

## Supporting information

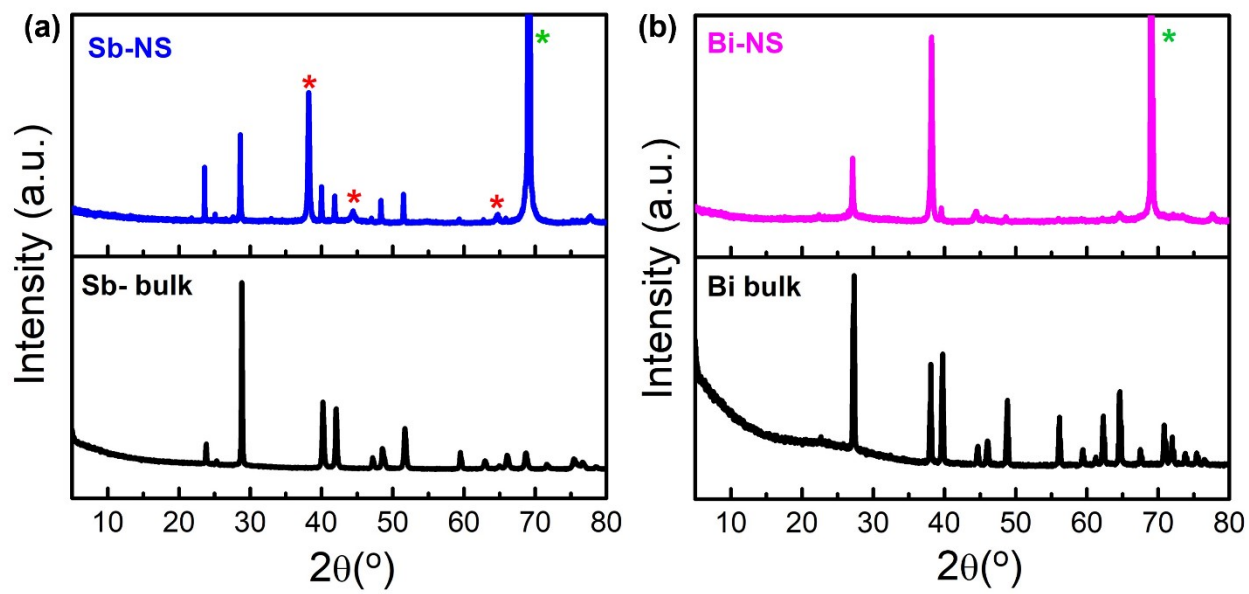
### Functionalization of Antimonene and Bismuthene with Lewis acids

*Manaswee Barua*‡, *Mohd Monis Ayyub*‡, *Shashidhara Acharya* and *C.N.R. Rao*\*

New Chemistry Unit, International Centre for Material Science and School of Advanced Materials,  
Jawaharlal Nehru Center for Advanced Scientific Research, Bangalore-560064, India

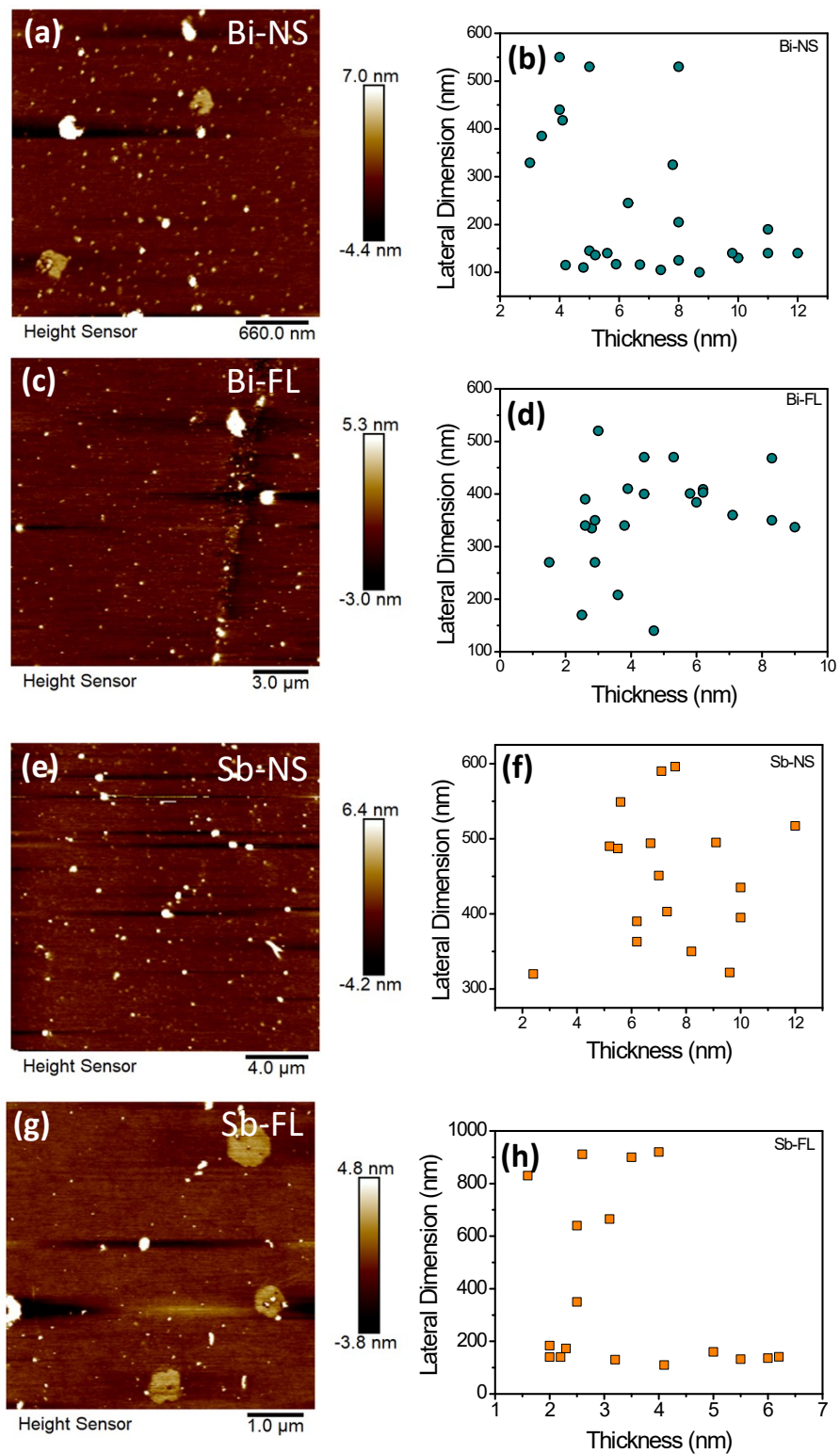
E-mail: [cnrrao@jncasr.ac.in](mailto:cnrrao@jncasr.ac.in)

‡ These authors contributed equally to this work.

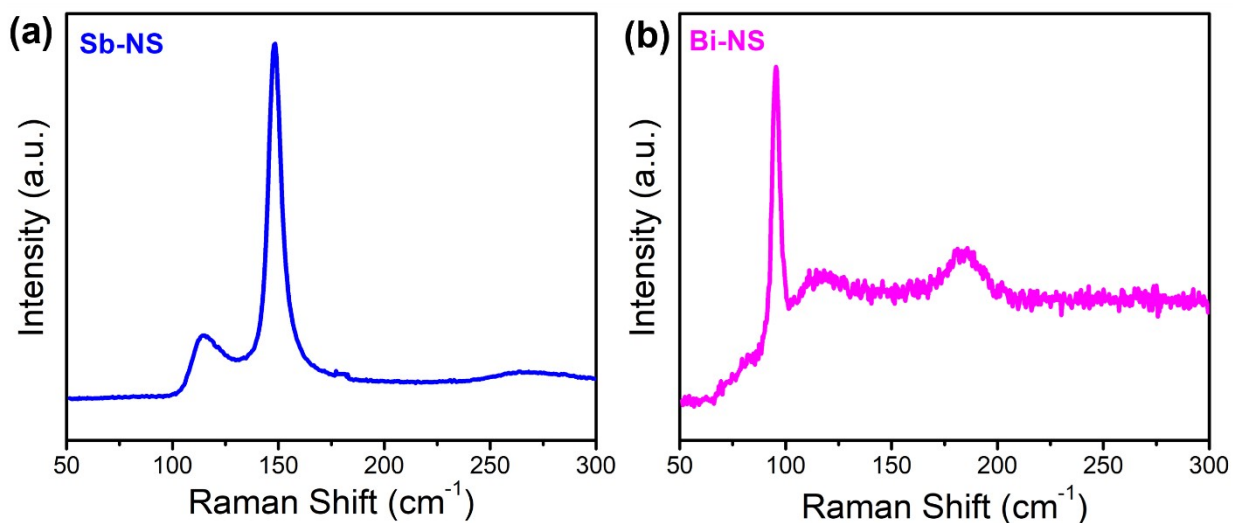


**Figure S1.** X-ray diffraction patterns of (a) Sb nanosheets (Sb-NS) in comparison with bulk Sb and (b) Bi nanosheets (Bi-NS) in comparison with bulk Bi.

\*Au peaks from substrate, \*Si substrate



**Figure S2.** Atomic force microscopy images of (a) Bi-NS, (c) Bi-FL, (e) Sb-NS and (g) Sb-FL; and their corresponding dimensional statistics



**Figure S3.** Raman spectra of (a) Sb nanosheets (Sb-NS) (under 514 nm laser) and (b) Bi nanosheets (Bi-NS) (under 633 nm laser) after being exposed to ambient conditions for over a year.

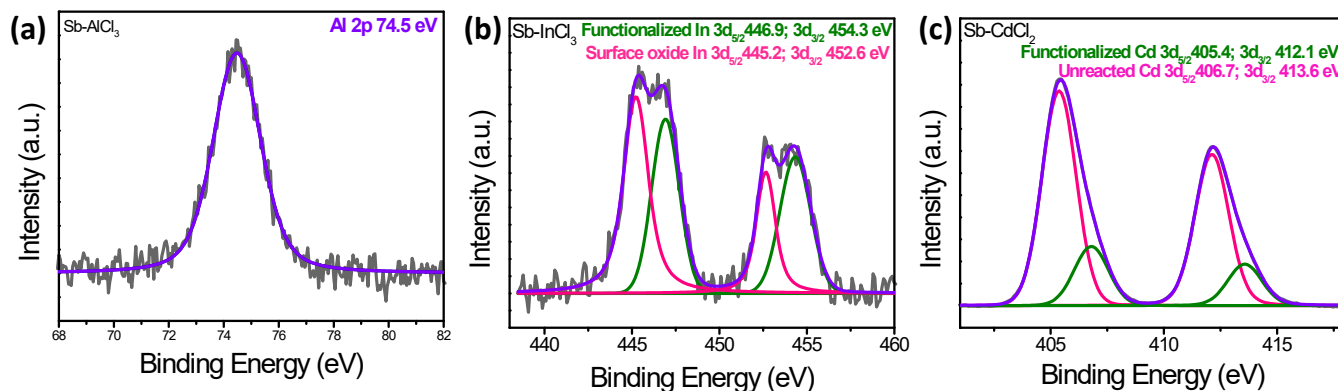
#### Note on XPS:

Bi 4f core level XPS consists of Bi  $4f_{7/2}$  and  $4f_{5/2}$  peaks. Bi  $4f_{7/2}$  core level spectra of Bi-NS show two peaks corresponding to Bi(0) and surface Bi-oxide species. On functionalization, Bi  $4f_{7/2}$  can be deconvoluted into two peaks corresponding to functionalized Bi and functionalized surface Bi-oxide species. Sb 3d core-level peak can be deconvoluted into Sb  $3d_{5/2}$  and  $3d_{3/2}$  peaks with a spin-orbit coupling of  $\sim 9.39$  eV. These peak intensities are approximately symmetric for Sb metal while for Sb-oxide it is asymmetric. The O1s core-level peak coincides with the Sb  $3d_{5/2}$  component and hence the Sb  $3d_{3/2}$  peak was used as a guide for fitting the other peak. The binding energy and peak intensities of Sb  $3d_{5/2}$  peaks for both Sb metal and Sb oxide were set according to the spin-orbit coupling considerations and relative intensities of the corresponding Sb  $3d_{3/2}$  peaks. Upon functionalization, the Sb 3d peaks can be deconvoluted into three peaks corresponding to

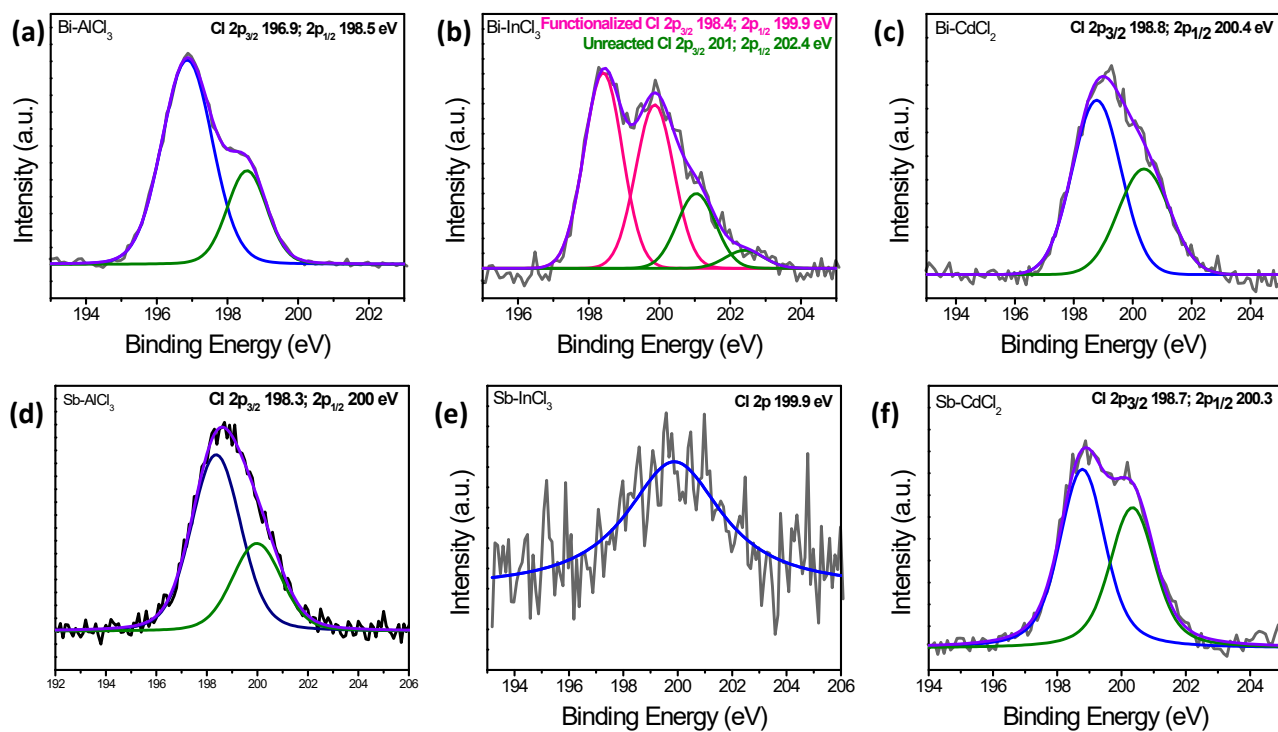
unreacted Sb(0), functionalized Sb, and functionalized Sb-oxide along with an additional peak corresponding to O1s for the Sb 3d<sub>5/2</sub> peak.

For Sb-AlCl<sub>3</sub> and Bi-AlCl<sub>3</sub>, Al 2p core-level XPS has two components 2p<sub>3/2</sub> and 2p<sub>1/2</sub> with a doublet splitting of ~0.4 eV. Due to very small doublet splitting, the components of Al 2p cannot be deconvoluted easily, therefore Al 2p is fitted with one component.

In 3d core-level spectrum in Bi-InCl<sub>3</sub> can be deconvoluted into In 3d<sub>5/2</sub> and 3d<sub>3/2</sub> and consists of small amounts of unreacted InCl<sub>3</sub>. The In 3d<sub>5/2</sub> peak in Bi-InCl<sub>3</sub> overlaps with Bi 4d<sub>5/2</sub> but Bi 4d<sub>3/2</sub> is out of range. For Sb-InCl<sub>3</sub>, the In 3d component has a significant amount of In-oxide species which could be due to exposure to air during sample storage. Bi-InCl<sub>3</sub> has a relatively lesser amount of surface In-oxide species. For Sb-CdCl<sub>2</sub> and Bi-CdCl<sub>2</sub>, the Cd 3d core-level spectra can be deconvoluted into 3d<sub>5/2</sub> and 3d<sub>3/2</sub> peaks along with small amounts of unreacted CdCl<sub>2</sub>.

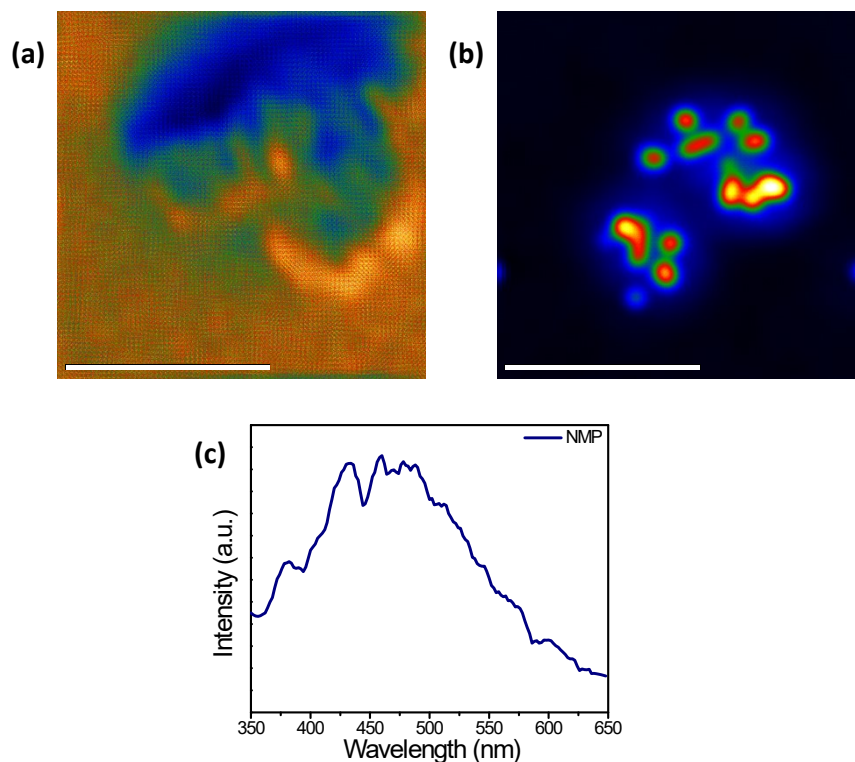


**Figure S4.** XPS core level spectra of (a) Al 2p Sb-AlCl<sub>3</sub>, (b) In 3d Sb-InCl<sub>3</sub> and (c) Cd 3d Sb-CdCl<sub>2</sub>.



**Figure S5.** XPS Cl 2p core level spectra of (a) Bi-AlCl<sub>3</sub>, (b) Bi-InCl<sub>3</sub>, (c) Bi-CdCl<sub>2</sub>, (d) Sb-AlCl<sub>3</sub>, (e) Sb-InCl<sub>3</sub> and (f) Sb-CdCl<sub>2</sub>.

## Note on cathodoluminescence spectroscopy:

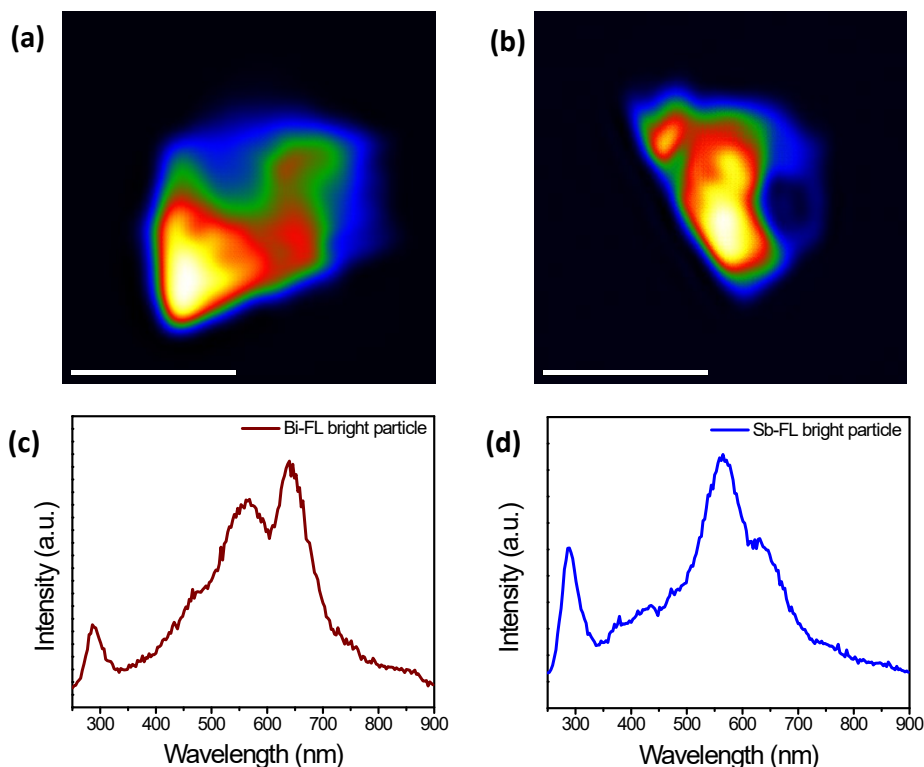


**Figure S6.** CL mapping of (a) NMP, (b) bright polymerized NMP particles, and (c) the corresponding CL spectra of bright polymerized NMP particles.

The solvent used for exfoliation of Sb and Bi is N-methyl pyrrolidone (NMP) is known to show fluorescence around 420 nm. Moreover, on being subjected to sonication NMP is known to polymerize and show emission in the range of 350-450 nm.<sup>1,2</sup> For our emission study, NMP was subjected to similar probe sonication conditions and drop coated on Si substrate and this spectrum was used as blank and other spectra were analyzed accordingly. In most regions, CL mapping of NMP sample did not show any emission (**Figure S4a**). However, in some places, we could observe some bright regions which according to literature could be polymerized NMP and we observe a sharp emission at around 475 nm with a shoulder at around 425 nm (**Figure S4b** and **4c**).

Moreover, the electron beam in SEM damages the NMP particles, which is not the case for Sb and Bi sheets.

While carrying out FESEM-cathodoluminescence (CL) measurements of Sb and Bi-FL, we could observe many weak emissive sheets and some bright sheets. CL spectra of the bright Bi sheets exhibit very sharp peaks at 290 nm, 530 nm, 590 nm, and 660 nm with a broad peak at ~450 nm (**Figure S5a and S5c**). And these peaks were used as the basis to deconvolute the broad CL spectra of the less-emissive sheets. CL spectra of all sheets have a broad feature between 250-900 nm. CL spectra of the bright Sb sheets exhibit very sharp peaks at 290 nm, 430 nm, 560 nm, 650 nm, and 750 nm (**Figure S5b and S5d**). We do not observe any prominent emission above 700 nm for bright sheets. The broad peak above 700 nm for the less emissive sheets could be due to



**Figure S7.** CL mapping of bright (a) Bi-FL , (b) Sb-FL and their corresponding CL spectra (c) Bi-FL and (d) Sb-FL



background correction. For the functionalization study, only these less emissive sheets were taken into consideration as these give a better representation of the sample.

## References

- 1 G. Song, Y. Lin, Z. Zhu, H. Zheng, J. Qiao, C. He and H. Wang, *Macromol. Rapid Commun.*, 2015, **36**, 278–285.
- 2 S. P. Ogilvie, M. J. Large, G. Fratta, M. Meloni, R. Canton-Vitoria, N. Tagmatarchis, F. Massuyeau, C. P. Ewels, A. A. K. King and A. B. Dalton, *Sci. Rep.* 2017, **7**, 1–7.