Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

Formation and properties of iodine- and acetonitrile-functionalized two-dimensional Si materials: a Density Functional Theory study

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Movies S1-S3: Ab initio molecular dynamics (AIMD) simulations for the Type 1 Si(MeCN) polymorph at 300 K (Movie S1), 600 K (Movie S2) and 1000 K (Movie S3) for a duration of 2 ps. Animations were rendered with the OVITO software[1] and are available as supplementary material.

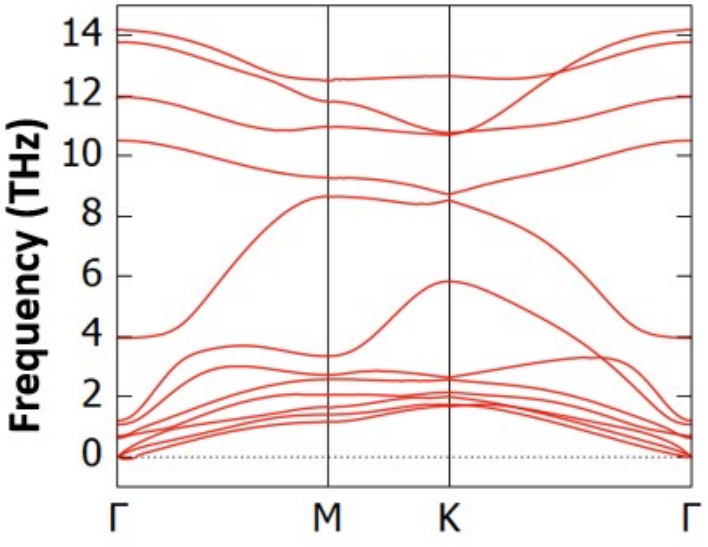

Fig. S1 Phonon band structure for the chair conformation of SiI calculated using the finite displacement method[2] in a 3x3x1 supercell.

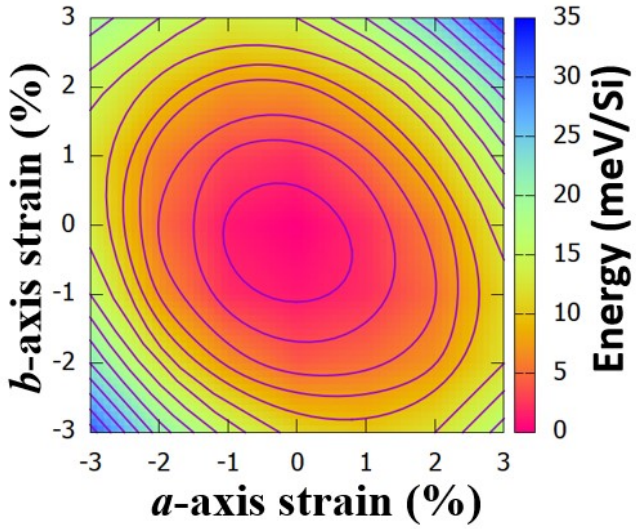

Fig. S2 Contour plot of the total energy per Si atom versus strain % applied along the a and b axes of the SiI chair polymorph shown in Figure 1(a).

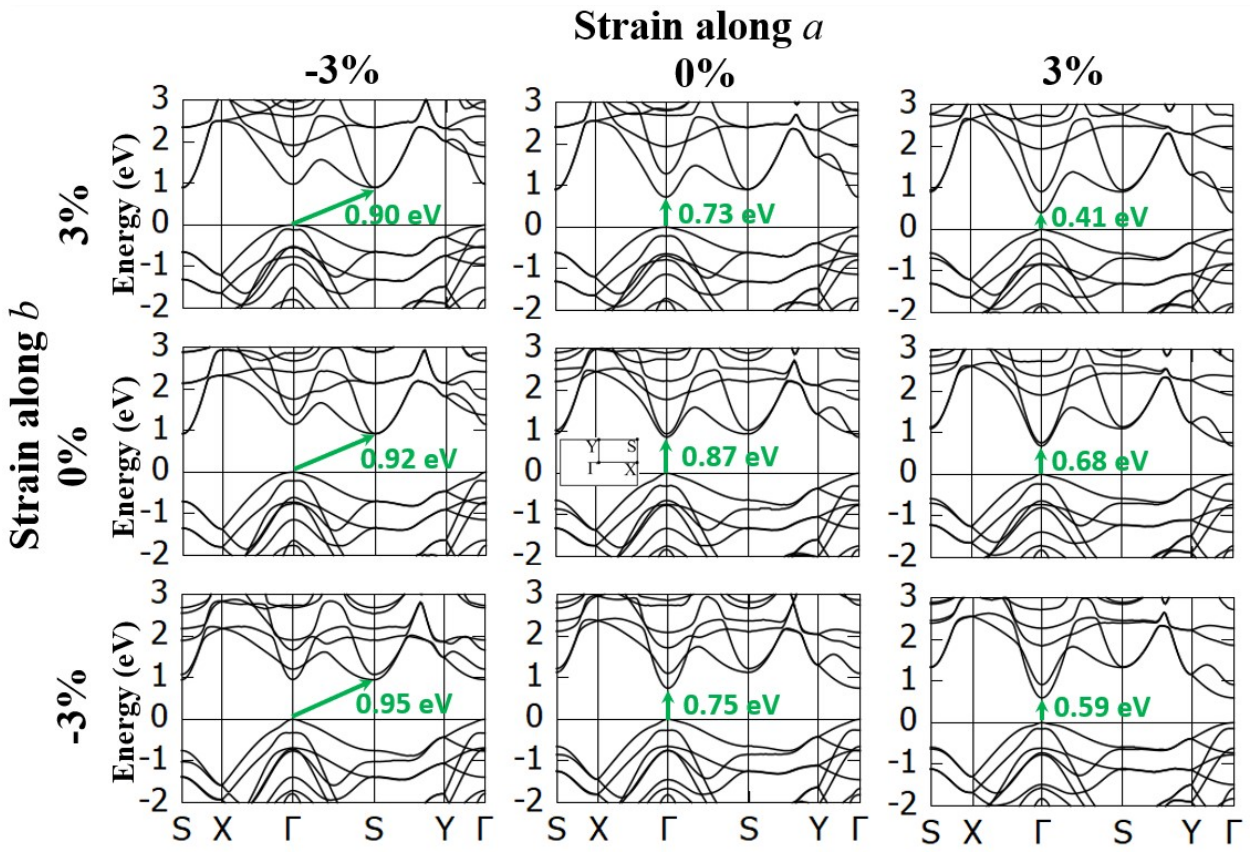

Fig. S3 Electronic band structure of the SiI chair polymorph [Figure 1(a)] for different strain levels applied along the a and b axes of the orthogonal conventional unit cell. The green arrows indicate the high symmetry points where the valence band maxima and conduction band minima are located in each case. The inset in the 0% strain diagram shows the corresponding Brillouin zone and high symmetry points.

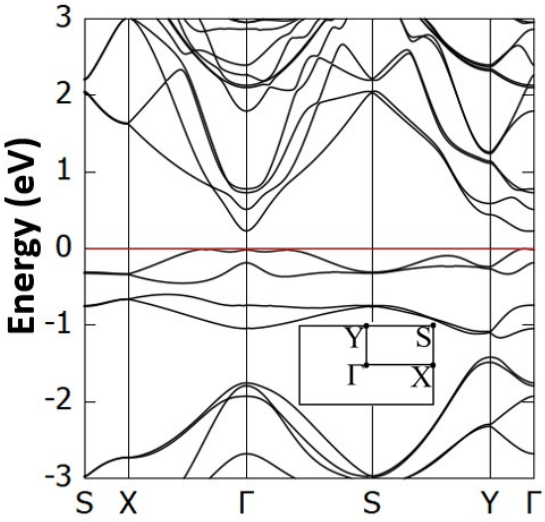

Fig. S4 Electronic band structure of the Type 1b Si(MeCN) sheet. The valence band maximum is set to 0 eV and the inset shows the first Brillouin zone and the corresponding high symmetry points.

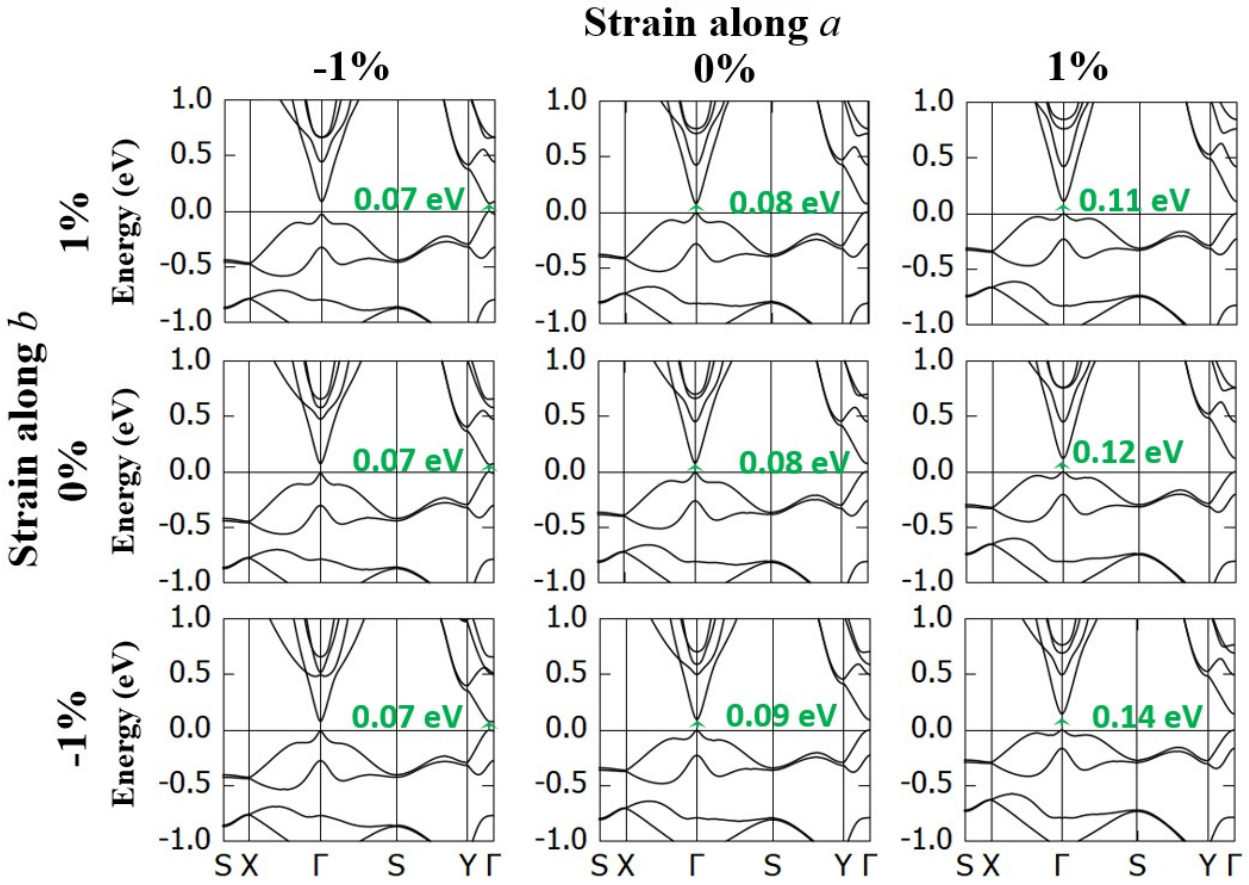

Fig. S5 Electronic band structure of the Type 1a Si(MeCN) polymorph (Figure 3) for different strain levels applied along the a and b axes of the unit cell. The green arrows indicate the high symmetry points where the valence band maxima and conduction band minima are located in each case. The inset in the 0% strain diagram shows the corresponding Brillouin zone and high symmetry points.

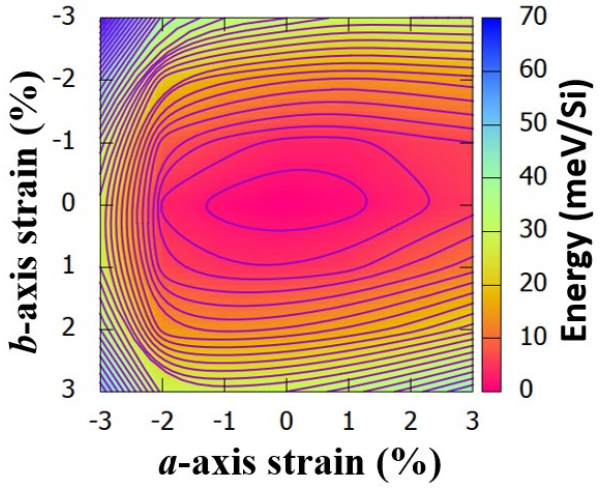

Fig. S6 Contour plot of the total energy per Si atom versus strain % applied along the a and b axes of the Type 1 Si(MeCN) polymorph (shown in Figure 3).

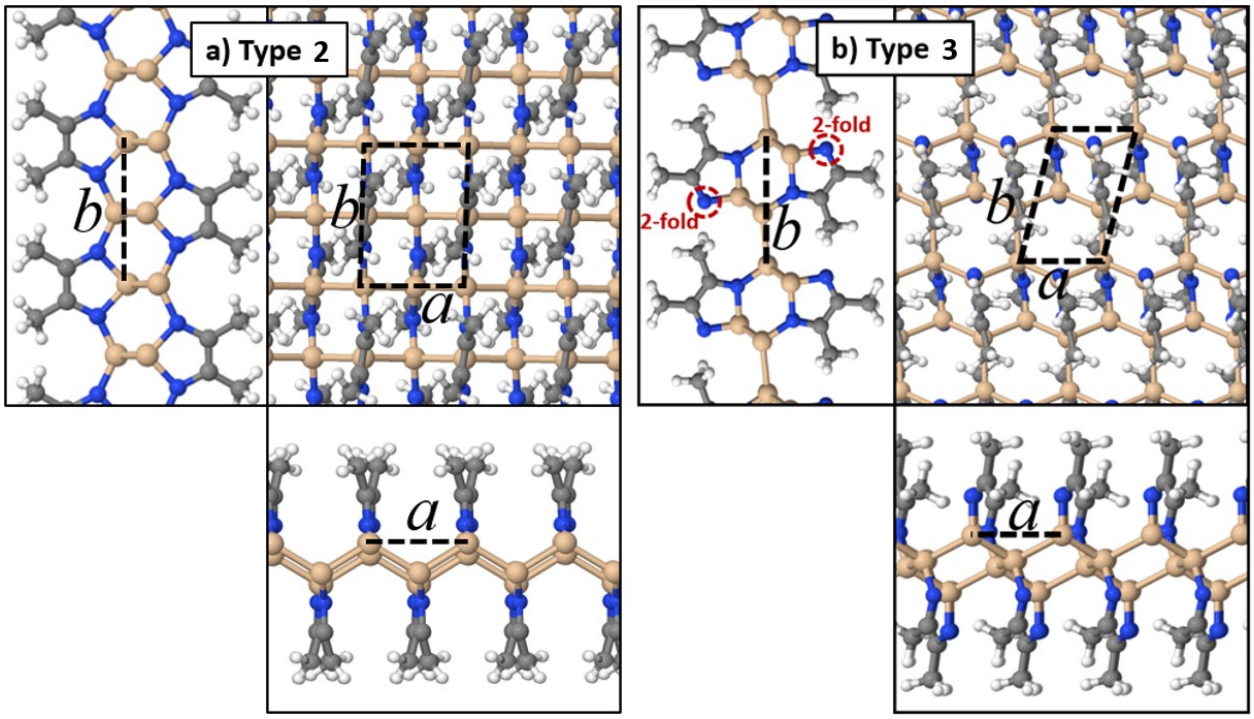

Fig. S7 Top and side views of different polymorphs of 2D-Si(MeCN) sheets (Si: orange, I: purple, N: blue, C: gray, H: white spheres).

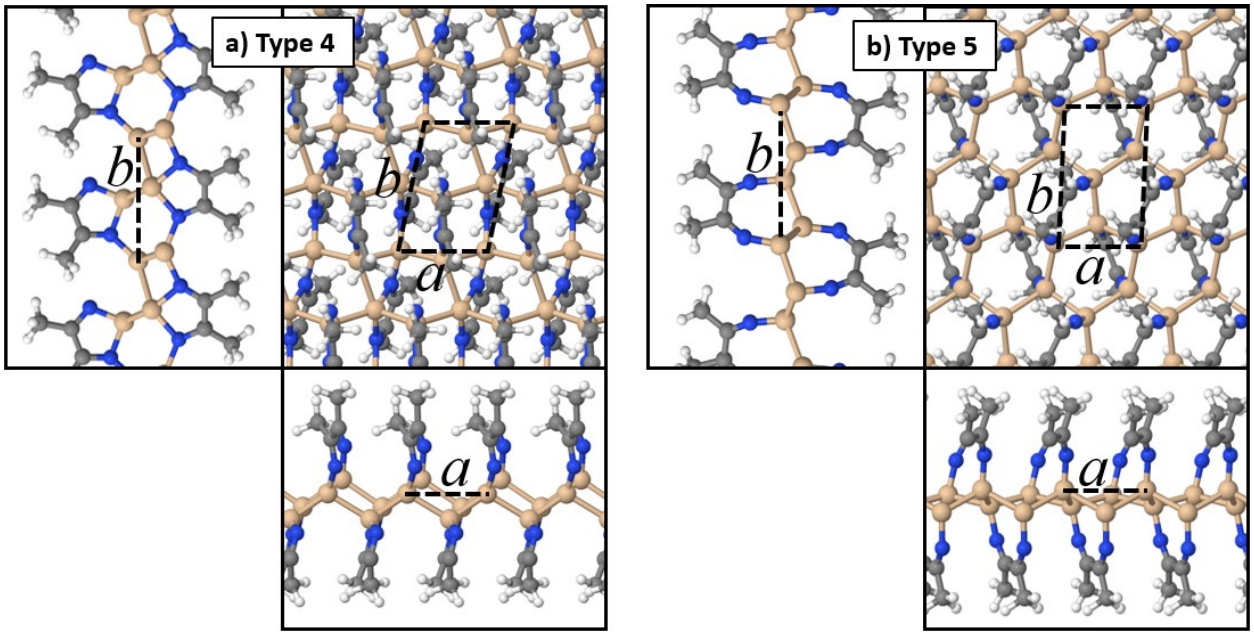

Fig. S8 Top and side views of different polymorphs of 2D-Si(MeCN) sheets (Si: orange, I: purple, N: blue, C: gray, H: white spheres).

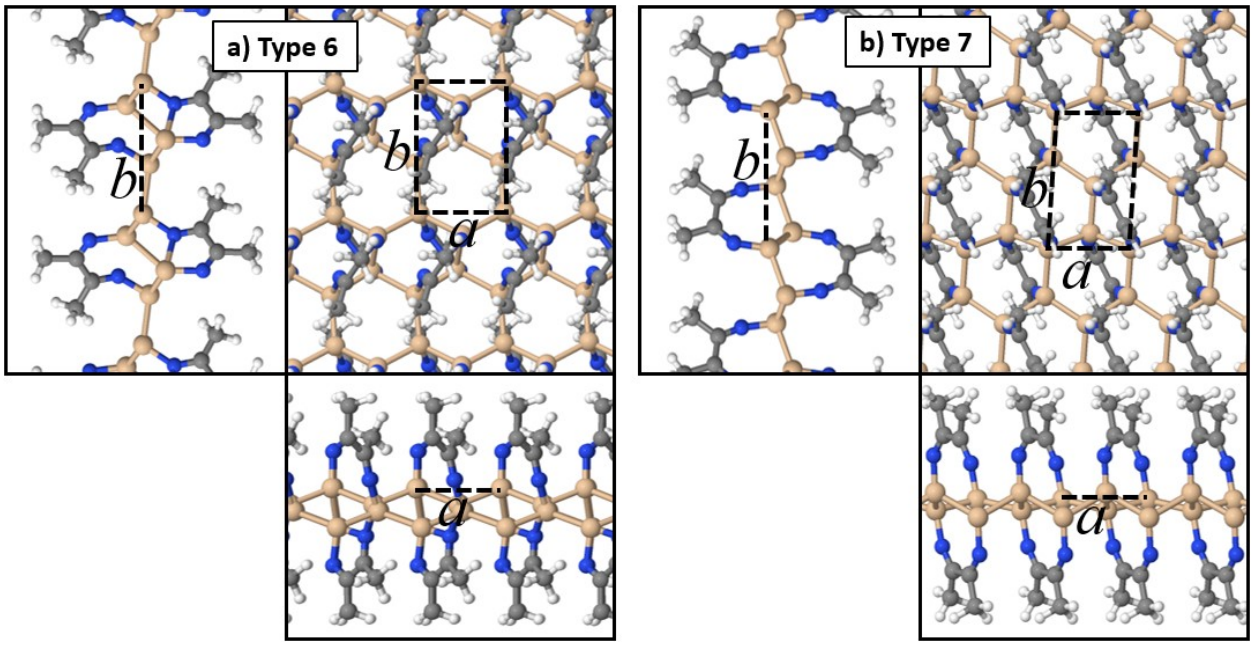

Fig. S9 Top and side views of different polymorphs of 2D-Si(MeCN) sheets (Si: orange, I: purple, N: blue, C: gray, H: white spheres).

Table S1 Lattice parameters (a, b), crystallographic angle (γ), total energy difference (ΔE) of each structure relative to Type 1, and band gaps of different polymorphs of 2D Si sheets functionalized with acetonitrile.

Polymorph	a (Å)	b (Å)	γ (◦)	ΔE (eV/Si)	E_{gap} (eV) (PBE-GGA)	E_{gap} (eV) (HSE06)
Type 2 Figure S1(a)	4.15	5.81	89.5	0.12	0.07	0.00
Type 3 Figure S1(b)	4.01	6.35	75.7	0.37	metallic	metallic
Type 4 Figure S2(a)	3.93	5.94	78.8	0.38	0.30	0.54
Type 5 Figure S2(b)	3.93	6.58	86.9	0.72	0.62	1.21
Type 6 Figure S3(a)	4.00	6.20	89.1	0.65	0.53	1.32
Type 7 Figure S3(b)	3.93	6.58	86.9	0.74	metallic	metallic

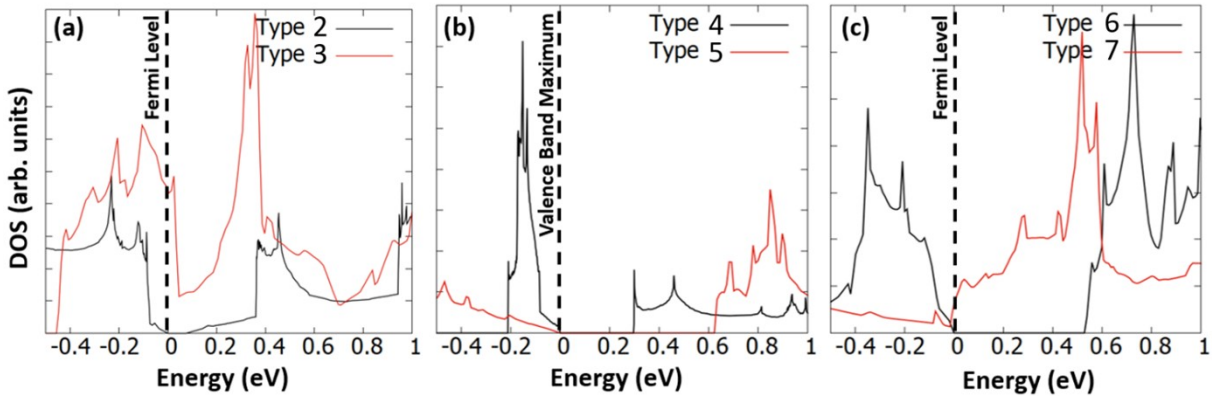

Fig. S10 Electronic density of states (DOS) for different polymorphs of Si(MeCN) sheets.

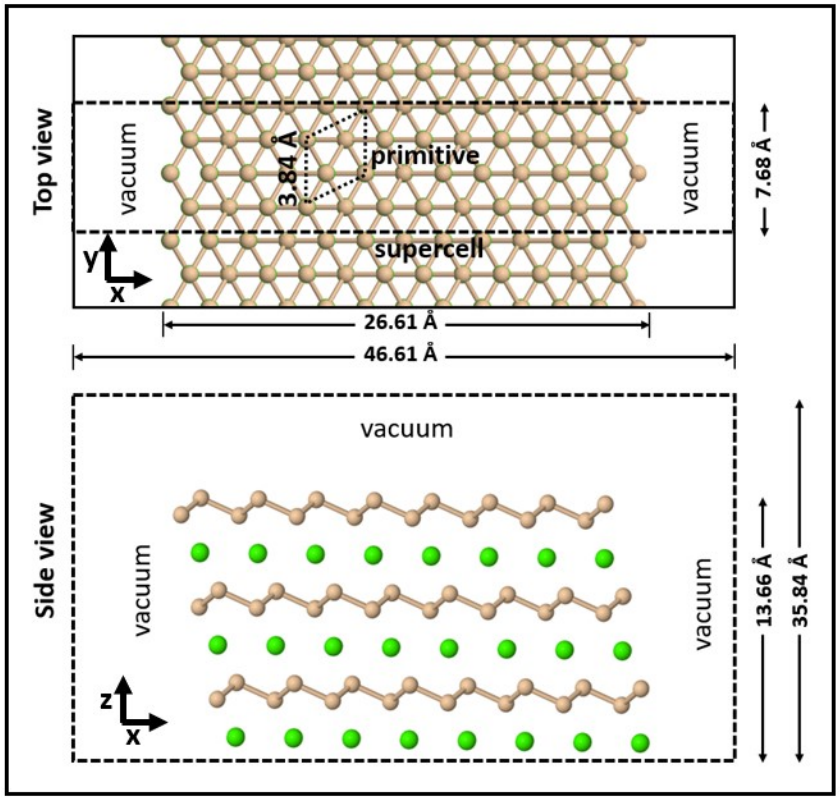

Fig. S11 The supercell used to simulate a slab of $CaSi_2$ crystal with exposed surfaces in the y and z directions with 20 Å of vacuum between adjacent images. The reported lengths do not correspond to the scale of the figure. The slab is periodic and continuous along the x direction. The atoms in the bottom Ca layer are kept fixed during structural relaxations (Ca: green, Si: orange spheres).

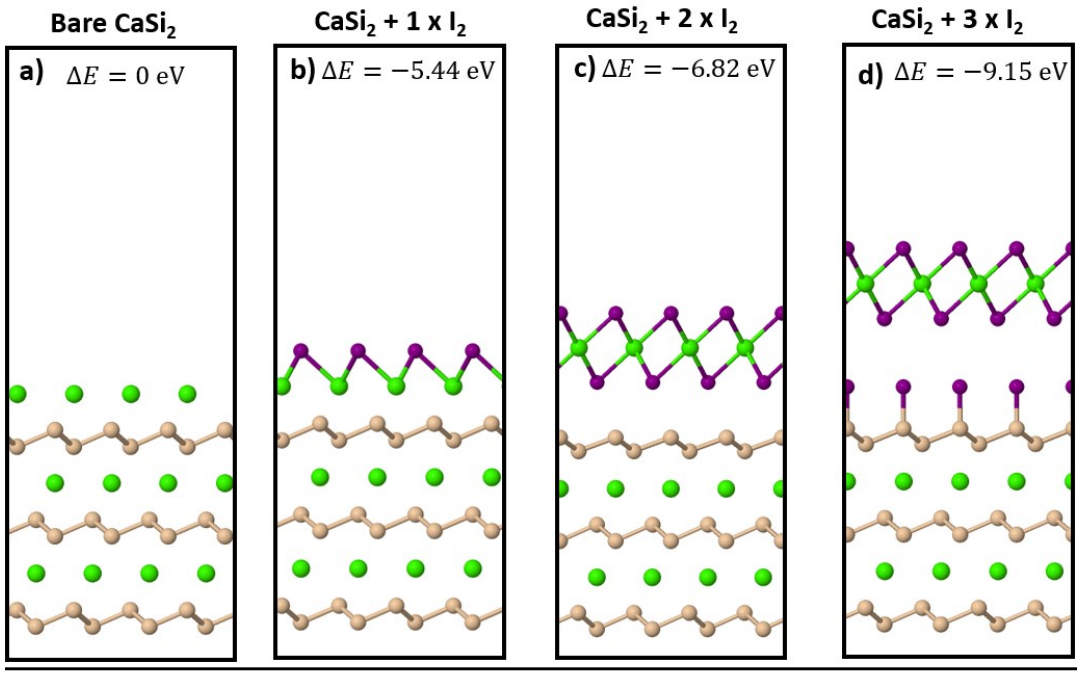

Fig. S12 Reactions of iodine with a Ca terminated $CaSi_2$ crystal using the orthogonal cell of Figure 6(a). ΔE is the change in total energy per cell relative to the bare surface of panel (a) calculated according to Equation 2. All steps are exothermic and lead to the desorption of the top Ca layer leaving exposed the Si layer below. In this way the reaction cycle of Figure 7 is reset. (Ca: green, Si: orange, I: purple spheres)

References

[1] A. Stukowski, Modelling Simul. Mater. Sci. Eng., 2009, **18**, 015012.

[2] A. Togo and I. Tanaka, Scr. Mater., 2015, **108**, 1-5.