

Supplementary Information

Two-dimensional covalent crystals by chemical conversion of thin van der Waals materials

Vishnu Sreepal^{1,2}, Mehmet Yagmurcukardes³, Kalangi S. Vasu^{1,2}, Daniel J. Kelly⁴, Sarah F. R. Taylor², Vasyl G. Kravets⁵, Zakhar Kudrynskyi⁶, Zakhar D. Kovalyuk⁷, Amalia Patanè⁶, Alexander N. Grigorenko⁵, Sarah J. Haigh^{1,4}, Christopher Hardacre², Laurence Eaves^{5,6}, Hasan Sahin⁸, Andre K. Geim⁵, Francois M. Peeters³, Rahul R. Nair^{1,2}*

¹National Graphene Institute, University of Manchester, Manchester, M13 9PL, UK.

²School of Chemical Engineering and Analytical Science, University of Manchester, Manchester, M13 9PL, UK.

³Department of Physics, University of Antwerpen, Groenenborgerlaan 171, B-2020 Antwerpen, Belgium.

⁴School of Materials, University of Manchester, Manchester, M13 9PL, UK.

⁵School of Physics and Astronomy, University of Manchester, Manchester, M13 9PL, UK.

⁶School of Physics and Astronomy, University of Nottingham, Nottingham, NG7 2RD, UK.

⁷Institute for Problems of Materials Science, The National Academy of Sciences of Ukraine, Chernivtsi Branch, Chernivtsi 58001, Ukraine.

⁸Department of Photonics, Izmir Institute of Technology, 35430, Izmir, Turkey.

Corresponding author

Email: rahul@manchester.ac.uk, Tel: +44 (0) 1613066574

Supplementary text

#1. Calculated Raman Spectrum of InF₃ and Se doped InF₃

The calculated Raman spectrum of pristine InF₃ reveals that it has a prominent peak located at 182.1 cm⁻¹, consistent with the experimental data, which is attributed to the in-plane vibrations of the F-atoms. Apart from this most prominent peak, there are some low intensity Raman-active modes at 230.7, 249.1, 251.2, 252.5, 259.6, 386.6, and 474.4 cm⁻¹ (Figure. 3c). Our calculation reveals that Se-doping results in additional Raman active modes. For a Se doping of 2.1%, a broad prominent peak centred at 250.6 cm⁻¹ is observed. Note that in the pure InF₃ structure, the Raman modes with frequencies 249.1, 251.2, 252.5, and 259.6 cm⁻¹ are non-degenerate, whereas in the Se-doped InF₃ structure, due to the 2×2×1 supercell, each mode has 4-fold-degeneracy. However, due to the small distortion in the supercell, the degeneracy of these modes is broken and 16 phonon modes appear, some of which are Raman inactive. Therefore, in the Raman spectrum of the Se-doped structure, the phonon modes around the broad peak at 250 cm⁻¹ are attributed to the modes arising from the InF₃ crystal. Moreover, the shoulder peak at 228.6 cm⁻¹ (experimentally found to be around ≈232 cm⁻¹) is attributed to the In-Se bond stretching. We have also noticed weaker modes around ≈495 cm⁻¹ that arise from bulk InF₃. Their intensities are very low and only become prominent after Se-doping (Figure. S2).

Supplementary Figures

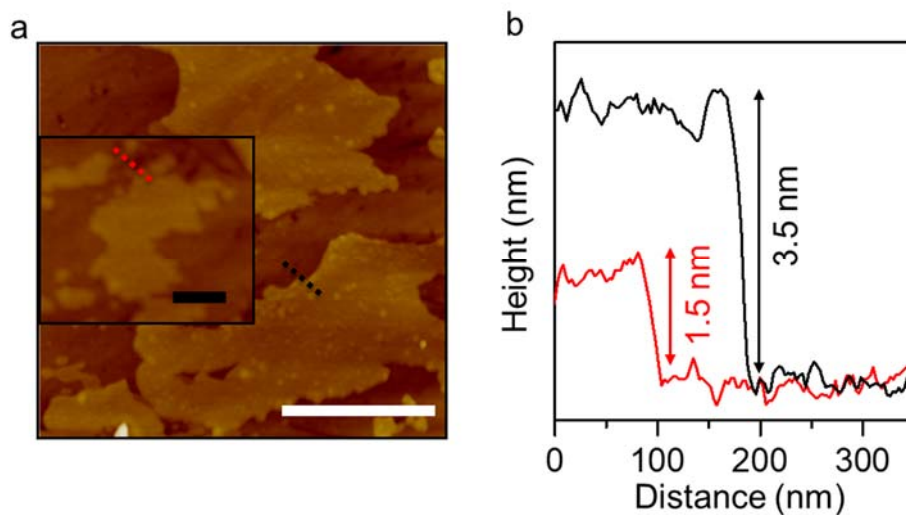


Figure S1. Atomic Force Microscopy (AFM) Image of thin InF_3 crystals. **a**, AFM image of 4 nm thick and 1.5 nm thick (inset. Scale bar, 0.5 μm) fluorinated InSe flakes. Scale bar, 1.5 μm . **b**, The height profile along the dotted lines in Figure S1a.

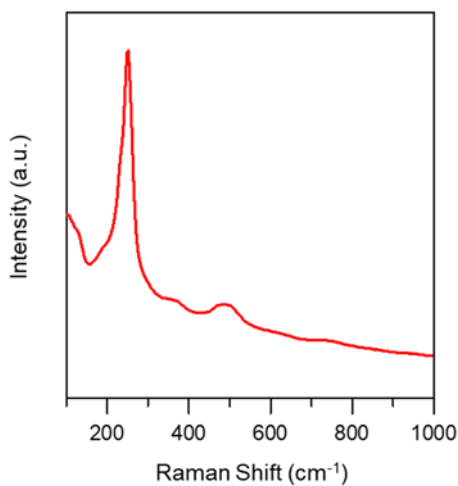


Figure S2. Raman spectrum of fluorinated InSe. Raman spectrum of fluorinated InSe over an extended range of wavenumbers.

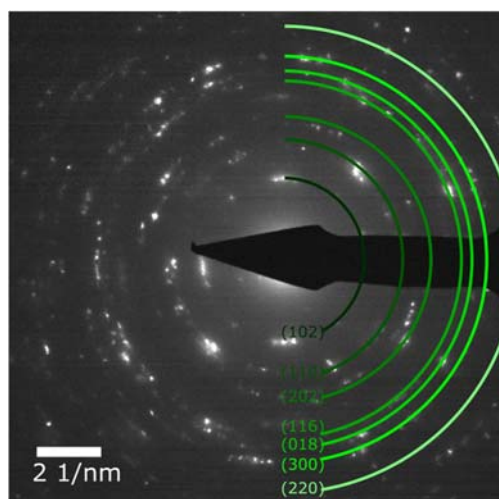


Figure S3. Selected Area Electron Diffraction (SAED) pattern of fluorinated InSe. SAED pattern obtained from a polycrystalline region of the fluorinated InSe sample. The labelled diffraction rings correspond to specific planes of the InF_3 crystal structure.

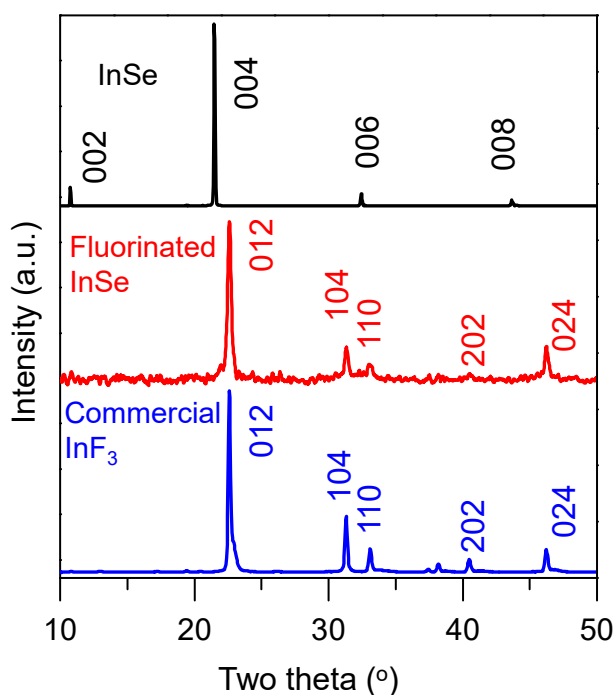


Figure S4. X-Ray Diffraction (XRD) characterization of fluorinated InSe. XRD spectra of pristine InSe, InSe after fluorination, and commercial InF_3 powder (colour-coded labels). The similar XRD spectra of fluorinated InSe and InF_3 indicate the conversion of InSe into InF_3 after the fluorination. The absence of any InSe diffraction peak in the fluorinated sample confirms the complete conversion of InSe into InF_3 . The Miller indices of the Bragg reflections are labelled.

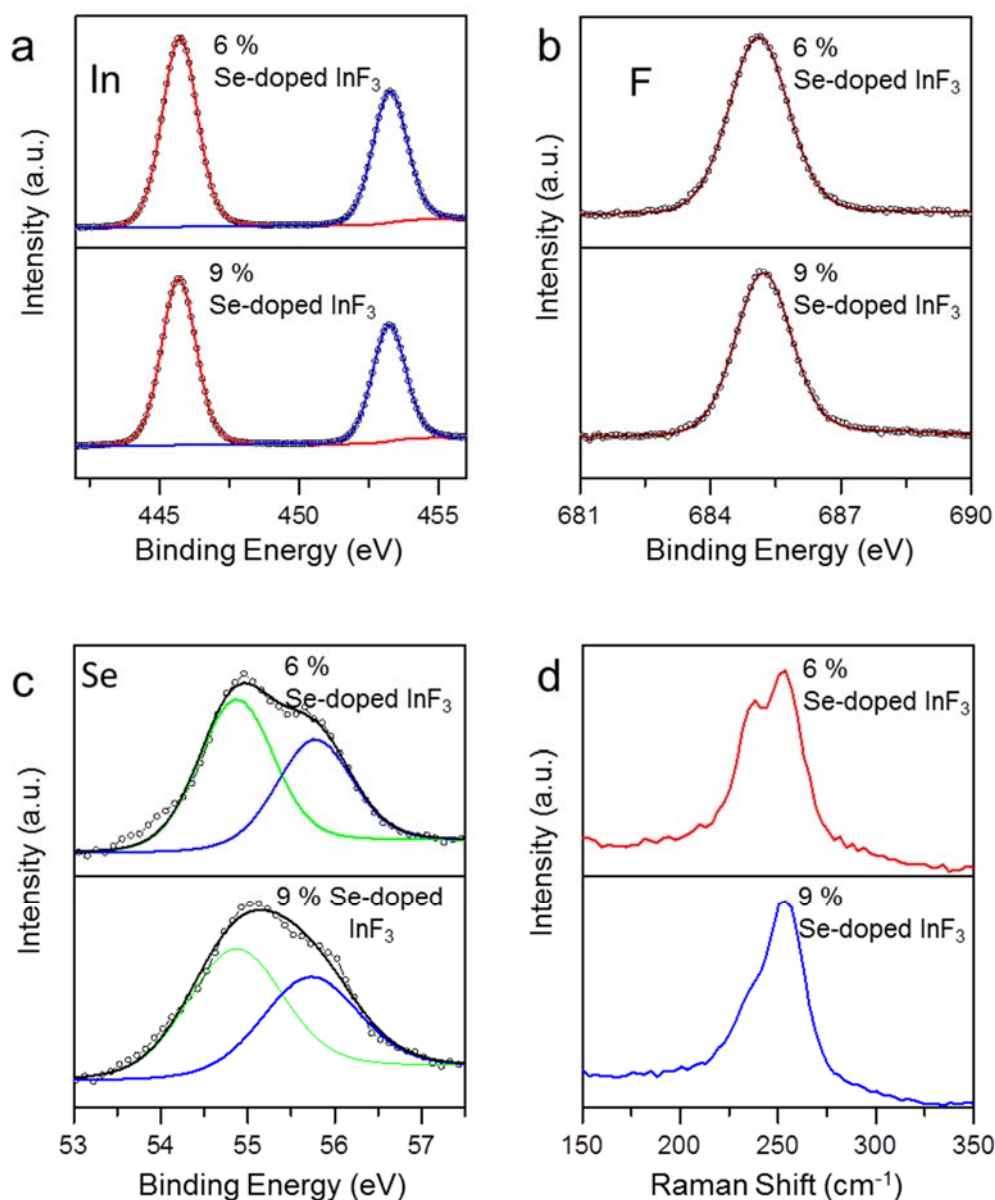


Figure S5. Tuning Se doping in InF_3 samples. XPS spectra of 6% and 9% Se doped InF_3 showing **a**, Indium, **b**, Fluorine and **c**, Selenium peaks. Se doping levels in the samples were controlled by the amount of XeF_2 crystals used for fluorination; higher XeF_2 leads to smaller doping level (~10 times by mass gives 9% Se doping and 40 times by mass gives 6% Se doping) **d**, Raman Spectra of 6% and 9% Se doped InF_3 at an excitation wavelength of 532 nm. No appreciable change in the Raman spectra is observed on varying the amount of Se doping.

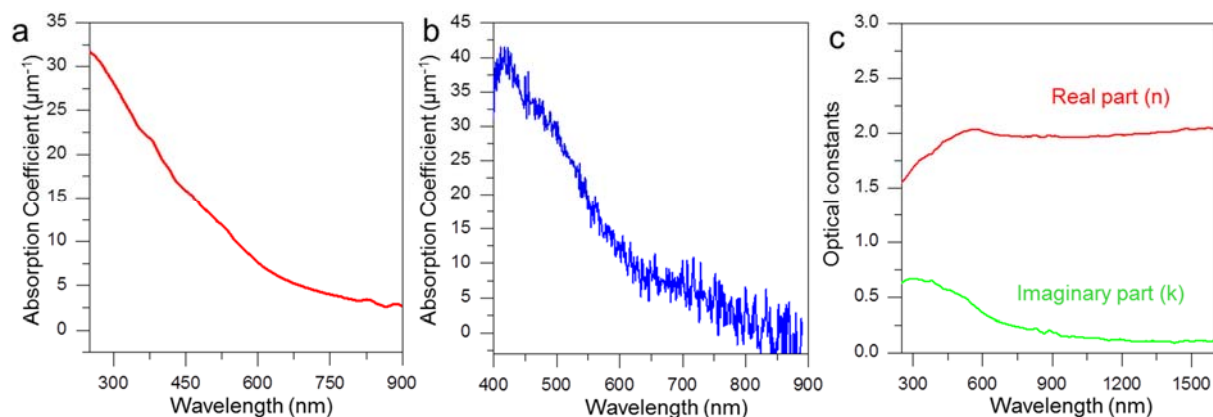


Figure S6. Optical characterisation of InF₃. Absorption coefficient of **a**, bulk InF₃ obtained by the fluorination of bulk InSe and **b**, InF₃ obtained by the fluorination of InSe flakes (≈ 10 nm thick). **c**, Optical constants of InF₃ crystal showing real and imaginary parts.

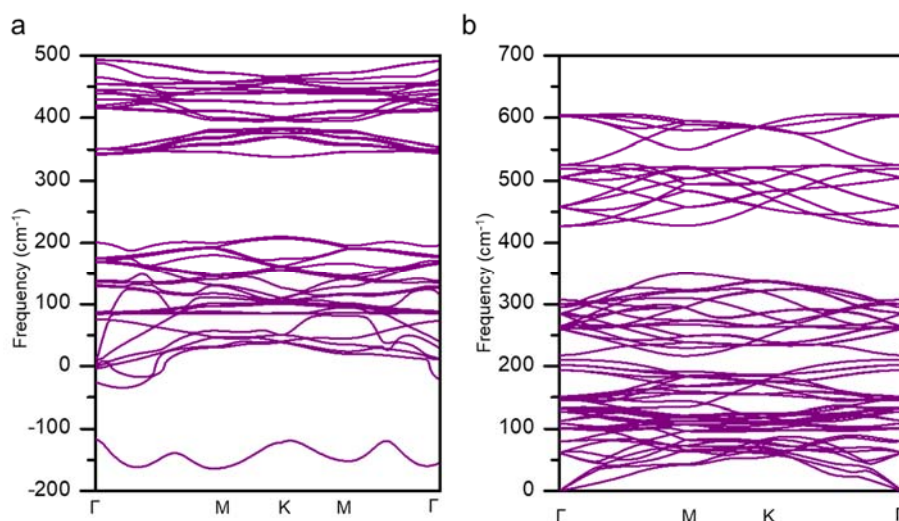


Figure S7. Phonon dispersion curve for thin InF₃ structures. Phonon dispersion curves for optimised structure of **a**, fully fluorinated bilayer InSe and **b**, fully fluorinated bulk InSe. Our structure optimisation calculation shows that fully fluorinated bilayer InSe is dynamically unstable. This is evident from the corresponding phonon dispersion curves which show a negative frequency throughout the Brillouin zone. Our calculations reveal that fluorination of bi- and monolayers of InSe does not lead to the formation of InF₃; however, fluorination of 3 and more layers of InSe leads to a stable InF₃ crystal structure. Furthermore, our calculations show that three-layer fluorinated InSe has 6-indium layers with a thickness of ≈ 1.4 nm, in agreement with the experimental results.

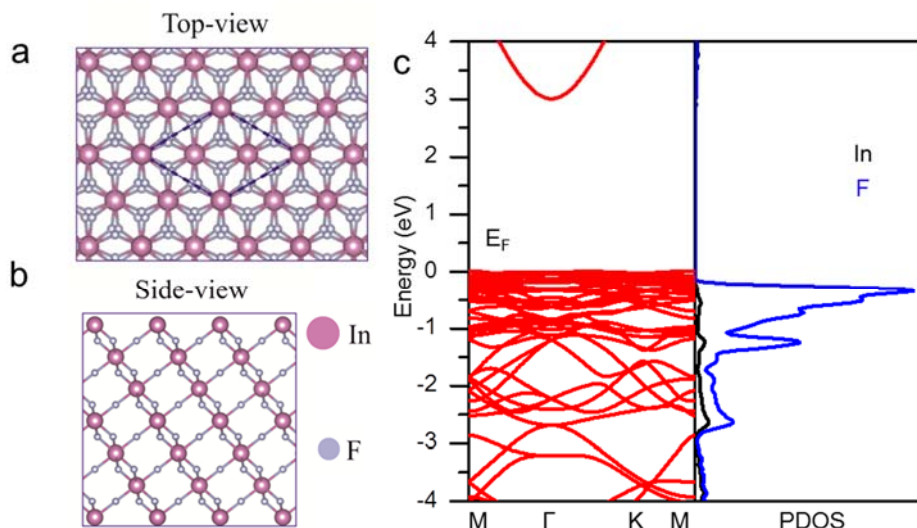


Figure S8. Bandstructure of InF₃. **a**, The crystal structure of pristine InF₃. **b**, Side view of the InF₃ crystal structure. **c**, Calculated band structure and the corresponding partial density of states (PDOS) of pristine InF₃ (colour-coded labels). The Fermi energy is set to 0 eV.

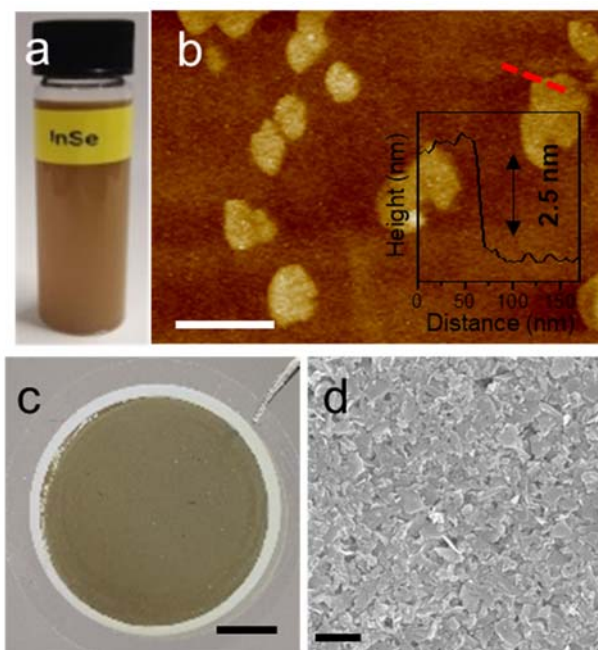


Figure S9. Liquid exfoliated InSe nanosheets. **a**, Photograph of liquid-exfoliated InSe suspension. **b**, AFM image showing few-layer thick liquid exfoliated InSe nanosheets. Scale bar, 200 nm. Height profile along the dashed line is given as inset. Majority of the flakes obtained by liquid exfoliation were found to be < 4 nm in thickness. Samples for AFM were obtained by drop-casting InSe suspension on an oxidised silicon wafer. **c**, Photograph of InSe laminate on Anodisc alumina filter obtained by vacuum filtering the InSe suspension. Scale bar, 5 mm. **d**, SEM image of InSe laminate. Scale bar, 400 nm.

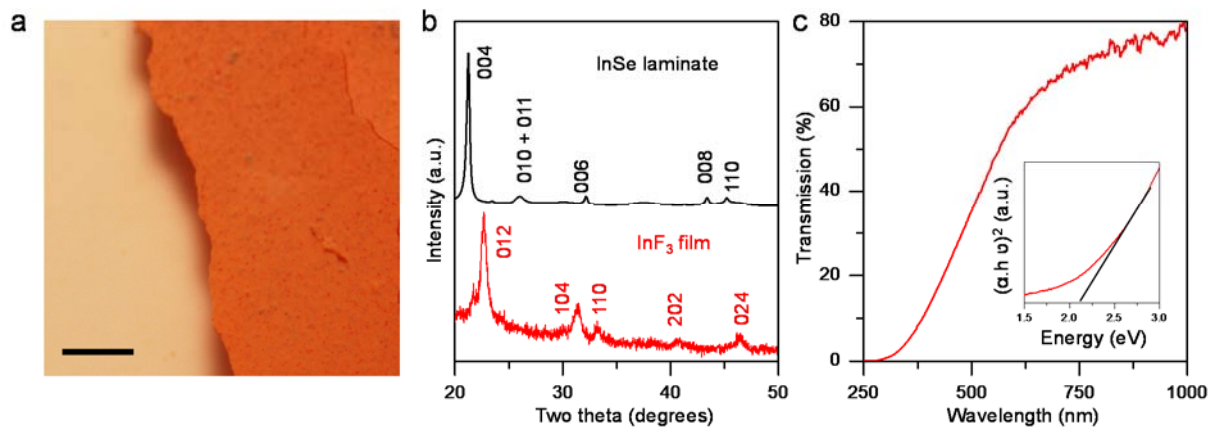


Figure S10. Large area InF₃ film. **a**, Photograph of a free-standing InF₃ film obtained by fluorinating an InSe laminate. Scale bar, 1 mm. **b**, XRD of InSe laminate and fluorinated InSe film. The Miller indices of the Bragg reflections are labelled. **c**, Optical transmission spectra of large area InF₃ film. Inset: the associated Tauc plot indicate a direct bandgap of 2.2 eV. Compared to the InF₃ crystal, the transition is noted to be broad in InF₃ thin films and this could be due to the polycrystallinity or the presence of defects in the sample.