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Supplementary Materials for

Water molecules in boron nitride interlayer space: ice and hydrolysis in super confinement

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Supplementary Descriptions

Figure S 1 depicts the process of applying pressure on the original water droplet. Figure S 1a shows the piston versus the fixed plate; the first and the final steps are shown with the primary and supporting nanosheets. Figure S 1b shows the MD simulation process in more detail, with multiple steps. As the interlayer distance falls from 24.4 to 3.4 Å, the droplet becomes flattened to one-layer ice and under high pressure, disintegrates.

Figure S 2 shows the details of the simulation cell used for DFT calculations. Figure S 2a shows a water molecule between two HBN sheets, with the moving upper sheet supported by another sheet spaced at 5 Å. The external pressure is applied with thus nanosheet as a mediator, to better distribute the pressure across the lower nanosheet. The height for the whole HBN-water-HBN-HBN system is 18 Å, 7 of which is the interlayer distance where water resides. Figure S 2b depicts

a similar cell, this time with 20 water molecules in between the principal HBN layers. As can be seen, the supporting sheet is fixed at 5 Å over the descending nanosheet. The goal of this section is for only one layer (sheet) to interact with the water, while the other layer is a stacked sheet of hBN. This approach was chosen to make the simulations more realistic. We followed an experimental setup to investigate an unknown phenomenon, aiming to replicate real conditions as closely as possible. Therefore, the stacked sheets of hBN represent the upper layer in the simulation.

Figure S 3 shows the external pressure corresponding with different levels of confinement, represented by the interlayer distance. Herein, two HBN sheets are forced into orbital overlap by increasing the external pressure. Although the pressure is increased to 90 GPa, which corresponds to a 2.33 Å interlayer distance, no bonding happens between the two nanosheets.

Figure S 4 shows the arrangement of hydroxyl functional groups on one of the HBN nanosheets after hydrolysis.

Figure S 5 shows the radial distribution function (RDF) values for a hydroxylated HBN, with one or two functionalized sides. In the main manuscript, we discuss the breaking down of the ice-like formation after the significant orbital overlap enforced by severe confinement, which is followed by hydroxylation of the HBN nanosheet. This also affects the B-N bond length distribution; as a result of hydroxylation, boron atoms change from sp2 to sp3 hybridization. The bond length provides a good representation of this phenomenon, as the share of longer bonds increases with the increase in the number of functional groups. This coincides with the breaking down of a well-ordered hexagonal B-N network, where the majority of bond length resides.

Figure S 6 shows the stress-strain curve of the hydroxylated HBN (functionalized through hydrolysis) obtained through DFT calculations. Both functionals show approximately the same ultimate stress for the produced hydroxylated HBN (one-side functionalized), which is around 46 GPa.

Figure S 7 shows the same curve as Figure S 6 but obtained through MD simulations. The ultimate stress is around 50 GPa for the one-side functionalized HBN. This value is around 40 GPa for the two-side functionalized HBN.

Supplementary Methods

Density functional theory

The interlayer for the latter part is 7 Å while the support and the upper layer are spaced at 5 Å. This design guarantees the real condition and eliminates all possible errors (Figure S7).

The strain was applied as tensile stress increments on the cell; the corresponding strain was calculated based on the change in the cell length. Equation (1) shows the stress tensor of the model which can be obtained using the virial expression (*25*)

$$\sigma_{ij} = -\frac{1}{\Omega}\left[\left(\sum_{i=1}^{N} m_i (v_i v_i^T)\right) + \left(\sum_{i<j} r_{ij} f_{ij}^T\right)\right] \qquad \text{Equation (1)}$$

where Ω is the system volume, m_i and v_i denote the mass and velocity of particle i; f_{ij} is the force component between atoms i and j, and r_{ij} represents the distance between particles i and j.

Molecular dynamics simulation

To build an accurate model, we tried to limit the effect of external factors. In this process, a droplet of water consisting of 700 molecules was placed between two HBN sheets extended 120 and 60 Å, along with X- and Y-axes. To limit the displacement of boron nitride sheets, two platelets were used on each side, with the inner nanosheet about 20% smaller than the outer membranes. The outer membranes were also the borders of the periodic space. The space created by this difference provided space for the displacement of extra water molecules to depart the interlayer area when the upper part (Figure S1) was moved down to reduce the interlayer space to the desired value; then, the distance between the layers was kept fixed. To ensure the distribution of water molecules in the interlayer region, the number of water molecules was more than enough to cover the surface, which highlights the importance of the difference in the length of the adjunct boron nitride sheets. With the inner sheets tied to the outer boron nitride sheets, we prevented them from slipping while their smaller size compared to the outer sheets provided space for excess water molecules (*6*). The MD simulations enabled the monitoring of the full reaction for a longer period, i.e. 1000 picoseconds, at 298 K (28, 29).

Supplementary Figures

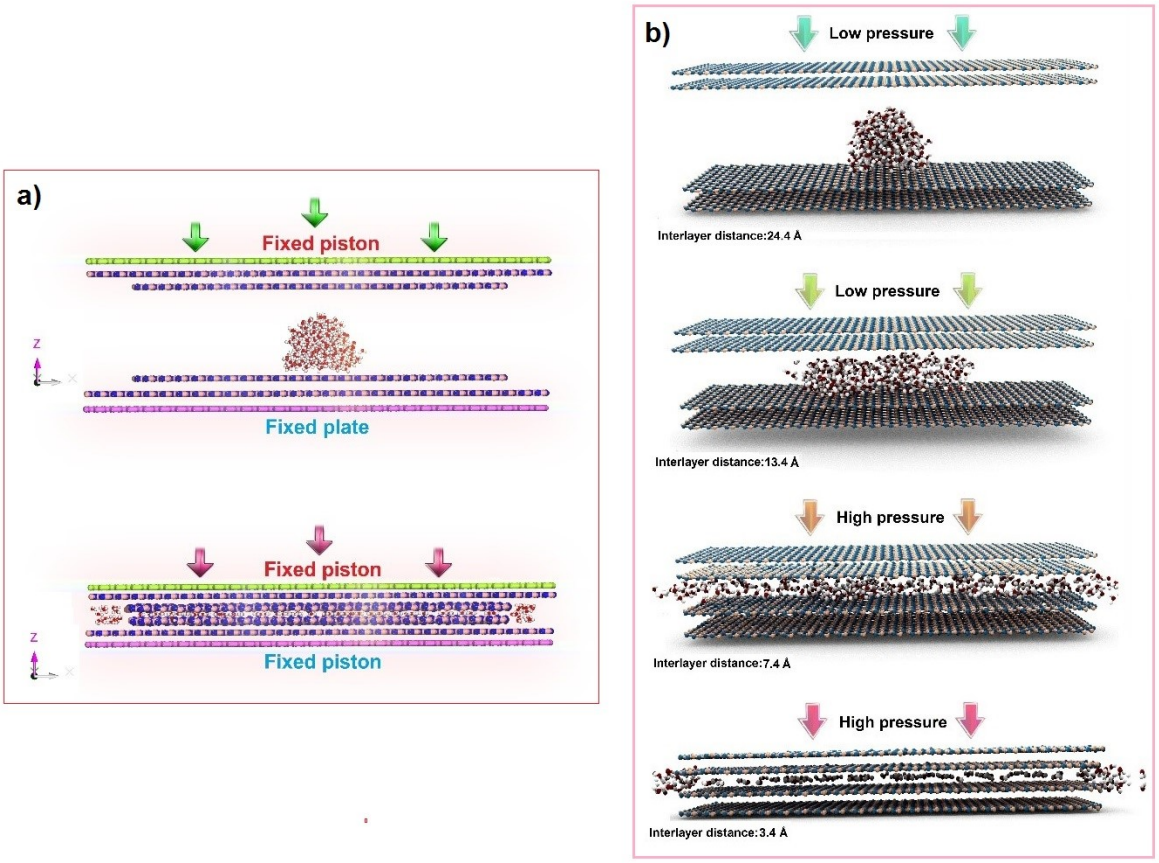

Figure S 1 The process of decreasing the interlayer distance to the desired value, shown in the original design of the model: (a) a drop of water confined between the moving upper platelet and the fixed platelet, and (b) the same droplet in different stages of confinement, marked with their corresponding interlayer distance values.

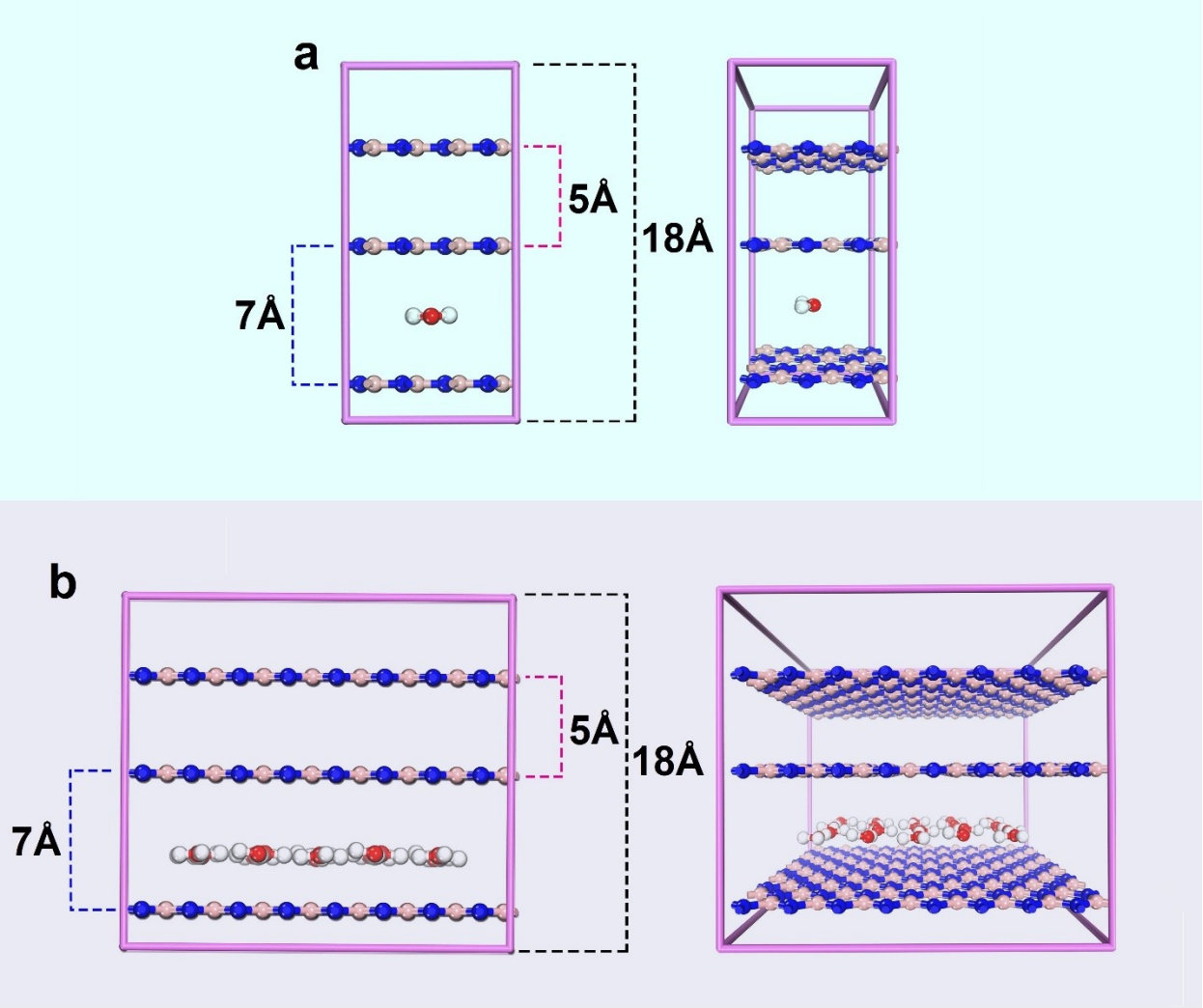

Figure S 2 The pattern of models DFT, shown in the original design: (a) one water molecule restrained between two 7.51 × 8.67 Å HBN sheets, and (b) 20 water molecules restrained between two 20.0 × 21.69 Å HBN sheets

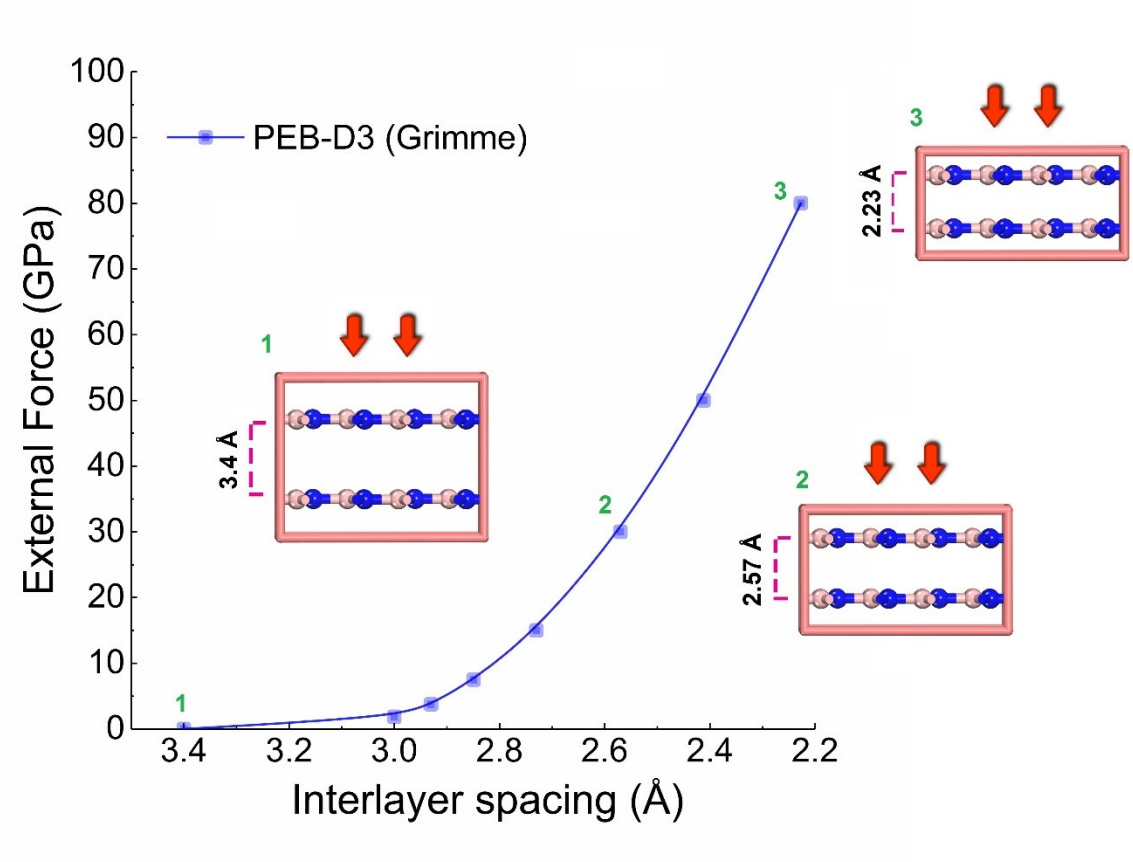

Figure S 3 Effect of external force on the interlayer distance of HBN sheets, calculated via PEB-D3 module

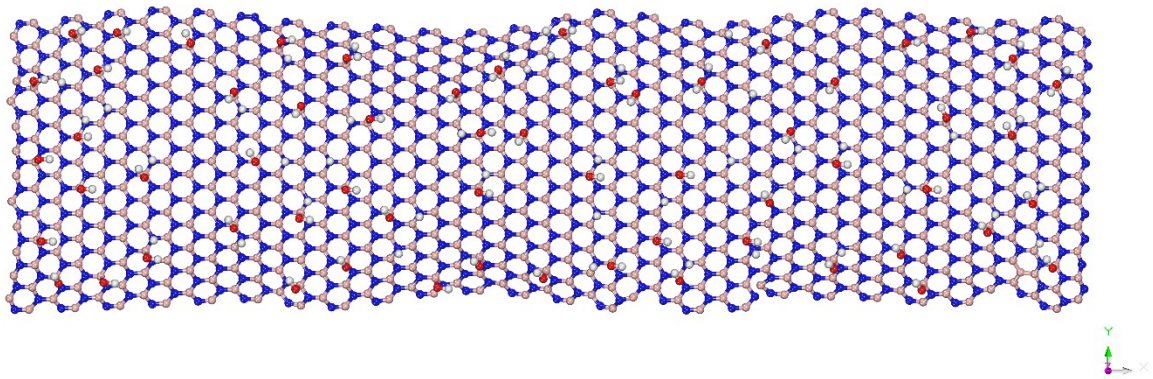

Figure S 4 HBN nanosheet after functionalization process, released after the last-stage confinement

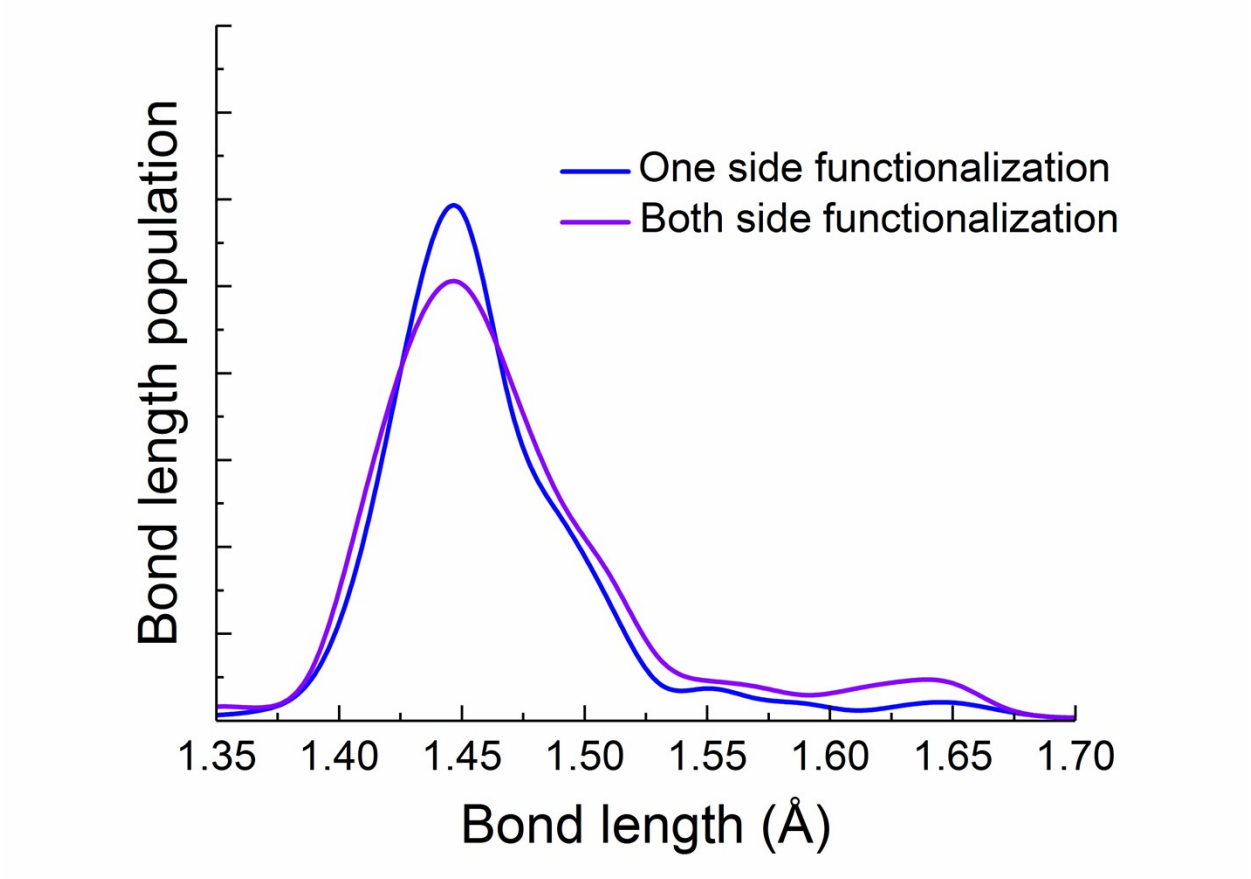

Figure S 5 bond length distribution for the functionalized HBN through hydrolysis.

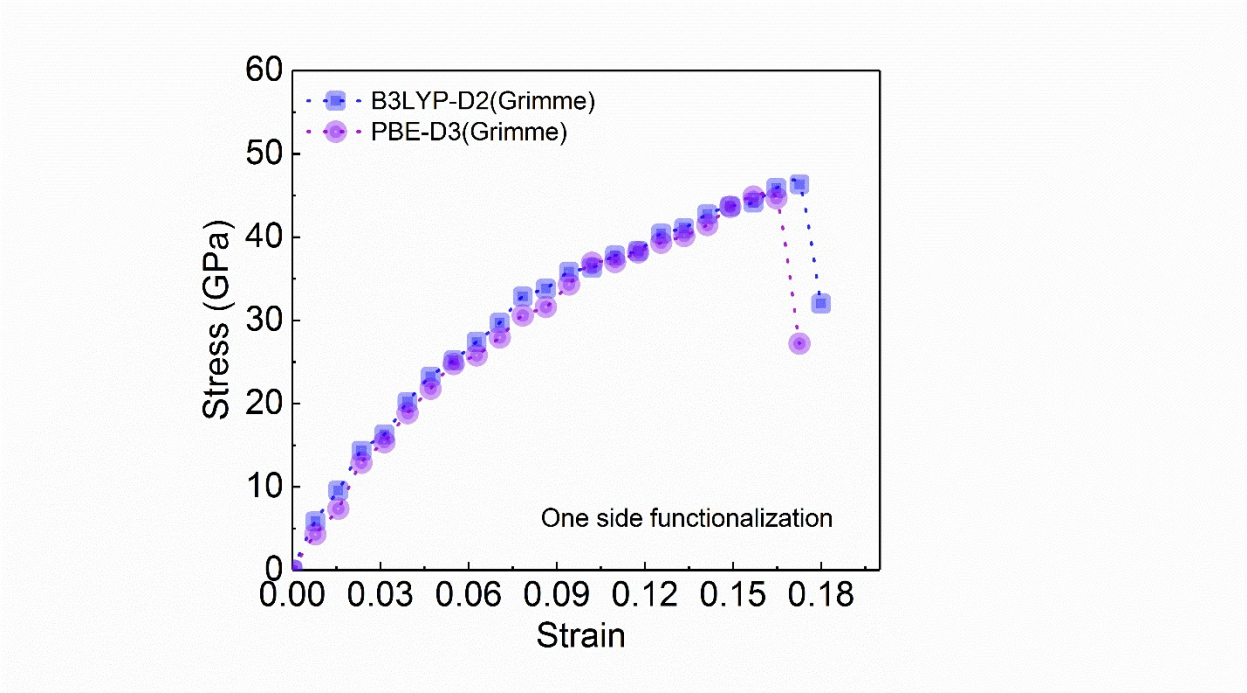

Figure S 6 stress-strain curve for HBN, functionalized through hydrolysis, obtained with DFT calculations through two different functionals

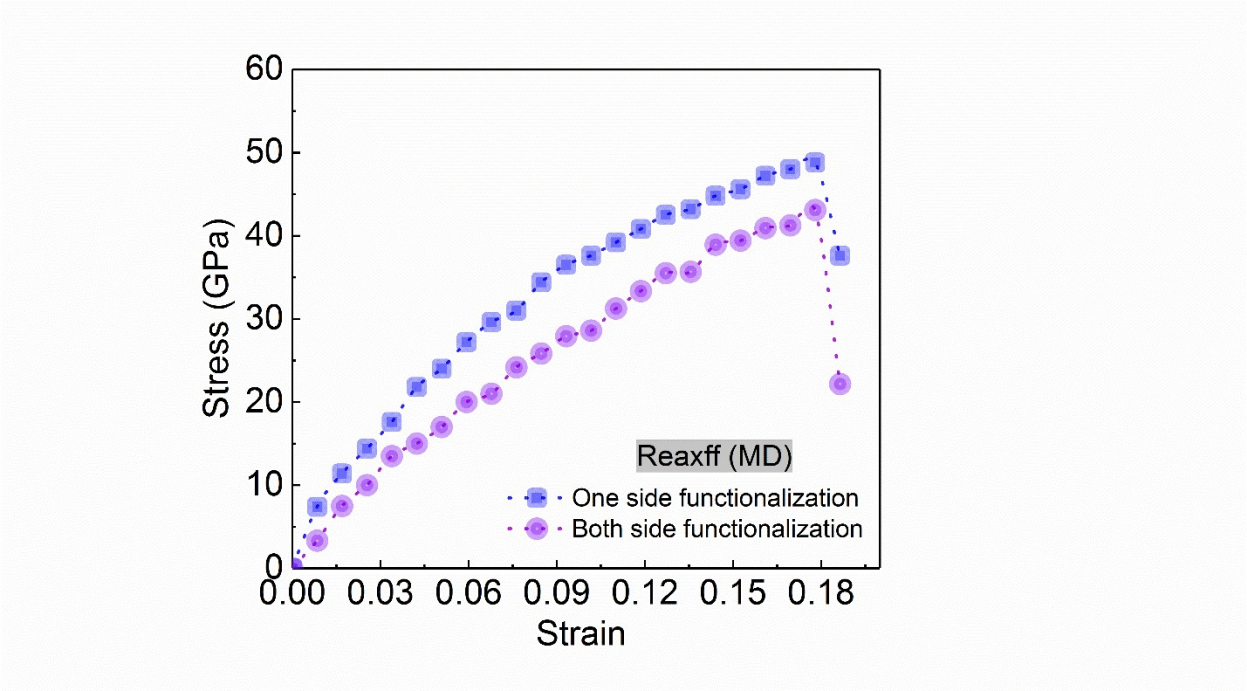

Figure S 7 Stress-strain curve of the HBN, functionalized through hydrolysis, obtained with MD simulations in Reaxx-FF