Supplementary Material: 180° Head-to-Head Flat Domain Walls in Single Crystal $BiFeO_3$

1. Piezo-response force microscopy

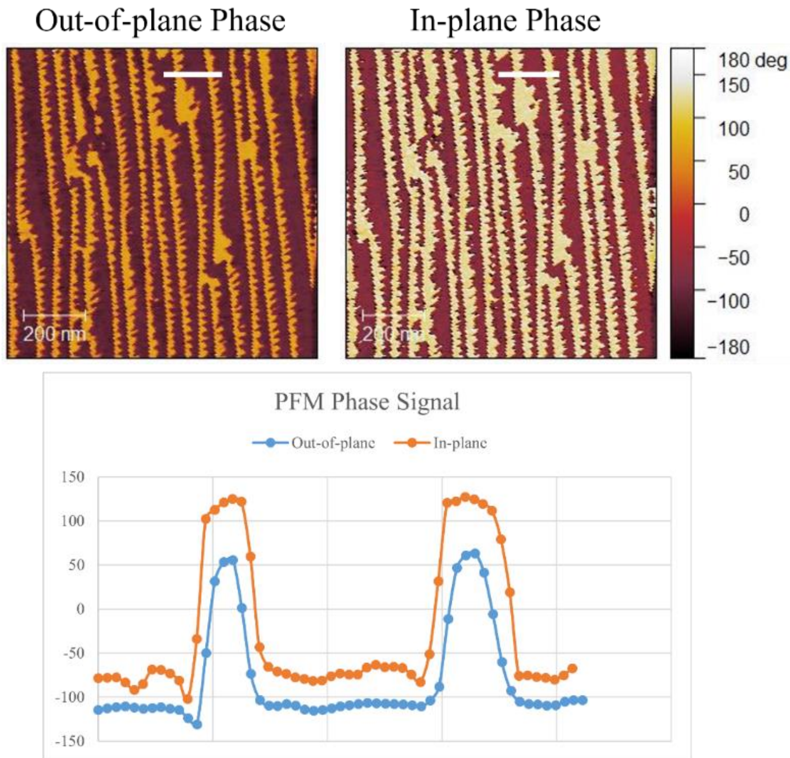

Figure S1a. A typical set of simultaneously collected PFM out-of-plane and in-plane phase signals on (001) surface, showing a 180° phase change at either sawtooth or flat domain walls. This result indicates that the domain structure can either be 109° or 180°.

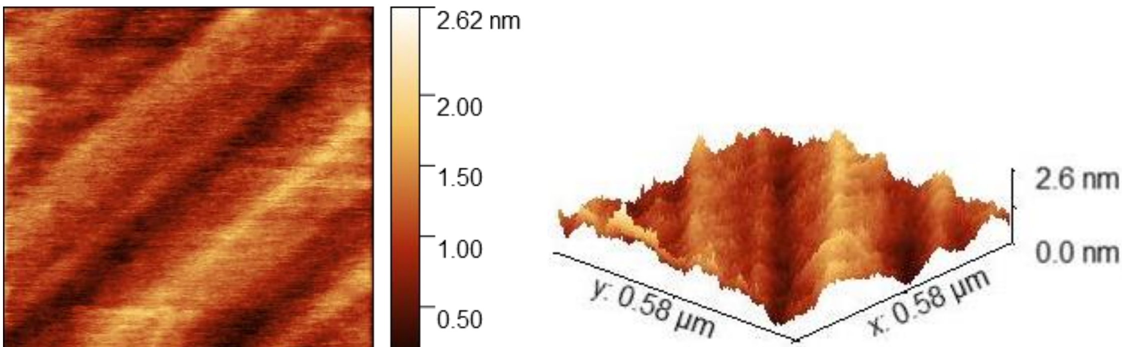

Figure S1b. Topographic image corresponding to Figure 1.

2. Tilted domain walls, steps, and the local ½[001] displacement

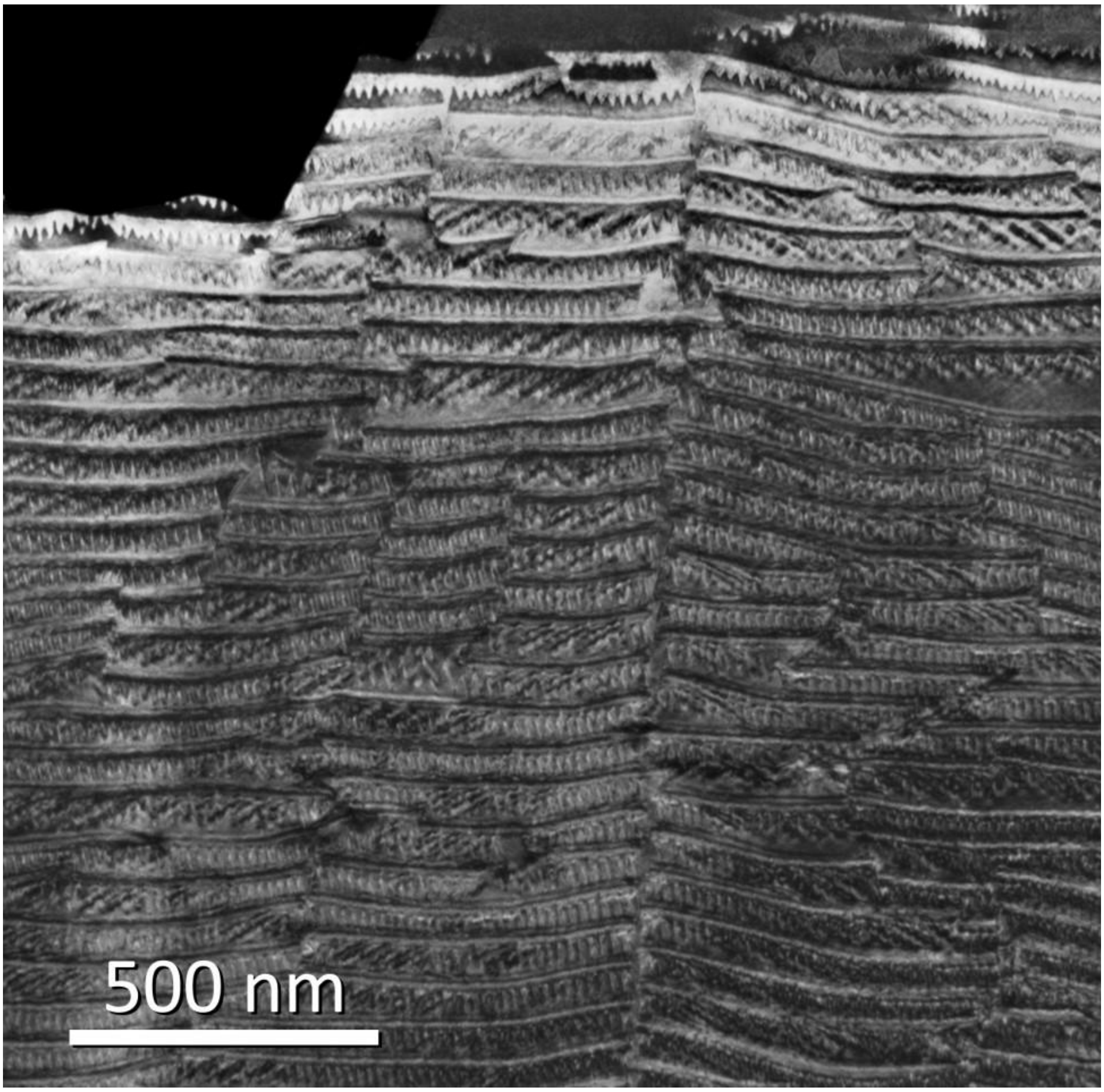

Figure S2a. Dark field [110] TEM image of the domain structure.

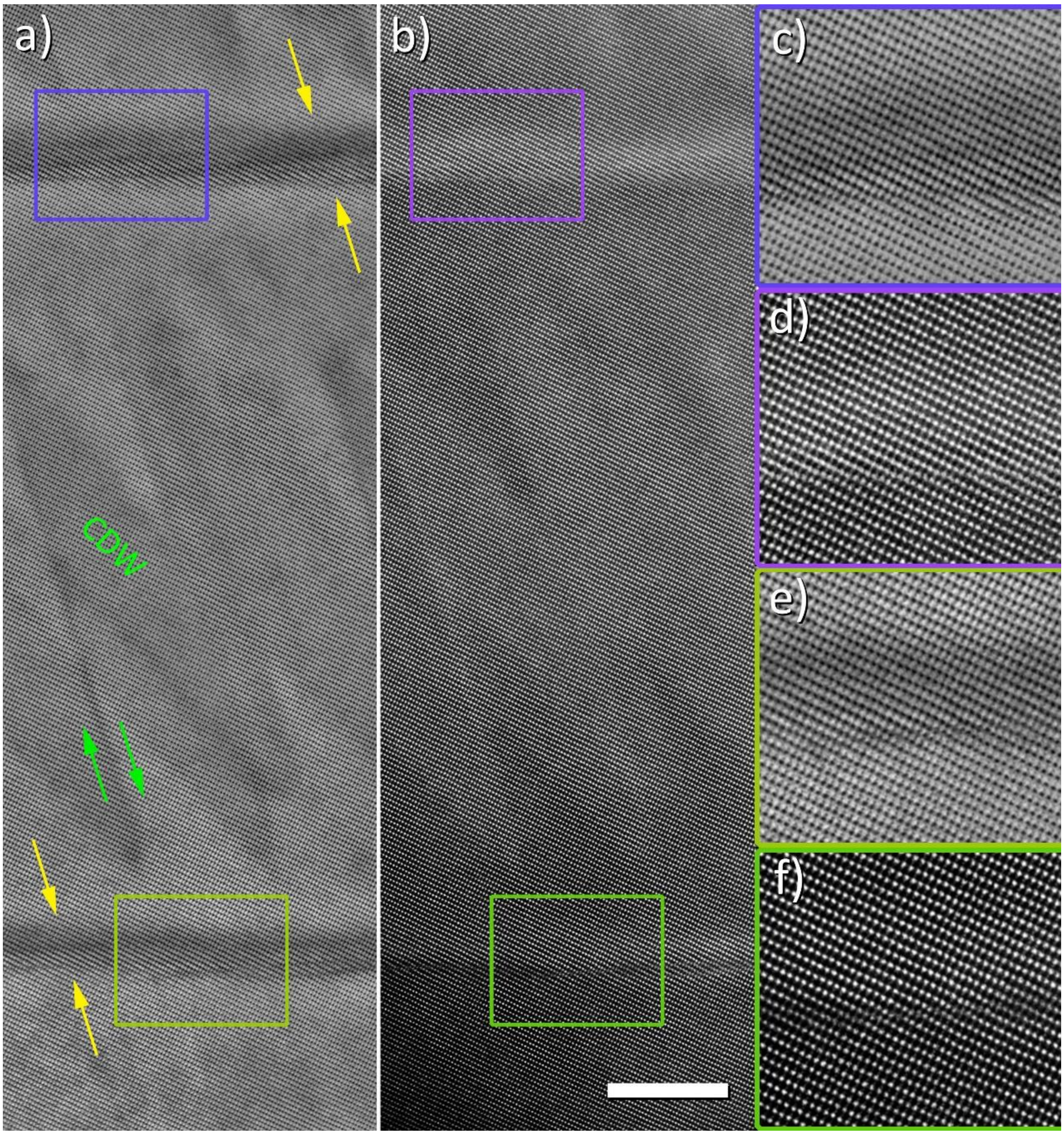

Figure S2b. a) Bright field (BF) and b) annular dark field (ADF) [1$\bar{1}$0] STEM images of the domain structure. Scale bar 10nm. The head-to-head domain charged walls (yellow arrows) are not seen edge-on since they appear as a band of contrast in the BF image. Their habit plane is thus close to, but not exactly, (112). The wider band for the upper head-to-head domain wall shows that the specimen is slightly thicker towards the top of the image. Arrows indicate the direction of polarisation. Overlapping facets of a single sawtooth tail-to-tail domain wall are seen in the centre, consisting of large (11$\bar{1}$) domain wall facets seen edge-on as a sharp line (green) and charged domain wall facets (CDW, green) seen in projection as a band of contrast. c) to f) show enlargements from a) and b) corresponding to the coloured boxes, showing atomic resolution images. Darker bands are visible in the ABF images where the domain wall is seen edge-on in this projection. Where the specimen is thin enough and with the aid of reduced depth of field in ADF images, the additional ½[001] displacement at the domain wall can be seen (centre of f). In places where the domain wall is not seen exactly edge-on, this displacement is not visible (d, edges of f).

3. Annular bright field ⟨110⟩ images

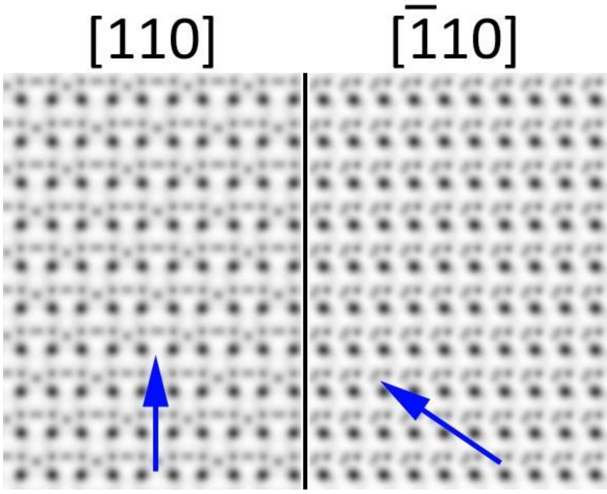

Figure S3. A pseudo-cubic ⟨110⟩ direction can either be at an angle of ~35° to the [111] polar axis (e.g. [110]) or perpendicular to it (e.g. [$\bar{1}$10]). The two possibilities give very different ABF-STEM images, as can be seen in these multislice simulations for specimen 20nm in thickness. The polar axis is marked in blue. It is completely in the image plane for [$\bar{1}$10] but has a component out of the image for [110].

4. Depth of field in HAADF images

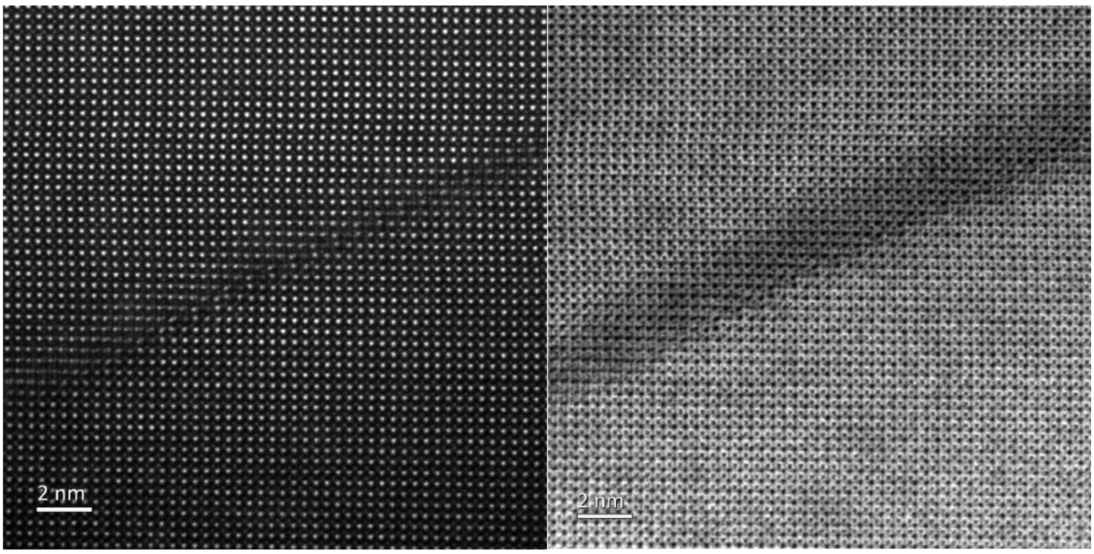

Figure S4. Simultaneously collected ADF (left) and BF (right) -STEM image of part of a flat domain wall in a (010) lamella. The projected width of the domain wall is visible as a band of dark contrast in the BF image, while the domain wall is sharply resolved in the ADF image. This is due to the reduced depth of field in an aberration-corrected STEM that results from the relatively large convergence angle of the electron probe.

5. Alignment of Bi columns at the wall

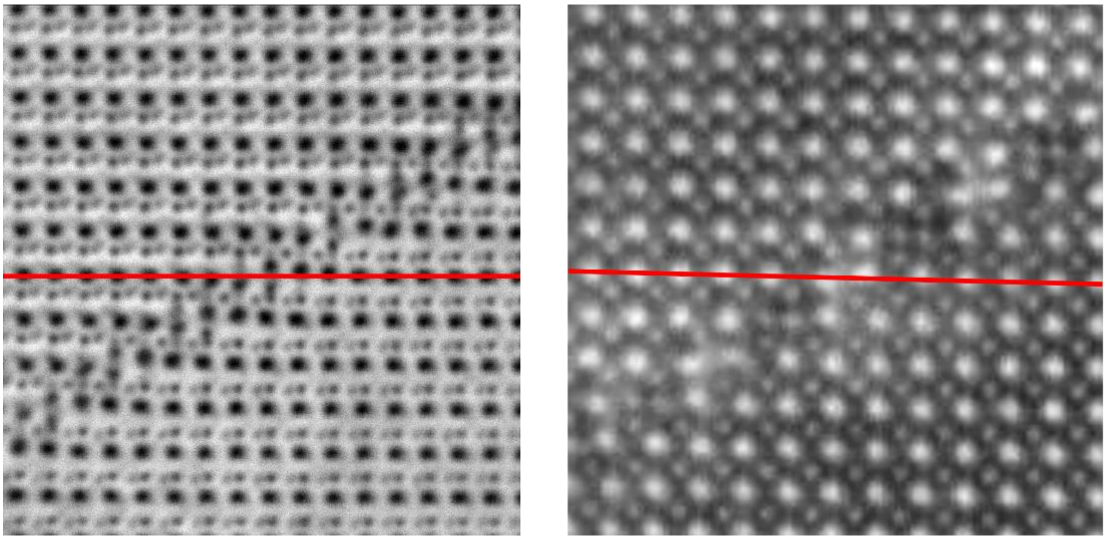

Figure S5. High magnification image of the flat wall from Figure 2c (left) and Figure 3a (right). Along the horizontal red (001) plane, it is apparent that the Bi columns go either downward or upward at the domain wall, although they are aligned at longer distances.

6. Core-loss EELS

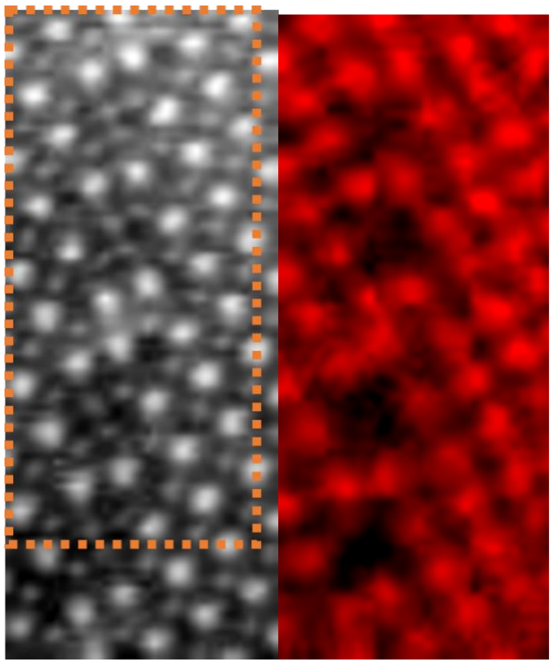

Figure S6. Core-loss EELS data taken at the domain wall along [$\bar{2}$01]. (left) ADF image and (right) element map of Bi. Although slightly different in the position of its boundaries, the boxed area in the ADF image is the same area as Figure 3c in the main text.