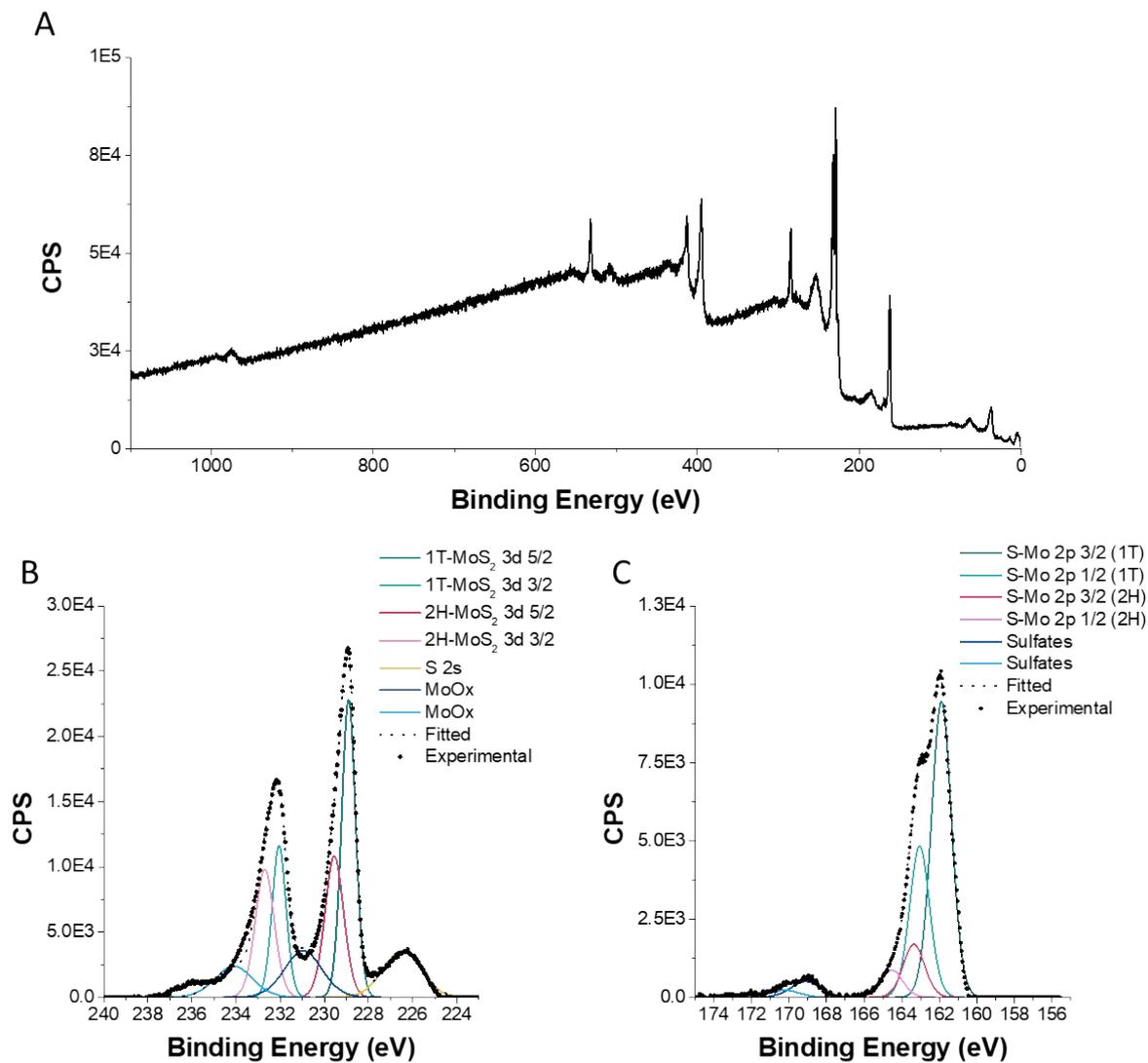


Figure S5 XPS spectra of 1T-MoS₂; survey spectrum (A), high-resolution spectrum of Molybdenum (B), and high-resolution spectrum of Sulphur (C). All binding energies were calibrated to adventitious carbon (284.8 eV).

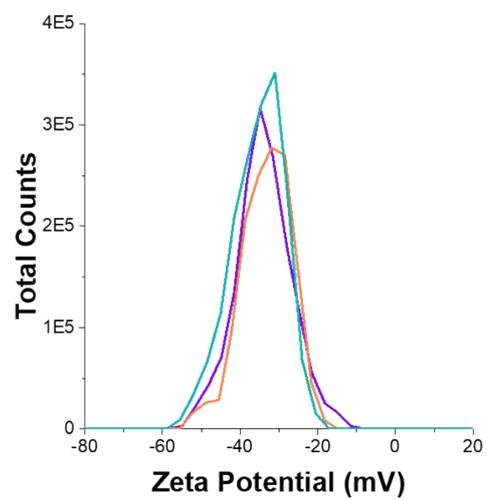
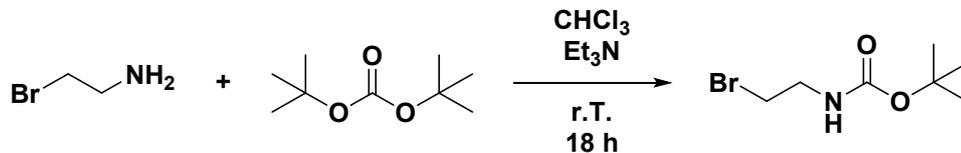


Figure S6 ζ -potential of 1T-MoS₂.

2. Synthesis of N',N',N'-triethylethane-1,2-diammonium (Et₃NEtNH₃)

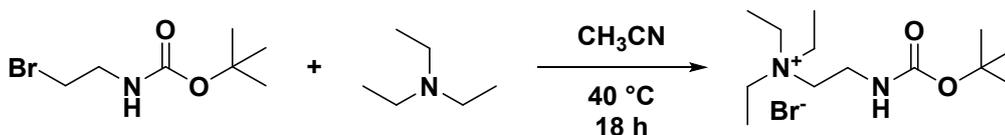
2.1. Synthesis of N-Boc-2-bromoethylamine



2-bromoethylamine hydrobromide (1 g, 8.06 mmol, 1 equiv.) was dissolved in chloroform (10 mL), and the resulting solution (sol. A) was left to stir at 0 °C. Subsequently, di-tert-butyl dicarbonate (1.92 g, 8.80 mmol, 1.1 equiv.) was dissolved in chloroform (10 mL) and triethylamine (2.24 mL, 16.12 mmol, 2 equiv.) was added to the resulting solution (sol. B). Sol. B was added dropwise to sol. A. over 0.5 h. Once sol. B was completely added, the reaction mixture was left to stir for 18 h, at room temperature. The mixture was extracted with ethyl acetate. The organic phase was washed twice with NH₄Cl saturated solution, twice with NaHCO₃ saturated solution and twice with brine. Then it was dried over sodium sulfate and the solvent was removed under reduced pressure.

¹H-NMR (400 MHz, CDCl₃): δ 1.40 (s, 9H), 3.40 (m, 2H), 3.48 (m, 2H), 5.03 (s, 1H).

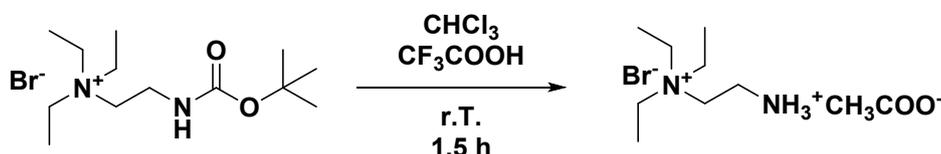
2.2. Synthesis of 2-((tert-butoxycarbonyl)amino)-N,N,N-triethylethanaminium bromide



According to a modified reported procedure, N-Boc-bromoethylamine (2.282 g, 10 mmol, 1 equiv.) was dissolved in acetonitrile (10 mL), then triethylamine (4.17 mL, 30 mmol, 3 equiv.) was added. The mixture was stirred at 40 °C for 18 h. The solvent was removed under reduced pressure and the product was recovered by precipitation in ethyl acetate.

¹H-NMR (400 MHz, D₂O): δ 1.30 (t, 9H), 1.45 (s, 9H), 3.35 (m, 8H), 3.50 (t, 2H).

2.3. Synthesis of N',N',N'-triethylethane-1,2-diaminium (Et₃NEtNH₃)



2-((tert-butoxycarbonyl)amino)-N,N,N-triethylethanaminium (924 mg, 2.84 mmol, 1 equiv.) was dissolved in CHCl₃ (7 mL) and cooled to 0 °C, then trifluoroacetic (5 mL, 91 mmol, 32 equiv.) was added dropwise. The reaction mixture was stirred at room temperature for 1.5 h. The solvent was removed under reduced pressure, yielding the product as a white solid.

¹H-NMR (400 MHz, D₂O): δ 1.35 (t, 9H), 3.42 (q, 6H), 3.54 (m, 4H).

3. ζ -potential titration

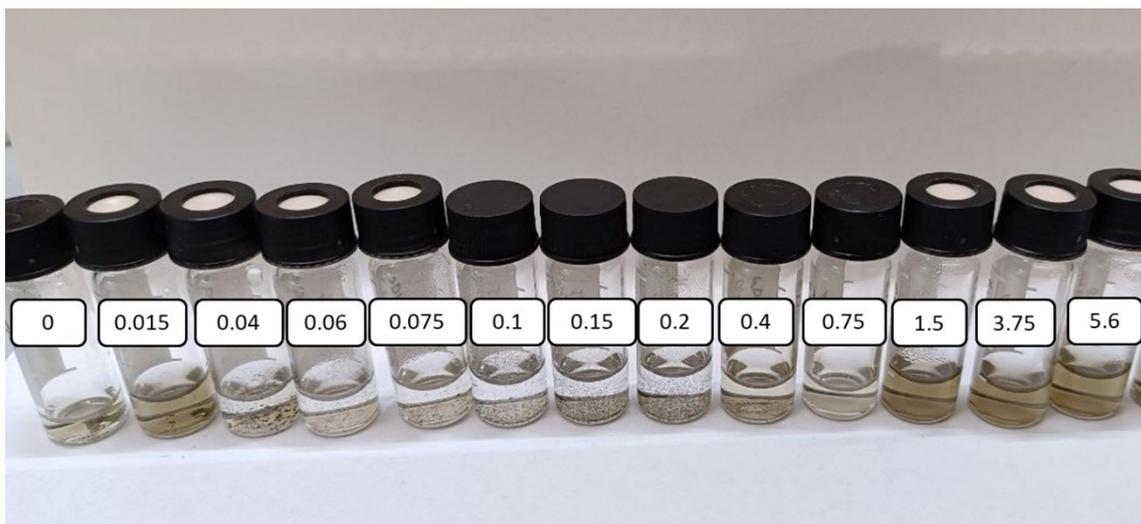


Figure S7 Photograph of 1T-MoS₂ suspensions with the addition of 0.015, 0.04, 0.06, 0.075, 0.1, 0.15, 0.2, 0.4, 0.75, 1.5, 3.75 and 5.6 equivalent of polyDADMAC.

4. Post-functionalization with pFBA

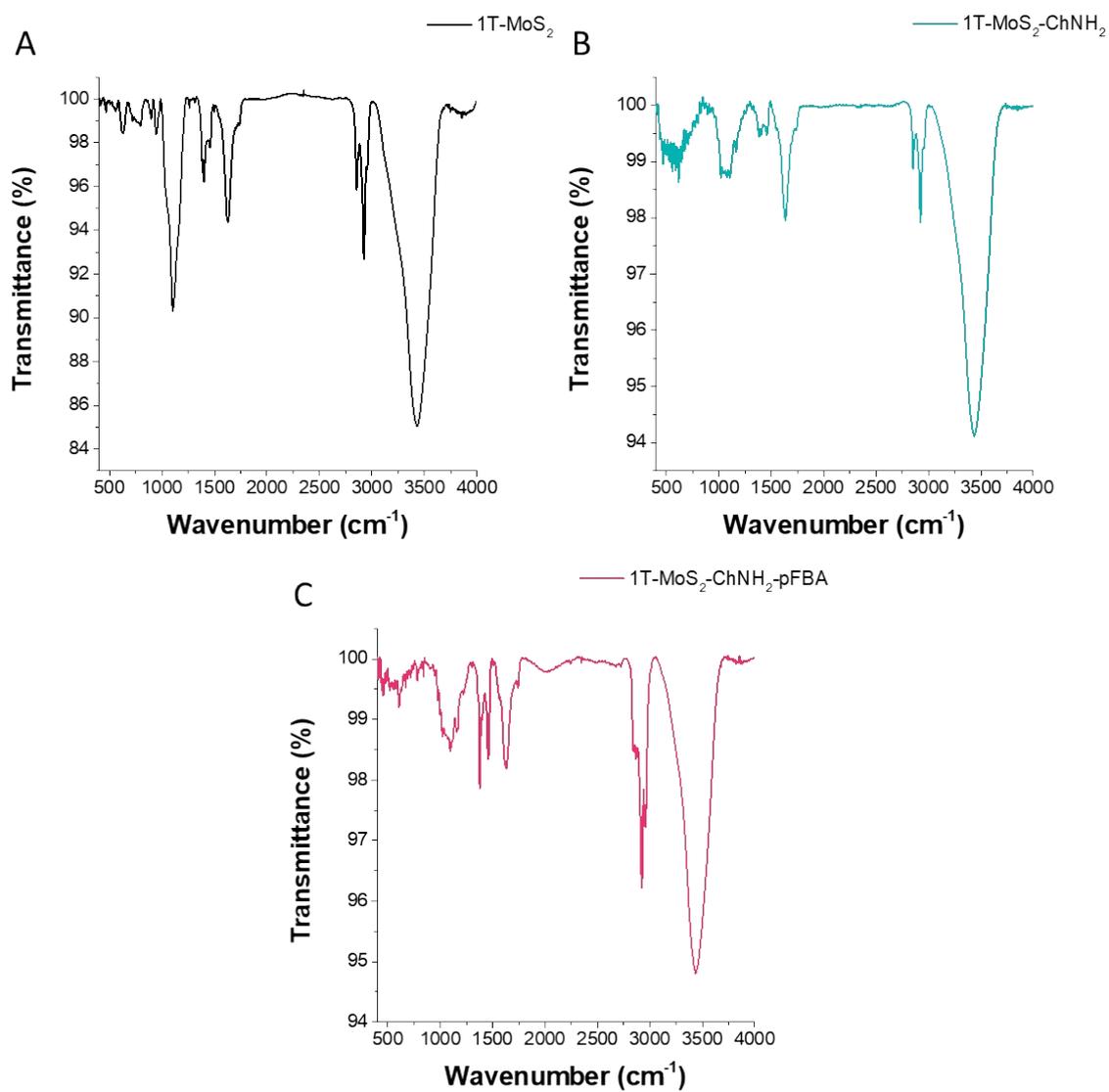


Figure S8 FT-IR spectra of 1T-MoS_2 (A), $1\text{T-MoS}_2\text{-ChNH}_2$ (B), $1\text{T-MoS}_2\text{-ChN=C-pFB}$ (C).

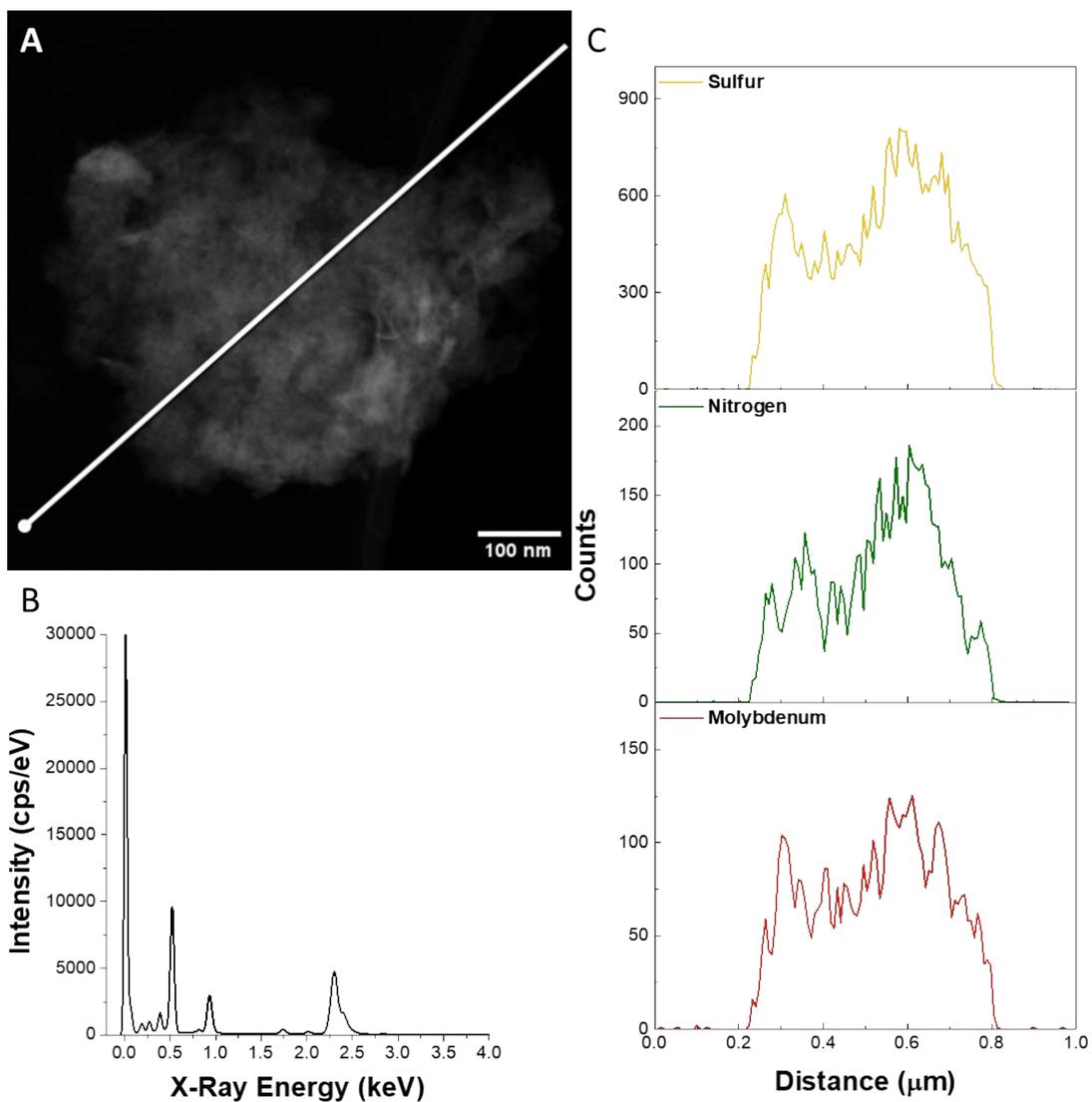


Figure S9 A) STEM micrograph of pristine 1T-MoS₂. The white line indicates the region where the EDX line scan was performed; B) Sum EDX spectrum of the line scan highlighted in panel A; C) Sulfur, Nitrogen, and Molybdenum profiles relative to the EDX line-scan highlighted in panel A.

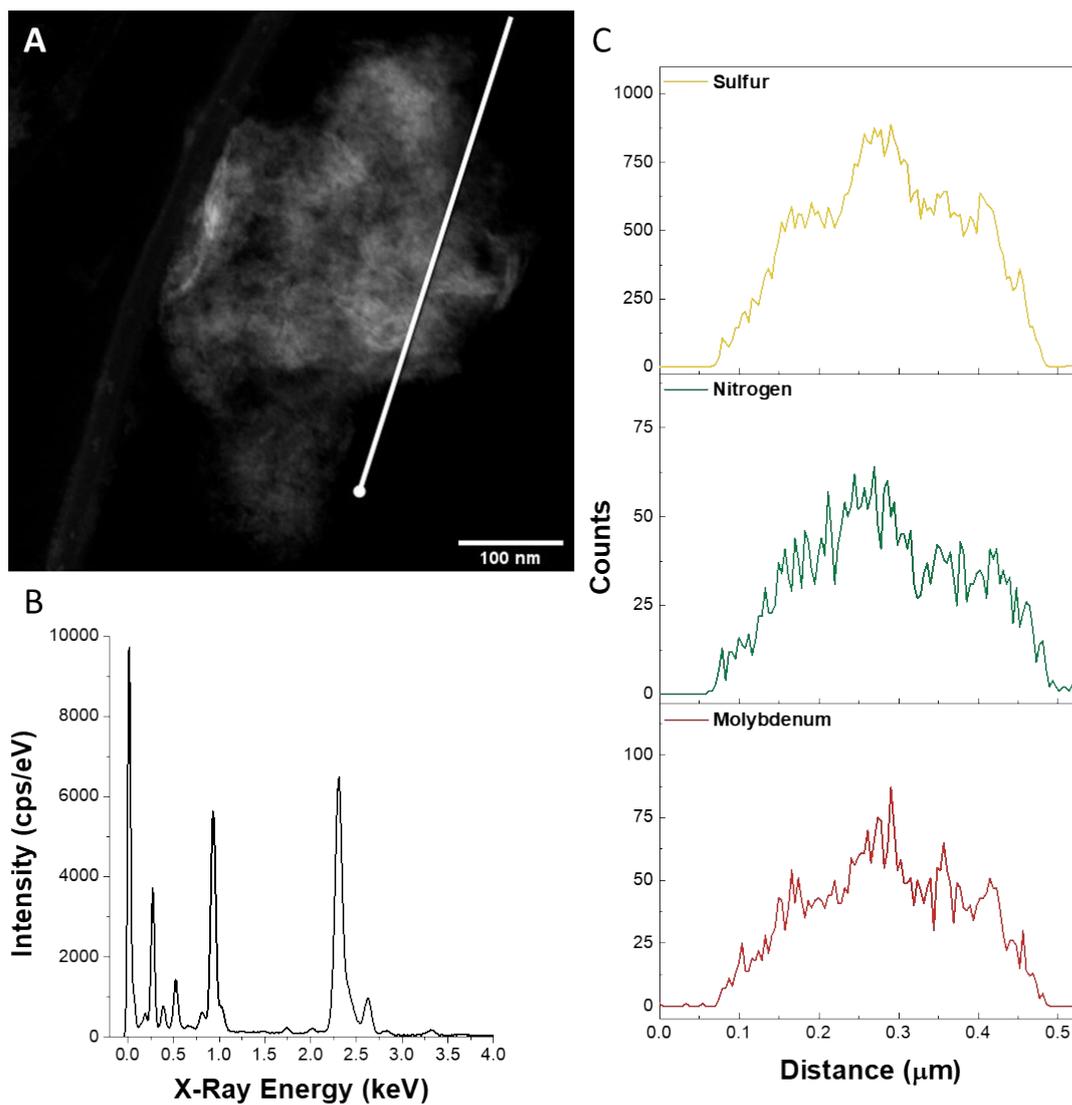


Figure S10 A) STEM micrograph of 1T-MoS₂-ChNH₂. The white line indicates the region where the EDX line scan was performed; B) Sum EDX spectrum of the line scan highlighted in panel A; C) Sulfur, Nitrogen, and Molybdenum profiles relative to the EDX line-scan highlighted in panel A.

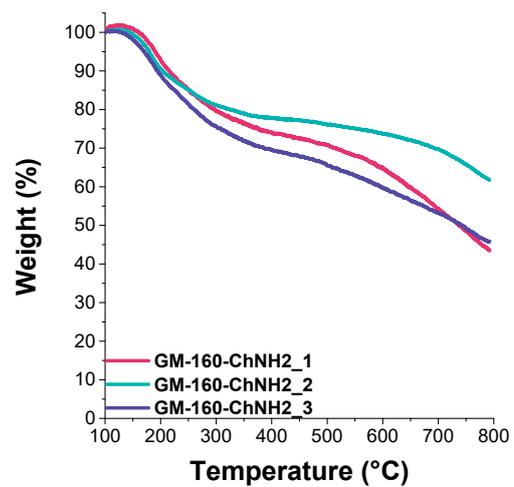


Figure S11 TGA of three functionalizations performed separately on a batch of 1T-MoS₂. The RSD calculated for the three functionalizations is 3.8%.