

Supplementary Information

Biofunctional Few-layer Metal Dichalcogenides and Related Heterostructures Produced by

Direct Aqueous Exfoliation Using Phospholipids

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Materials

All starting materials and solvents were used as received. MoS₂ (purum), WS₂ (2 μm, 99%), TiS₂ (-200 mesh, 99.9%), MoSe₂ (-325 mesh, 99.9%) and BN (1 μm, 98%) powders were purchased from Sigma-Aldrich. Graphite powder (grade 2369) was obtained from Graphexel Ltd (UK). 1,2-dioleoyl-*sn*-glycero-3-phosphocholine (DOPC) (≥ 99%) was purchased from Sigma-Aldrich and kept refrigerated.

Preparation of dispersions

In a typical experiment, DOPC was dispersed in 10 mL of ultra-pure water (18 MΩ cm, Milli-Q Direct 8, Millipore, USA) at a concentration of 0.2 mg mL⁻¹ in a 20 mL glass vial. The inorganic material, in powder form, was sieved before use through a 500 μm pore-size mesh in order to remove large particles, and subsequently added to the phospholipid/water solution at a concentration of 5 mg mL⁻¹. The mixture was shaken and then sonicated in an ultrasonic bath for 12 hours (Elmasonic P, Elma, Germany. Frequency = 37 kHz, power equivalent = 40%, true power ≈ 34 W) at a constant bath temperature of 20 °C, after which the resulting dispersion was left standing for 24 hours to allow for the sedimentation of large aggregates. The supernatant was subsequently removed and centrifuged at 6000 rpm for 30 min, with the process being repeated once more to produce a dispersion. The amount of dispersed material was calculated by carefully separating the supernatants from the sediment after centrifugation. The volume of dispersion was measured and the undispersed mass was dried in a vacuum oven (Gallenkamp, UK) at 120 °C. For the preparation of DOPC/MX₂:MX₂ heterostructure dispersions, \mathcal{X} and \mathcal{Y} volume ratios of the desired parent DOPC/MX₂ dispersions were mixed and subsequently sonicated for 10 minutes.

Thermogravimetric analysis (TGA)

15 mL aliquots of supernatants were freeze dried in a 50 mL Falcon tube (Fisherbrand, polypropylene) using a Genevac evaporator (EZ-2 series); the resulting solids were transferred to a cellulose filter, repeatedly washed with ultrapure water and allowed to dry in a vacuum oven at 120 °C for 24 hrs. TGA measurements were performed on a Q500 instrument (TA Instruments, USA) under a nitrogen atmosphere and at 10 °C min⁻¹ using a temperature range of 20-1000 °C.

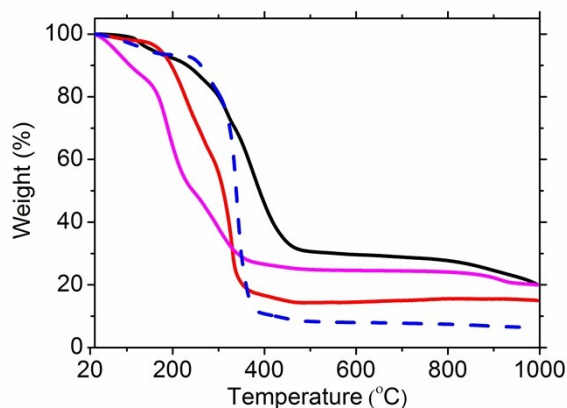


Figure S1: TGA of DOPC/MoS₂ dispersions (black solid line), DOPC/TiS₂ dispersions (red solid line), DOPC/WS₂ dispersions (purple solid line) and of pure DOPC (blue dashed line).

UV-Vis spectroscopy

UV-visible absorption spectra were recorded on a USB2000+UV-VIS fibre-optic spectrometer using a DH-2000-BAL deuterium-halogen light source (Ocean Optics).

Dynamic light scattering (DLS) and Zeta-potential measurements

A Malvern Zetasizer Nano ZS was operated in backscatter mode (173°), using a 633 nm HeNe laser. The 2D-material/DOPC dispersions were diluted in ultra-pure water (1:10 dilution) and equilibrated by the instrument to 25 °C for each measurement. The zeta potential was calculated by Malvern software using the Smoluchowski model.

X-ray photoelectron spectroscopy (XPS)

Samples were prepared by drop casting 100 μL of fresh dispersions onto 1 cm^2 Si/SiO₂ substrates (pre-cleaned by sonication in ethanol and acetone for 10 min), which were allowed to dry overnight. Spectra were measured using an AXIS Nova (Kratos Analytical, UK) with a monochromatic AlK α source operated at 225 W (15 kV and 15 mA). Analysis was performed using CasaXPS software, utilizing Shirley background subtraction and the appropriate relative sensitivity factors.

XPS: MoSe₂

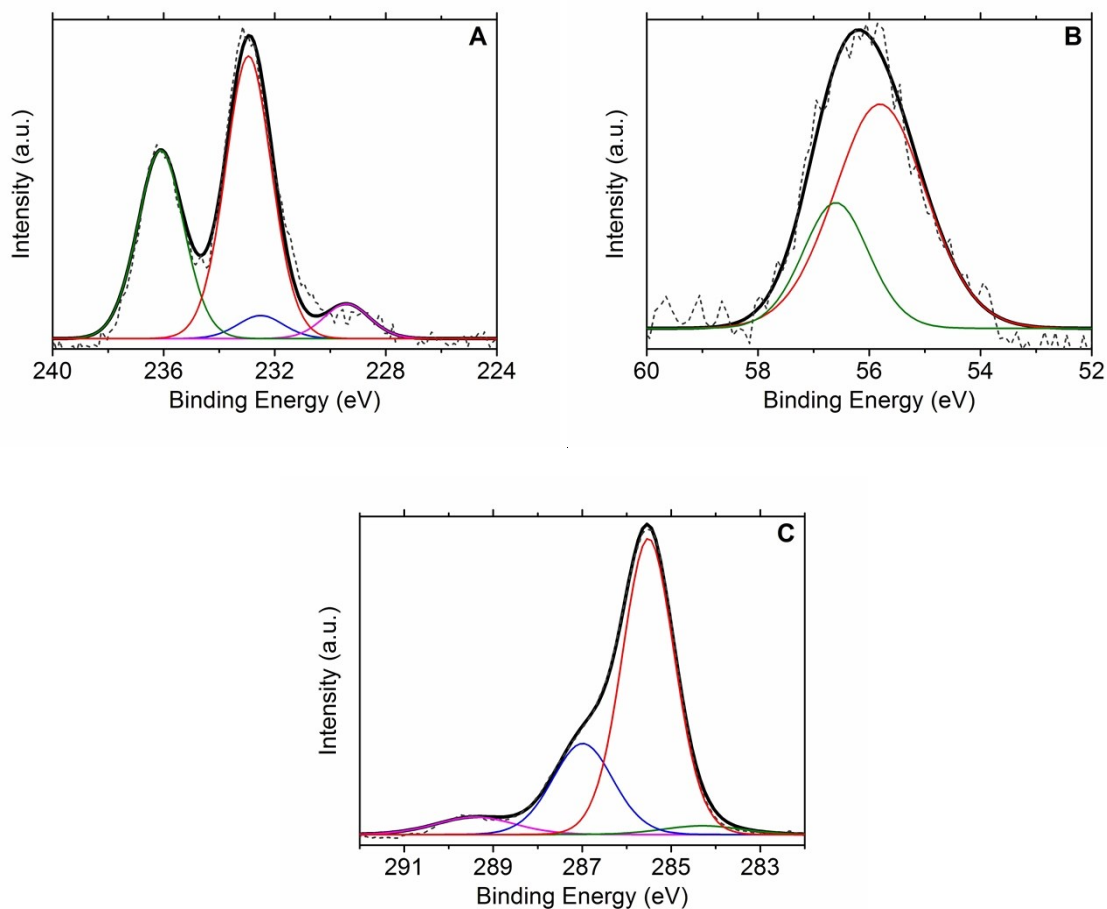


Fig. S2: (A) Mo3d XPS spectrum of a DOPC/MoSe₂ dispersion drop cast onto Si/SiO₂ substrate. In the fitting, the purple line corresponds to the Mo⁴⁺3d_{5/2} peak, the blue line to the Mo⁴⁺3d_{3/2} peak, the red line to the Mo⁶⁺3d_{5/2} peak and the green line to the Mo⁶⁺3d_{3/2} peak. (B) Se3d XPS spectrum of a DOPC/MoSe₂ dispersion drop cast onto Si/SiO₂ substrate. The fitting is for the Se3d doublet, with the red line depicting the Se3d_{5/2} peak and the green line the Se3d_{3/2} peak. (C) C1s XPS spectrum of a DOPC/MoSe₂ dispersion drop cast onto Si/SiO₂ substrate. In the fitting, the green line corresponds to the C-C sp² peak, the red line to the C-C sp³ peak, the blue line to the C-O/C-N peak and the purple line to the O-C=O peak.

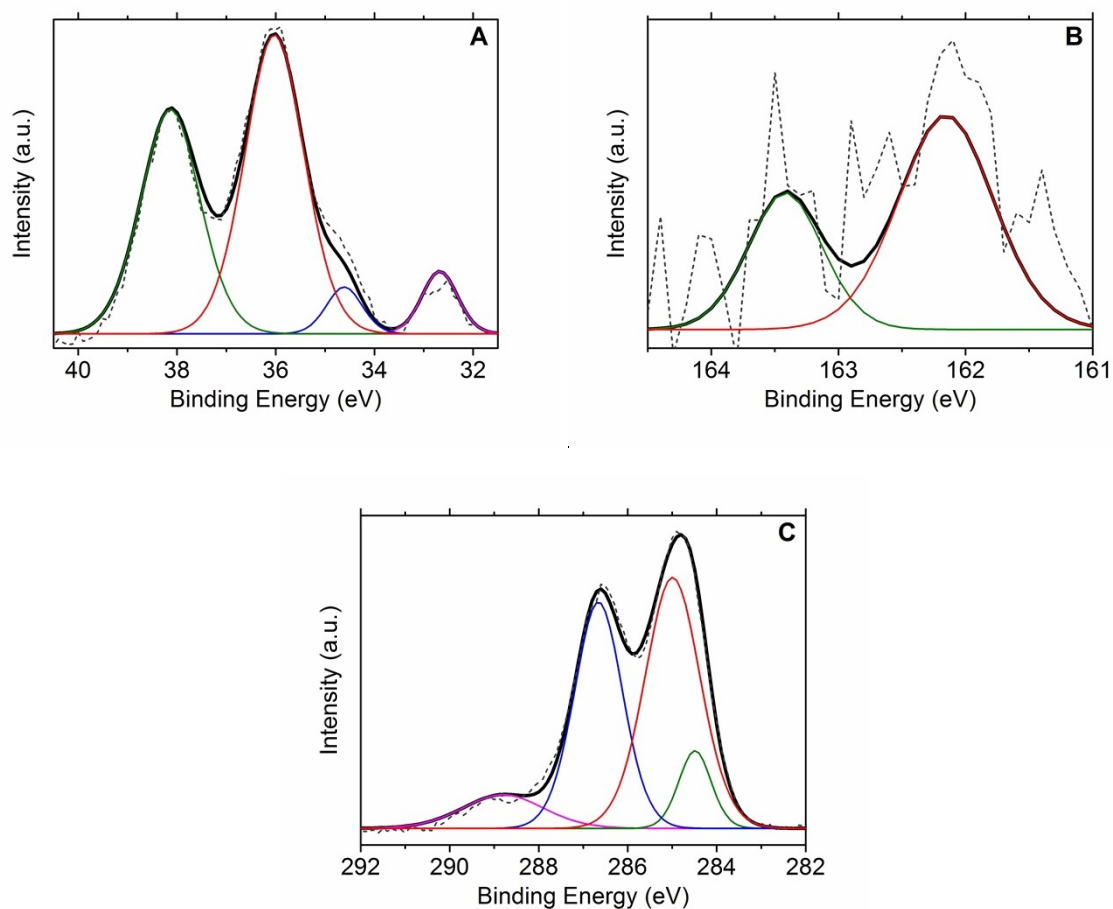


Fig. S3: **(A)** W4f XPS spectrum of a DOPC/WS₂ dispersion drop cast onto Si/SiO₂ substrate. In the fitting, the purple line corresponds to the W⁴⁺4f_{7/2} peak, the blue line to the W⁴⁺4f_{5/2} peak, the red line to the W⁶⁺4f_{7/2} peak and the green line to the W⁶⁺4f_{5/2} peak. **(B)** S2p XPS spectrum of a DOPC/WS₂ dispersion drop cast onto Si/SiO₂ substrate. The fitting is for the S2p doublet, with the red line depicting the S2p_{3/2} peak and the green line the S2p_{1/2} peak. **(C)** C1s XPS spectrum of a DOPC/WS₂ dispersion drop cast onto Si/SiO₂ substrate. In the fitting, the green line corresponds to the C-C sp² peak, the red line to the C-C sp³ peak, the blue line to the C-O/C-N peak and the purple line to the O-C=O peak.

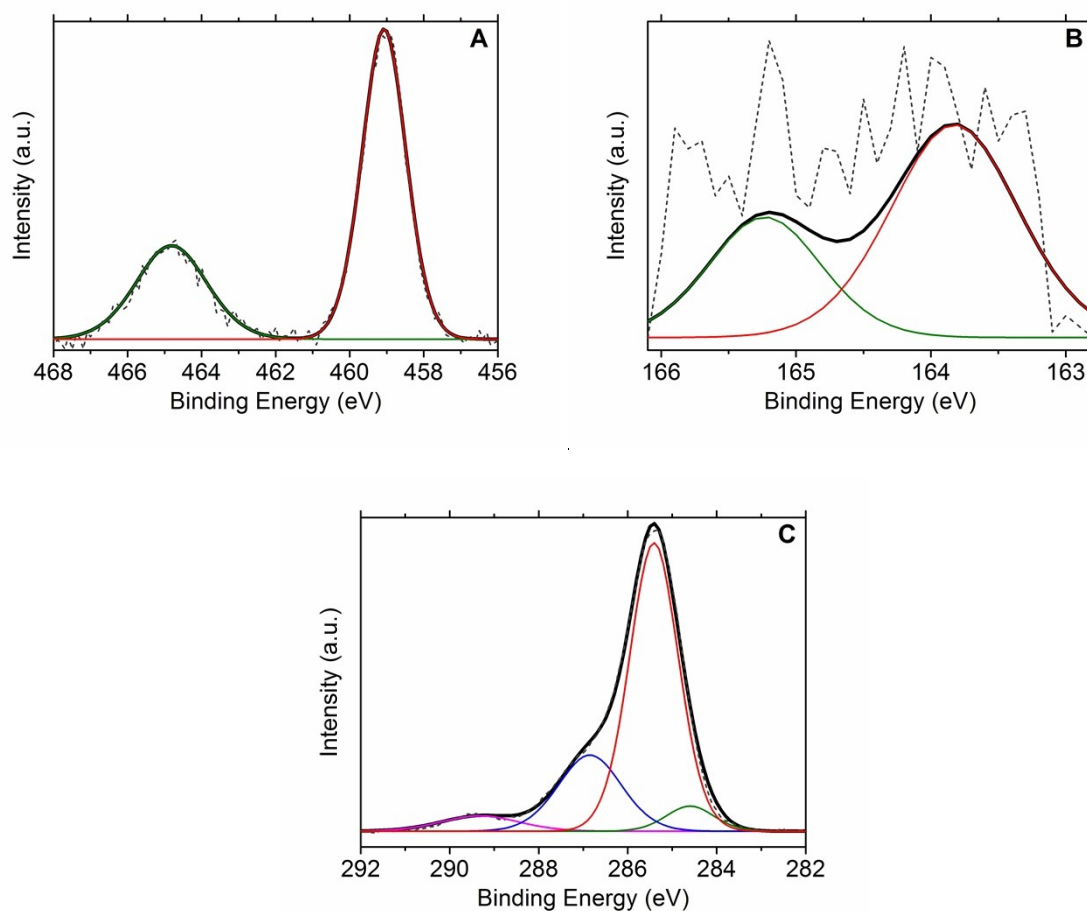


Fig. S4: (A) Ti2p XPS spectrum of a DOPC/TiS₂ dispersion drop cast onto Si/SiO₂ substrate. In the fitting, the red line corresponds to the Ti2p_{3/2} peak and the green line to the Ti2p_{1/2} peak. (B) S2p XPS spectrum of a DOPC/TiS₂ dispersion drop cast onto Si/SiO₂ substrate. The fitting is for the S2p doublet, with the red line depicting the S2p_{3/2} peak and the green line the S2p_{1/2} peak. (C) C1s XPS spectrum of a DOPC/TiS₂ dispersion drop cast onto Si/SiO₂ substrate. In the fitting, the green line corresponds to the C-C sp² peak, the red line to the C-C sp³ peak, the blue line to the C-O/C-N peak and the purple line to the O-C=O peak.

Raman spectroscopy

Samples were prepared by drop casting 100 μL of fresh dispersions onto 1 cm^2 Si/SiO₂ substrates (pre-cleaned by sonication in ethanol and acetone for 10 min), followed by drying at 70 $^\circ\text{C}$ for approximately 10 min. Powder samples were used to obtain spectra for the bulk starting-materials. Raman spectra and photoluminescence (PL) measurements were taken on a Renishaw inVia system using 532 nm (2.33 eV) excitation energy (laser power of 1.8 mW) and a 100 \times objective (numerical aperture of 0.9), giving a spot size of approximately of 1 μm . This system uses a high-resolution grating of 1800 g mm^{-1} , giving a spectral resolution $\leq 1 \text{ cm}^{-1}$. Spectra represent three accumulations at 5 s of exposure time.

Raman and PL Spectra: MoS₂

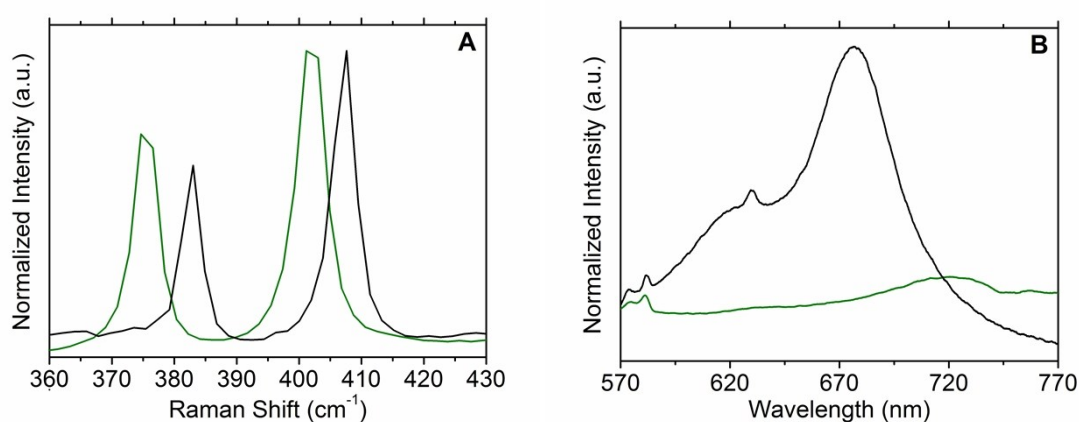


Fig. S5: (A) Raman spectra of the DOPC/MoS₂ dispersion drop cast onto Si/SiO₂ substrate (black line) and the bulk (powder) starting-material (green line); normalized to the A_{1g} peak. (B) PL spectra of the DOPC/MoS₂ dispersion drop cast onto Si/SiO₂ substrate (black line) and the bulk (powder) starting-material (green line); normalized to the A_{1g} peak.

Raman and PL Spectra: WS₂

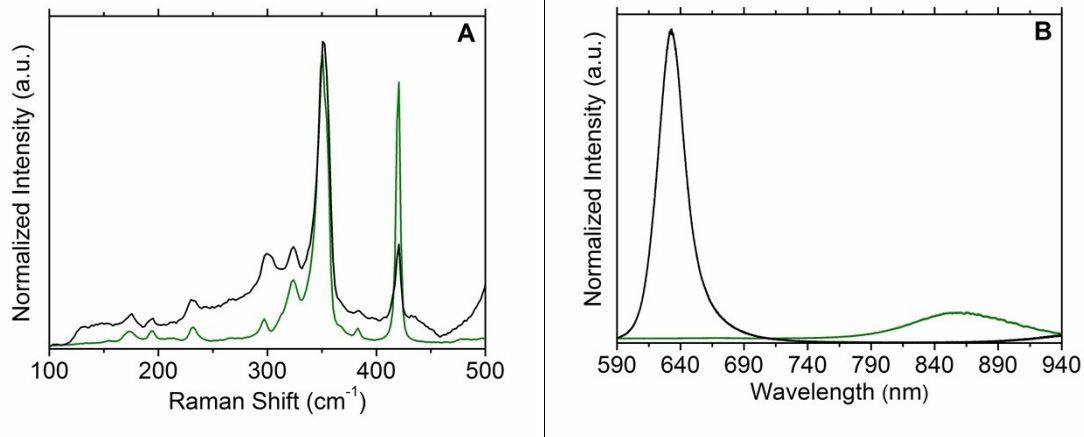


Fig. S6: (A) Raman spectra of the DOPC/WS₂ dispersion drop cast onto Si/SiO₂ substrate (black line) and the bulk (powder) starting-material (green line); normalized to the E_{2g} peak. (B) PL spectra of the DOPC/WS₂ dispersion drop cast onto Si/SiO₂ substrate (black line) and the bulk (powder) starting-material (green line); normalized to the E_{2g} peak.

Raman and PL Spectra: MoSe₂

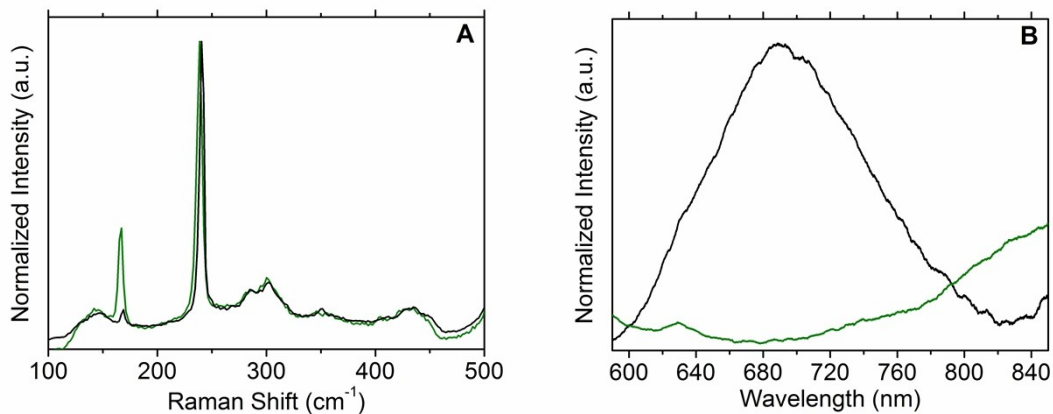


Fig. S7: (A) Raman spectra of the DOPC/MoSe₂ dispersion drop cast onto Si/SiO₂ substrate (black line) and the bulk (powder) starting-material (green line); normalized to the A_{1g} peak. (B) PL spectra of the DOPC/MoSe₂ dispersion drop cast onto Si/SiO₂ substrate (black line) and the bulk (powder) starting-material (green line); normalized to the A_{1g} peak.

Raman and PL Spectra: TiS₂

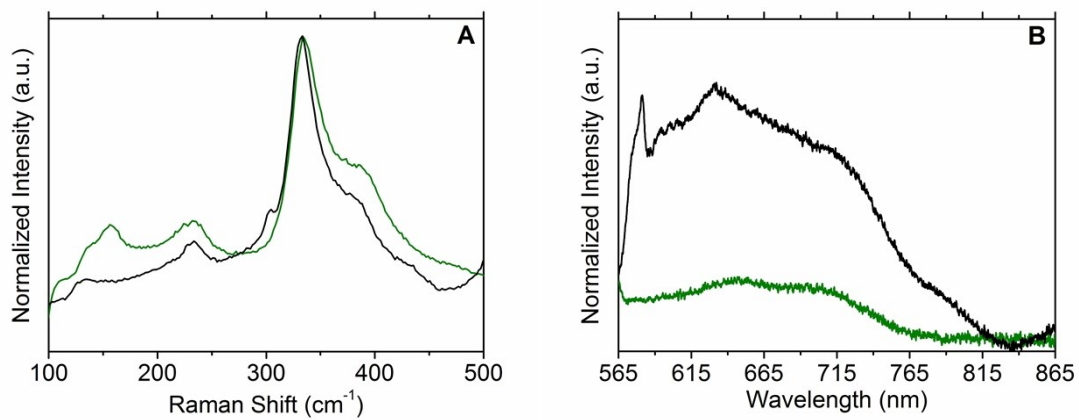


Fig. S8: (A) Raman spectra of the DOPC/TiS₂ dispersion drop cast onto Si/SiO₂ substrate (black line) and the bulk (powder) starting-material (green line); normalized to the A_{1g} peak. (B) PL spectra of the DOPC/TiS₂ dispersion drop cast onto Si/SiO₂ substrate (black line) and the bulk (powder) starting-material (green line); normalized to the A_{1g} peak.

Atomic force microscopy (AFM)

Samples were prepared by drop casting 100 μL of fresh dispersions onto 1 cm^2 clean mica substrates, which were allowed to dry overnight. AFM measurements were performed in peak-force tapping mode using silicon nitride SNL-10 cantilevers with a Multimode 8 AFM (Bruker, UK).

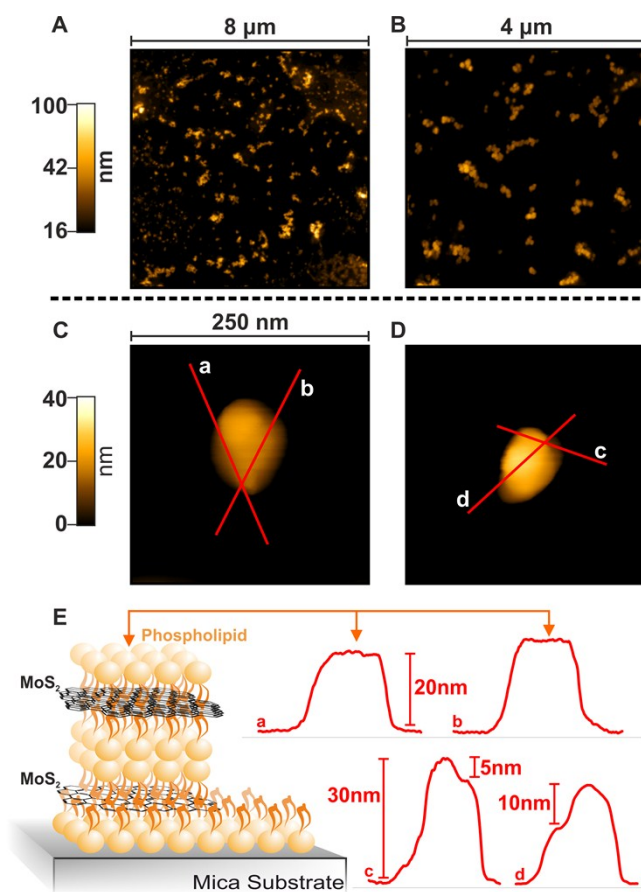


Fig. S9: Height AFM images of DOPC-coated MoS₂ for areas: 8 x 8 μm (A) and 4 x 4 μm (B). The objects are characterised by an average height of 40 nm. Profiles acquired on single objects (C & D) showed “steps” of 5 nm in height (or multiples of 5 nm) (E) which we ascribe to a DOPC bilayer between MoS₂ sheets, as proposed in the schematic presented in (E).