**Electronic Supplementary Information (ESI)** *for*

# Isolation of pristine MXene from $Nb_4AlC_3$ MAX phase: A first-principles study

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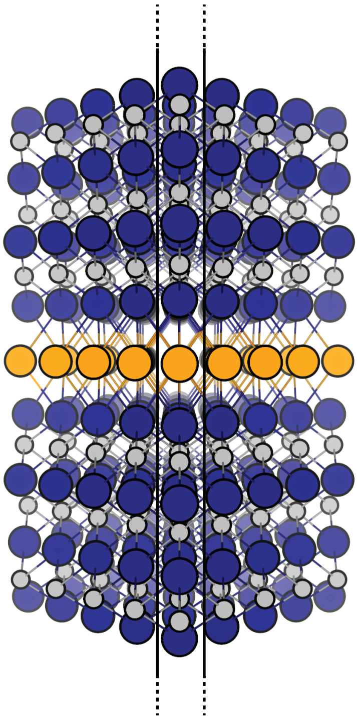

Figure S1: Model structure (vacuum-MXene-Al-MXene-vacuum) taken for the calculation of BDE of bonds in $Nb_4AlC_3$. The two $Nb_4C_3$ layer are interleaved with atomically thin Al layer. Black lines represent the unit cell of $Nb_4AlC_3$. For the insertion of guest species same geometry has been used. Nb, C and Al atoms are shown by blue, grey and orange balls, respectively.

## Structure of $Nb_4AlC_3$ with and without intercalants

The MAX phase of $Nb_4AlC_3$ has layered hexagonal structure with $P6_3/mmc$ space group. Figure S2a is showing the unit cell of the MAX phase. The Al atom stays over the Nb top site of the second sublayer of both MXene layers. The equilibrium interlayer and vertical distance between $Nb_4C_3$ layer and Al are D = 5.22 Å and $d_e$ = 2.26 Å, respectively.

Figure S2b shows the relaxed structure of $Nb_4AlC_3$ with HF. As apparent from the figure, HF intercalation introduces asymmetry in the structure; the stacking sequence after HF insertion deviates from the AA stacking of $Nb_4AlC_3$. H and F occupies the Nb top site in $\text{MXene}_{top}$ and

MXene$_{bottom}$ layers respectively, and Al remains at same position. The interlayer distance (D) increases to 6.20 Å and d$_e$ of H−MXene, F−H, Al−F and Al−MXene$_{bottom}$ are 0.75, 1.58, 1.75 and 2.11 Å, respectively.

Figure S2c shows the structure of $Nb_4AlC_3$ with Li, similar to HF, Li insertion also disturbs the stacking of the MXene layers. Li atom occupies C-top site (top MXene layer) between Al and MXene$_{top}$ layer, the interlayer distance (D) increases to 7.15 Å, and the d$_e$ for Al−MXene$_{bottom}$, Al−Li and Li−MXene$_{top}$ becomes 2.30, 2.31, 2.54 Å, respectively.

Figure S2d shows the relaxed structure of $Nb_4AlC_3$ after LiF insertion. The interlayer distance (D) increases to 7.70 Å, and the d$_e$ for Al−MXene$_{bottom}$, Al−F, Li−F and Li−MXene$_{top}$ becomes 2.08, 1.89, 1.06 and 2.90 Å, respectively. The intercalation of LiF also destructs the AA stacking of the MAX phase, and occupies a position in between Al and MXene layer such that the Li and Al atoms are bonded to MXene$_{top}$ and MXene$_{bottom}$ layers respectively, with F atom sandwiched between them.

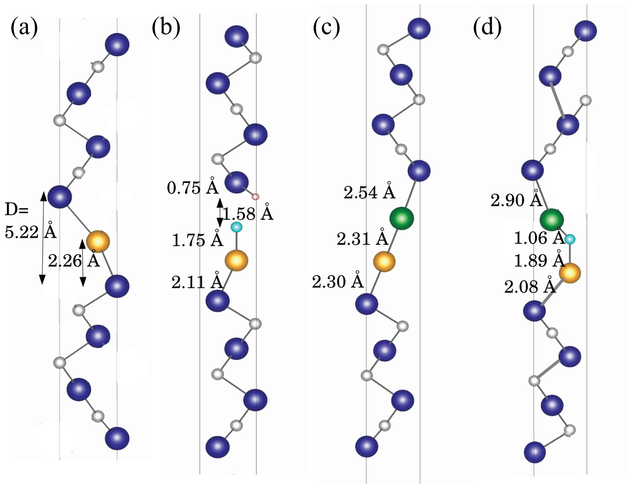

Figure S2: Optimized structures of (a) $Nb_4AlC_3$ without and, with (b) Li (c) HF and (d) LiF. Nb, C, Al, Li, F, and H atoms are shown by blue, grey, orange, green, cyan, and pink balls, respectively.

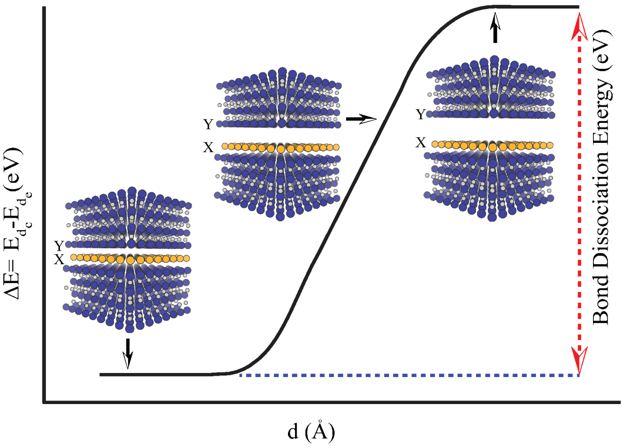

Figure S3: Method to calculate the bond-dissociation energy for the X-Y bond. The distance between the plane containing X and Y atoms are increased from $d_e$ to $d_c$. The position of other atoms, relative to X or Y, are kept fixed. We also checked the layer number dependence of BDE. We have found that BDE changes by 0.06 eV ($\sim$ 2% of BDE of Al−MXene bond) when the number of layers were increased from two to four in the model system. Therefore, we have adopted the two-layer MAX structure for our study.

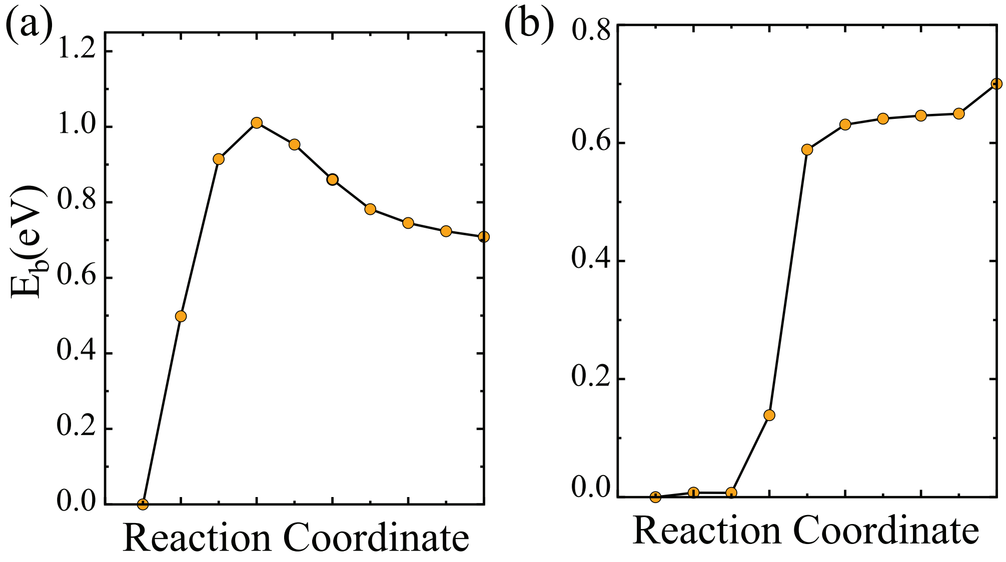

Figure S4: Energy barriers for the dissociation of (a) F−Al and (b)Li−MXene bonds in LiF inserted MAX phase calculated using CI-NEB method.

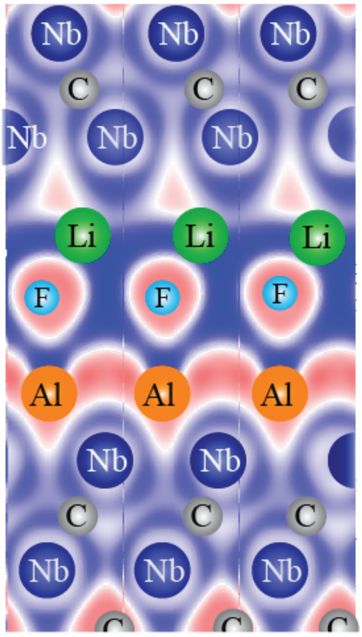

Figure S5: ELF contour plots projected on XZ-plane passing through Li for $Nb_4AlC_3$ after LiF insertion. Nb, C, Al, Li and F atoms are shown by blue, grey, orange, green and cyan balls, respectively.

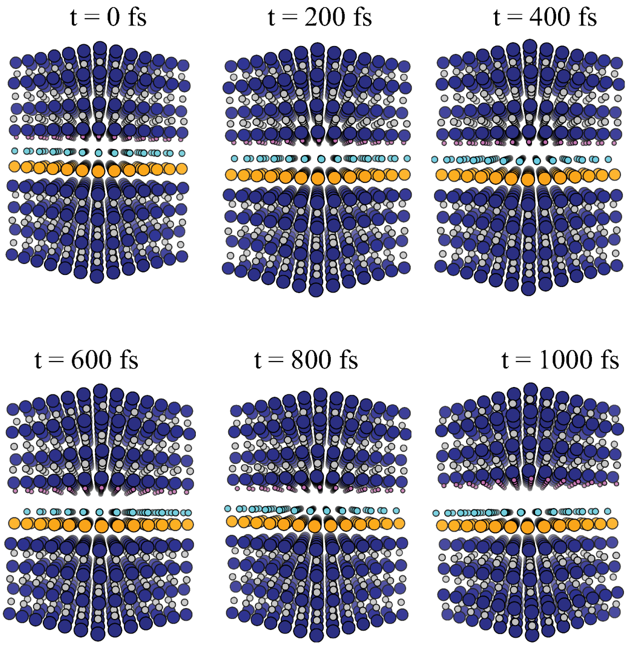

Figure S6: AIMD snapshots for $Nb_4AlC_3$ with HF at 500 K. Nb, C, Al, F, and H atoms are shown by blue, grey, orange, cyan, and pink balls, respectively.

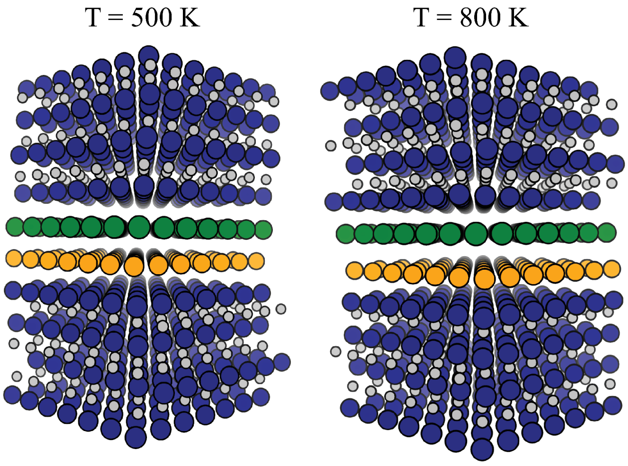

Figure S7: AIMD snapshots at t= 30 ps for $Nb_4AlC_3$ with Li at temperature 500 K and 800 K. Nb, C, Al and Li atoms are shown by blue, grey, orange and green balls, respectively.

Table S1: Interlayer distance (D) and, $d_e$ for alkali−$Nb_{top}$, Nb−Al and Al−alkali bonds are given here.

| Alkali | D (Å) | $d_e$ (Alkali−Nb) (Å) | $d_e$ (Nb−Al) (Å) | $d_e$ (Al−alkali) (Å) |
|---|---|---|---|---|
| Li | 7.15 | 2.54 | 2.30 | 2.31 |
| Na | 8.02 | 2.94 | 2.30 | 2.80 |
| K | 8.80 | 3.36 | 2.31 | 3.13 |

## Alkali-fluoride insertion

The charge transfer from Al to electronegative F weakens its binding with the $MXene_{top}$. Moreover the electropositive element (alkali) are bonded with $MXene_{top}$ via weak metallic bonding (Figure S7). Therefore fluorides of alkalis (Figure S7) can facilitate the chemical transformation of MAX phase into pristine MXene under some external perturbation, e.g., heating or sonication.

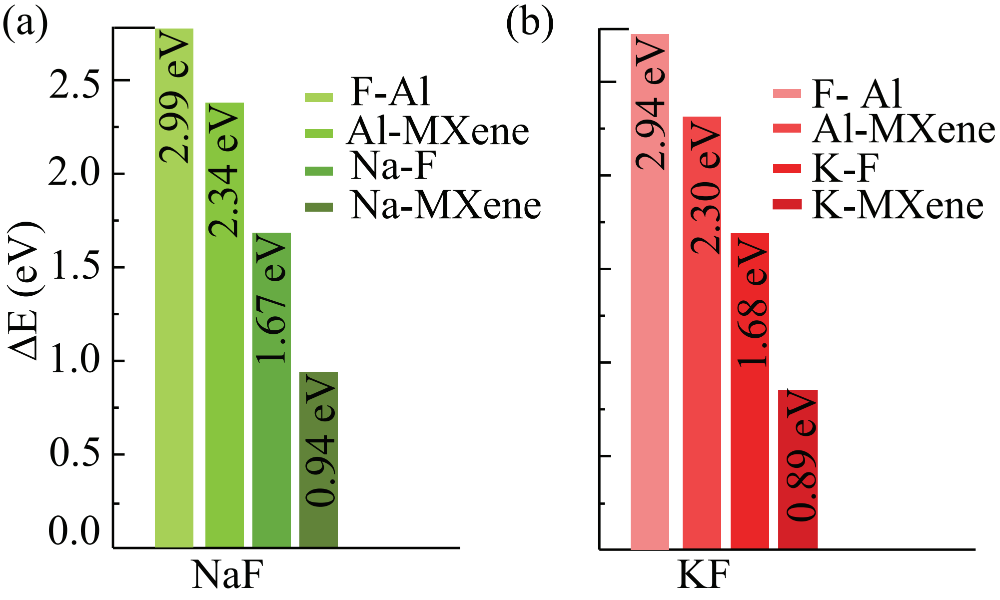

Figure S8: Bond-dissociation energies of various bonds formed in $Nb_4AlC_3$ upon (a) NaF and (b) KF insertion.