Supporting Information for

Effects of Doped N, B, P, and S atoms on Graphene towards Oxygen Evolution Reactions

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1. Classical Molecular Dynamics Simulations

The initial structure for FPMD was obtained from classical molecular dynamics (CMD) simulation run using the large-scale atomic molecular massively parallel simulator (LAMMPS)\(^1\). A 6 x 6 supercell of graphene consisting of 72 atoms was considered. A water box of 15 x 15 x 15 Å\(^3\) consisting of 100 water molecules was prepared using PACKMOL\(^2\) and equilibrated using SPC/E\(^3\) parameters. Each of the doped sheets was simulated for 500 ps with 1 fs timestep using isochoric-isothermal ensemble NVT using Nose-Hoover\(^4,5\) thermostat. Then the preequilibrated water box was placed along the z-direction of the doped graphene sheet figuratively depicted in Figure 1a. The density of the box was maintained at 1 g cm\(^{-3}\). A vacuum layer of 2 Å was maintained between sheet and water box. The box dimension of the complete setup is 15 x 15 x 18 Å\(^3\). While classically simulating a complex system like solid-liquid interfaces such as graphene-water system the conventional general amber force fields (GAFF)\(^6,7\), and optimized potentials for liquid simulations (OPLS)\(^8,9\) are not enough. To realize carbon-carbon short- and long-range interactions in the graphene sheet adaptive intermolecular reactive empirical bond order (AIREBO)\(^10\) was used for all the doped sheets. For N-doped graphene (NGr) and B-doped graphene (BGr), the empirical reactive force field TERSOFF\(^11,12\) was used for C-N and C-B interaction. For PGr and SGr, the P-C and S-C interactions are defined by GAFF parameters generated using ANTECHAMBER. The size parameters (\(\sigma_{ij}\)) and energy parameters (\(\epsilon_{ij}\)) for P-C are 3.571 Å, 0.131 kcal mol\(^{-1}\) respectively and for S-C are 3.482 Å, 0.146 kcal mol\(^{-1}\) respectively. For defining the non-bonded interaction between the sheet elements with the oxygen and hydrogen of water molecule the Lorentz-Berthelot mixing rule\(^13-15\) is used, according to which, \(\sigma_{ij} = \frac{1}{2} [\sigma_{ii} + \sigma_{jj}] \) (in Å) and \(\epsilon_{ij} = \sqrt{\epsilon_{ii}\epsilon_{jj}} \) (in kcal mol\(^{-1}\)), (where \(i = C_a/N/S/P\) and \(j = O_w/H_w\)). The \(\sigma_{ii}\) for the sheet, elements are the GAFF parameters, whereas \(\sigma_{jj}\) for O\(_w\) and H\(_w\) are obtained from SPC/E parameters. Since GAFF and OPLS parameters are not available for boron, we used previously defined dreading parameters\(^16\) for B-O\(_w\) and B-H\(_w\) interaction. The size parameters and energy parameters, \(\sigma_{ij}\) and \(\epsilon_{ij}\) (i = C/N/B/S/P and j = H\(_w\)/O\(_w\)) are tabulated in the Table S1. The classical simulations are performed on the charge neutral systems.

Table S1. The pairwise interaction term for sheet element and O\(_w\) and H\(_w\) for classical simulation.

|       | \(\sigma_{ij}\) (in Å) | \(\epsilon_{ij}\) (in kcal mol\(^{-1}\)) | \(\sigma_{ij}\) (in Å) | \(\epsilon_{ij}\) (in kcal mol\(^{-1}\)) |
|-------|------------------------|----------------------------------------|------------------------|----------------------------------------|
| O\(_w\) |                        |                                        |                        |                                        |
| C     | 3.283                  | 0.093                                  | 1.699                  | 0.000                                  |
| N     | 3.208                  | 0.163                                  | 1.625                  | 0.000                                  |
| B     | 3.310                  | 0.121                                  | 3.310                  | 0.121                                  |
| S     | 3.365                  | 0.196                                  | 1.782                  | 0.000                                  |
| P     | 3.454                  | 0.176                                  | 1.871                  | 0.000                                  |
| H\(_w\) |                        |                                        |                        |                                        |
2. First Principles Molecular Dynamics Simulations: Details of Density-functional tight-binding approach

Density functional tight-binding (DFTB)\textsuperscript{17,18} is an alternate technique for the expensive DFT method and is successful in explaining several chemical behaviors such as surface-mediated reactions, proton transfer, reactions concerning hydrocarbons.\textsuperscript{19,20} DFTB along with self-consistent charge modification (SCC-DFTB)\textsuperscript{21} is also implemented in explaining the electronic and mechanical phenomena in graphene-based material\textsuperscript{22,23}. It has been established that SCC-DFTB is 3- to 4-fold faster in estimating single point energy and barriers.\textsuperscript{24} We performed the metadynamics simulation using SCC-DFTB with D3 dispersion correction\textsuperscript{25,26}. Instead of solving the total Kohn-Sham energy SCC-DFTB is defined as 2nd order expansion of DFT energy concerning the charge density fluctuation around a reference density and the total energy is given by the equation,

\[
E_{\text{tot}}^{\text{SCC-DFTB}} = \sum_{\mu \nu} c_{\mu}^i \chi_{\mu}^0 H_{\mu \nu}^0 + \frac{1}{2} \sum_{\alpha \beta} \gamma_{\alpha \beta} \Delta q_\alpha \Delta q_\beta + E_{\text{rep}}
\]  

(1)

Where \(H_{\mu \nu}^0\) = elements of the Hamiltonian matrix, comprising of pair-wise terms. \(c_{\mu}^i\) and \(c_{\nu}^i\) are the wave function expansion coefficient, \(\Delta q_\alpha\) and \(\Delta q_\beta\) are the fluctuation terms for charges of \(\alpha\) and \(\beta\), respectively, and \(E_{\text{rep}}\) a function of density is an approximation of the short-range repulsion term. The \(\gamma_{\alpha \beta}\) is a two-term expression given as,

\[
\gamma_{\alpha \beta} = \frac{1}{r_{\alpha \beta}} - S_{\alpha \beta}
\]  

(2)

where \(r_{\alpha \beta}\) = interatomic distance between \(\alpha\) and \(\beta\) and \(S_{\alpha \beta}\) = is a short-range correction term between the two nuclei which decays exponentially.

Publicly available Slater-Koster (SK) parameters are used for calculating the pairwise interaction terms among \(i - j\), where \(i = j = \text{C/N/B/P/S/Ow/Hw}\). The Ow-Ow, Ow-Hw, Hw-Hw interactions are realized by implementing "mio-1-1"\textsuperscript{21} parameters. The bonded and non-bonded interaction among sheet elements C\textsuperscript{21}, N\textsuperscript{21}, B\textsuperscript{27}, S\textsuperscript{21}, and P\textsuperscript{28} with each other, as well as with Ow and Hw of water, are defined using “mio-1-1”, “matsci-o-3”. Interaction of Na\textsuperscript{+} with the rest of the atoms in the systems is defined using the parameters developed by Kubillus et al.\textsuperscript{29} In the case of BGr due to the unavailability of B-Na interaction parameters, we used H\textsuperscript{+} as the cationic counterpart for OH\textsuperscript{-}. For three independent metadynamics simulations, three different starting structures are used. The two collective variables (CVs) defined concerning the physical attributes are the same as the ones used for the PBE-D3 method. Also, the parameters for p and q are used for defining the coordination number between the interacting atoms used as the CV in individual steps of the 4e\textsuperscript{-} transfer pathway and are tabulated in Table S2. CV2 for Step 1 does not have any parameters defined as it is in terms of the dihedral angle. For certain steps, we used wall potentials during metadynamics simulation for proper reactant and product sampling, and the values are tabulated in Table S3.

3. Metadynamics Simulations
Metadynamics method is an effective method for tracing the free energy barrier of a chemical event by considering the important physical alteration. Instead of visiting all 3N degrees of freedom, energy is biased along the direction of relevant degrees of freedom known as the collective variable defined in terms of distance, angle, dihedral angle, and coordination number. The coordination number as a collective variable is defined by,

\[
CN = \frac{1 - (d_{AB}/d_0)^p}{1 - (d_{AB}/d_0)^{p+q}}
\]  

(3)

Here \(d_{AB}\) = the distance between atom A and B

\(d_0 = \) cut-off parameter or the reference distance

\(p, q=\) parameters to distinguish between bonded and non-bonded system.

The external potential energy applied as bias is given by,

\[
V_G(S(x), t) = \sum_{t' = \tau_G}^{2\tau_G} \ldots \exp \left( -\frac{(S(x) - s(t'))^2}{2\delta s^2} \right),
\]  

(4)

where \(s(t) = S(x(t))\) is the CV value at time t, \(\omega = \) height of Gaussian, \(\delta s = \) width of Gaussian, and \(\tau_G = \) frequency of MD steps at which Gaussians are added. The free energy well thus filled by adding Gaussian hills. The free energy \(F(s)\) is given by,

\[
F(s) = -T \ln \left( \int dx \exp \left( \frac{-V(x)}{T} \right) \delta(s - S(x)) \right),
\]  

(5)

where \(S = \) the function of coordinate \(S(x)\) and \(s = \) the value of the CV.

Table S2. The \(p\) and \(q\) for collective variables defined for running metadynamics simulation.

|       | NGr |       | BGr |       | SGr |       | PGr |
|-------|-----|-------|-----|-------|-----|-------|-----|
|       | PBE | DFTB | PBE | DFTB | PBE | DFTB | PBE | DFTB |
| Step 1 |     |       |     |       |     |       |     |       |
| CV1   | 10  | 22   | 10  | 22   | 10  | 22   | 8   | 16   |
| CV2   | -   | -    | -   | -    | -   | -    | -   | -    |
| Step 2 |     |       |     |       |     |       |     |       |
| CV1   | 8   | 16   | 8   | 16   | 8   | 16   | 8   | 16   |
| CV2   | 8   | 16   | 8   | 16   | 8   | 16   | 8   | 16   |
| Step 3 |     |       |     |       |     |       |     |       |
| CV1   | 8   | 18   | 8   | 18   | 8   | 18   | 8   | 18   |
| CV2   | 10  | 24   | 10  | 24   | 10  | 24   | 10  | 24   |
| Step 4 |     |       |     |       |     |       |     |       |
| CV1   | 10  | 24   | 10  | 24   | 10  | 24   | 10  | 24   |
| CV2   | 8   | 18   | 8   | 18   | 10  | 24   | 10  | 24   |

For a valid comparative study, the Gaussian hill height spawned (with scaling factor = 0.1) and the frequency of hill addition (Table S3) was the same as the metadynamics simulation performed using PBE.
The free energy landscape was presented from the simulations of 1500 steps. The fixed distance cutoff parameter ($d_0$) along with the free energy barrier for independent metadynamics simulation of each step for NGr, BGr, SGr, and PGr are tabulated in Table S4.

4. Results

**NGr**: We plotted the three free energy surfaces obtained from 3 independent metadynamics simulations and explored to obtain the energy barriers for each step. The activation energy for step 1, 2, 3, and 4 are $4.87\pm0.38$, $4.02\pm0.13$, $17.91\pm0.56$, and $3.51\pm0.55$ kcal mol$^{-1}$. The reactant, transition state, and product snapshots are depicted in Figure S1, panel a-c, d-f, g-i, and j-l for step 1, step 2, step 3, and step 4 respectively. The free energy contour plots for each step are plotted simultaneously are presented in Figure S1(m-p) for steps 1-4 respectively. Figure S1q represents the complete 2D energy profile.

**BGr**: The three free energy surfaces are plotted and the stepwise barriers are calculated. The activation energy for step 1, 2, 3, and 4 are $3.13\pm0.14$, $1.84\pm0.29$, $15.22\pm0.87$, and $2.19\pm0.11$ kcal mol$^{-1}$ respectively. The reactant, transition state, and product snapshots are depicted in Figure S2 panel a-c, d-f, g-i, and j-l for step 1, step 2, step 3, and step 4 respectively. The free energy contour plots and 2D energy profile are presented in Figure S2(m-p) and Figure S2q for steps 1-4 respectively.

**SGr**: We plotted a free energy surface and explored to obtain the energy barriers for each step. The activation energy for step 1, 2, 3, and 4 are $4.29\pm0.24$, $2.96\pm0.35$, $14.94\pm0.41$, and $3.96\pm0.17$ kcal mol$^{-1}$. The $\Delta G$ values calculated from PBE are close in values to the ones calculated using SCC-DFTB. The reactant, transition state, and product snapshots are depicted in Figure S3 panel a-c, d-f, g-i, and j-l for step 1, step 2, step 3, and step 4 respectively. The free energy contour plots are presented in Figure S3(m-p) for steps 1-4 respectively. Figure S3q represents the complete 2D energy profile.

**PGr**: We plotted a free energy surface and explored to obtain the energy barriers for each step. The activation energy for step 1, 2, 3, and 4 are $4.24\pm0.02$, $3.05\pm1.41$, $17.34\pm1.06$, and $1.95\pm0.13$ kcal mol$^{-1}$ respectively. We observed a similarity in the values obtained from PBE and SCC-DFTB. The reactant, transition state, and product snapshots are depicted in Figure S4 panel a-c, d-f, g-i, and j-l for step 1, step 2, step 3, and step 4 respectively. The free energy contour plots are presented in Figure S4(m-p) for steps 1-4 respectively. The 2D energy profiles for PGr is depicted in Figure S4q.
Table S3. The electronic parameters used for running metadynamics simulation. The stepwise Gaussian hill height, frequency of hill addition, and scale are the same irrespective of the dopant.

| Step | CV1 | CV2 | NGr | BGr | PGr | SGr | K for quadratic wall (in kcal mol⁻¹) | Hill height (kcal mol⁻¹) | Frequency of hill addition | Scale |
|------|-----|-----|-----|-----|-----|-----|-----------------------------------|--------------------------|----------------------------|-------|
| 1    | 1.2 | -   | 1.2 | -   | 0.7 | -   | 1.2                               | 0.6                      | 5                          | 0.1   |
|      | 1.2 | -   | 0.7 | -   | -   | 0.7 |                                   |                          |                            |       |
|      |     |     |    |     |     |     |                                   |                          |                            |       |
| 2    | 2.0 | -   | 2.0 | -   | 2.0 | -   | 2.0                               | 2.0                      | 5                          | 0.1   |
|      | 2.0 | -   | 2.0 | -   | 2.0 | -   |                                   |                          |                            |       |
|      |     |     |    |     |     |     |                                   |                          |                            |       |
| 3    | 1.2 | -   | -   | -   | -   | -   | 1.2                               | 1.2                      | 5                          | 0.1   |
|      | 1.2 | -   | -   | -   | -   | -   |                                   |                          |                            |       |
| 4    | 1.2 | -   | -   | -   | -   | -   | 0.6                               | 0.6                      | 5                          | 0.1   |
|      | 1.2 | -   | -   | -   | -   | -   |                                   |                          |                            |       |
Table S4. The energy barriers obtained from the metadynamics simulation run using PBE and SCC-DFTB for step 1 to step 4 of the OER catalytic cycle mediated by NGr, BGr, SGr, and PGr.

|       | PBE                                | DFTB                                |
|-------|------------------------------------|------------------------------------|
|       | Set 1                              | Set 2                              | Set 3                              | Set 1                              | Set 2                              | Set 3                              |
|       | d_{c}^{CV1}/d_{c}^{CV2} | ΔG     | d_{c}^{CV1}/d_{c}^{CV2} | ΔG     | d_{c}^{CV1}/d_{c}^{CV2} | ΔG     | d_{c}^{CV1}/d_{c}^{CV2} | ΔG     | d_{c}^{CV1}/d_{c}^{CV2} | ΔG     | d_{c}^{CV1}/d_{c}^{CV2} | ΔG     | d_{c}^{CV1}/d_{c}^{CV2} | ΔG     |
| NGr   | Step 1                             | 2.25/-                            | 4.73                              | 2.35/-                            | 4.73                              |
|       |                                    | 2.53                              | 5.37                              | 5.11±0.33                         | 4.54                              | 2.35/-                            | 4.79                              | 2.45/-                            | 5.30                              | 4.87±0.38                         |
|       | 1.60/1.40                          | 2.65/1.60                         | 3.04/1.60                         | 2.96                              | 2.66±0.24                         | 1.55/1.40                         | 3.88/1.60                         | 1.60/1.50                         | 4.04/1.50                         | 4.15/1.40                         | 4.02±0.13                         |
|       | 2.25/3.70                          | 18.18/18.73                       | 2.40/3.45                         | 17.77/3.45                        | 18.23±0.48                        | 2.20/3.70                         | 18.55/3.35                        | 2.30/3.55                         | 17.67/3.35                        | 17.50/3.55                        | 17.91±0.56                        |
|       | 1.60/1.45                          | 2.33/1.55                         | 2.47/1.60                         | 2.74                              | 2.51±0.21                         | 2.00/1.50                         | 2.91/1.60                         | 2.00/1.60                         | 3.61/1.65                         | 4.00/1.45                         | 3.51±0.55                         |
| BGr   | Step 1                             | 2.15/-                            | 3.40                              | 2.88                              | 3.87                              | 3.71±0.27                         | 2.15/1.50                         | 2.98/1.50                         | 2.25/-                            | 3.17/1.50                         | 3.25/1.44                         | 3.13±0.14                         |
|       |                                    | 1.76/1.40                         | 1.70/1.40                         | 1.90                              | 1.79±0.10                         | 1.60/1.30                         | 1.93/1.40                         | 1.45/1.51                         | 1.51/1.40                         | 2.08/1.50                         | 1.84±0.29                         |
|       | 2.30/3.65                          | 15.42/16.05                       | 2.50/3.45                         | 16.42/3.45                        | 15.97±0.51                        | 2.30/3.65                         | 14.25/3.45                        | 2.40/3.55                         | 15.44/3.55                        | 15.96/3.55                        | 15.22±0.87                        |
|       | 1.70/1.55                          | 2.36/1.60                         | 2.31/1.60                         | 2.64                              | 2.42±0.16                         | 1.70/1.55                         | 2.31/1.60                         | 1.70/1.60                         | 2.09/1.60                         | 1.80/1.60                         | 2.18/0.11                         |
| SGr   | Step 1                             | 2.05/-                            | 4.29                              | 2.15/-                            | 4.40                              | 2.25/-                            | 5.13                              | 4.61±0.46                         | 4.20/1.42                         | 4.18/1.41                         | 4.47/0.24                         | 4.29±0.24                         |
|       |                                    | 1.50/1.40                         | 2.36/1.50                         | 2.12/1.60                         | 3.21/1.60                         | 2.56±0.57                         | 1.50/1.40                         | 2.61/1.50                         | 1.45/1.50                         | 2.97/1.50                         | 1.50/0.35                         | 2.96±0.35                         |
|       | 2.30/3.60                          | 13.79/14.74                       | 2.50/3.44                         | 15.64/3.44                        | 14.73±0.92                        | 2.20/3.60                         | 14.47/3.40                        | 2.30/3.50                         | 15.14/3.40                        | 15.21/3.40                        | 14.94±0.41                        |
|       | 1.90/1.40                          | 2.33/1.45                         | 3.87/1.50                         | 4.01/1.50                         | 3.40±0.93                         | 1.95/1.65                         | 4.01/1.70                         | 3.71/1.70                         | 1.95/1.75                         | 4.11/0.17                         | 3.96±0.17                         |
| PGr   | Step 1                             | 2.15/-                            | 3.77                              | 2.25/-                            | 3.59/1.80                         | 2.40/1.90                         | 4.40/1.90                         | 3.92±0.43                         | 2.15/1.75                         | 4.23/1.75                         | 4.24/-                            | 4.24/0.02                         |
|       |                                    | 1.50/1.40                         | 1.65/1.55                         | 1.66/1.60                         | 1.75/1.70                         | 1.69±0.05                         | 1.50/1.40                         | 2.05/1.50                         | 1.55/1.50                         | 2.45/1.50                         | 1.65/1.41                         | 3.05±1.41                         |
|       | 2.35/3.50                          | 17.17/18.69                       | 2.55/3.30                         | 17.75/3.30                        | 17.88±0.76                        | 2.30/3.50                         | 18.39/3.30                        | 2.40/3.40                         | 17.38/3.30                        | 16.26/3.30                        | 17.34±1.06                        |
|       | 1.80/1.75                          | 3.10/1.80                         | 2.30/1.80                         | 2.84                              | 2.74±0.41                         | 1.80/1.75                         | 1.93/1.80                         | 1.80/1.80                         | 2.09/1.80                         | 1.84/1.80                         | 1.95±0.13                         |
Figure S1. (a-c), (d-f), (g-i), and (j-l) depicts the snapshots of the reactant [R], transition state [TS], and product [P] obtained from the metadynamics simulation of step 1, step 2, step 3, and step 4 of OER assisted by the NGr using DFTB method. The surface plots of the free energy hence obtained are presented in (m-p) for step (1-4) respectively. (q) is the 2D energy profile for the same presenting the reaction energy barriers for the 4 elementary steps. The blue, green, red, and white ball represents N, C, O, and H respectively.

Figure S2. (a-c), (d-f), (g-i), and (j-l) depicts the snapshots of the reactant [R], transition state [TS], and product [P] obtained from the metadynamics simulation of step 1, step 2, step 3, and step 4 of OER assisted by the BGr using DFTB method. The surface plots of the free energy hence obtained are presented in (m-p) for step (1-4) respectively. (q) is the 2D energy profile for the same presenting the reaction energy barriers for the 4 elementary steps. The pink, green, red, and white ball represents B, C, O, and H respectively.
Figure S3. (a-c), (d-f), (g-i), and (j-l) depicts the snapshots of the reactant [R], transition state [TS], and product [P] obtained from the metadynamics simulation using the DFTB method of step 1, step 2, step 3, and step 4 of OER assisted by the SGr. The surface plots of the free energy hence obtained are presented in (m-p) for step (1-4) respectively. (q) is the 2D energy profile for the same presenting the reaction energy barriers for the 4 elementary steps. The yellow, green, red, and white ball represents S, C, O, and H respectively.

Figure S4. (a-c), (d-f), (g-i), and (j-l) depicts the snapshots of the reactant [R], transition state [TS], and product [P] obtained from the metadynamics simulation using the DFTB method of step 1, step 2, step 3, and step 4 of OER assisted by the PGr. The surface plots of the free energy hence obtained are presented in (m-p) for step (1-4) respectively. (q) is the 2D energy profile for the same presenting the reaction energy barriers for the 4 elementary steps. The olive, green, red, and white ball represents P, C, O, and H respectively.
5. Electronic Property

We calculated the Mulliken\textsuperscript{33} and Lowdin charge to have a closer insight into how the electron density changes as the reaction proceeds. In Figure S5 (a1-a4), (c1-c4), (e1-e4), and (g1-g4) for NGr, BGr, SGr, and PGr we have presented the change in the Mulliken charge as the reaction metadynamics simulation proceeds for each step in the catalytic cycle. Similarly, the Lowdin charge distributions are presented in Figure S5 (b1-b4), (d1-d4), (f1-f4), and (h1-h4) for NGr, BGr, SGr, and PGr respectively.

**Figure S5.** Represents the Mulliken and Löwdin charge change of the reactive species, and active site in the 4 elementary paths of OER to the MD steps. a1-a4, c1-c4, e1-e4, and g1-g4 presents the change in the Mulliken charge for NGr, BGr, SGr, and PGr. The Lowdin charged are presented in b1-b4, d1-d4, f1-f4, and h1-h4 for NGr, BGr, SGr, and PGr respectively. The reactive species O\textsubscript{a}, O\textsubscript{b}, O\textsubscript{c}, and O\textsubscript{e} irrespective of catalyst, are presented by red, blue, magenta, and brown lines respectively.
Figure S6. The RDF of oxygen of water with respect to the 3 randomly chosen carbon atom $C_1$ (black line), $C_2$ (red line), $C_3$ (green line) from the bulk positions of undoped graphene, and the entire graphene sheet (blue line).
REFERENCES:

(S1) Plimpton, S. Fast Parallel Algorithms for Short-Range Molecular Dynamics. *J. Comput. Phys.* **1995**, *117*, 1–19.

(S2) Martínez, L.; Andrade, R.; Birgin, E. G.; Martínez, J. M. PACKMOL: A package for building initial configurations for molecular dynamics simulations. *J. Comput. Chem.* **2009**, *30*, 2157–2164.

(S3) Berendsen, H. J. C.; Grigera, J. R.; Straatsma, T. P. The Missing Term in Effective Pair Potentials. *J. Phys. Chem.* **1987**, *91*, 6269–6271.

(S4) Hoover, W. G. Canonical Dynamics: Equilibrium Phase-Space Distributions. *Phys. Rev. A* **1985**, *31*, 1695–1697.

(S5) Martyna, G. J.; Klein, M. L.; Tuckerman, M. Nosé–Hoover Chains: The Canonical Ensemble via Continuous Dynamics. *J. Chem. Phys.* **1992**, *97*, 2635–2643.

(S6) Wang, J.; Wolf, R. M.; Caldwell, J. W.; Kollman, P. A.; Case, D. A. Development and Testing of a General Amber Force Field. *J. Comput. Chem.* **2004**, *25*, 1157–1174.

(S7) Wang, J.; Wang, W.; Kollman, P. A.; Case, D. A. Automatic Atom Type and Bond Type Perception in Molecular Mechanical Calculations. *J. Mol. Graph. Model.* **2006**, *25*, 247–260.

(S8) Jorgensen, W. L.; Tirado-Rives, J. The OPLS [Optimized Potentials for Liquid Simulations] Potential Functions for Proteins, Energy Minimizations for Crystals of Cyclic Peptides and Crambin. *J. Am. Chem. Soc.* **1988**, *110*, 1657–1666.

(S9) Jorgensen, W. L.; Maxwell, D. S.; Tirado-Rives, J. Development and Testing of the OPLS All-Atom Force Field on Conformational Energetics and Properties of Organic Liquids. *J. Am. Chem. Soc.* **1996**, *118*, 11225–11236.

(S10) Stuart, S. J.; Tutein, A. B.; Harrison, J. A. A Reactive Potential for Hydrocarbons with Intermolecular Interactions. *J. Chem. Phys.* **2000**, *112*, 6472–6486.

(S11) Tersoff, J. New Empirical Approach for the Structure and Energy of Covalent Systems. *Phys. Rev. B* **1988**, *37*, 6991–7000.

(S12) Tersoff, J. Modeling Solid-State Chemistry: Interatomic Potentials for Multicomponent Systems. *Phys. Rev. B* **1989**, *39*, 5566–5568.

(S13) Al-Matar, A. K.; Rockstraw, D. A. A Generating Equation for Mixing Rules and Two New Mixing Rules for Interatomic Potential Energy Parameters. *J. Comput. Chem.* **2004**, *25*, 660–668.

(S14) Kolafa, J.; Nezbeda, I.; Pavlíček, J.; Smith, W. R. Global Phase Diagrams of Model and Real Binary Fluid Mixtures: Lorentz–Berthelot Mixture of Attractive Hard Spheres. *Fluid Phase Equilib.* **1998**, *146*, 103–121.

(S15) Zarkova, L.; Hohm, U.; Damyanova, M. Comparison of Lorentz–Berthelot and Tang–Toennies Mixing Rules Using an Isotropic Temperature-Dependent Potential Applied to the Thermophysical Properties of Binary Gas Mixtures of CH4, CF4, SF6, and C(CH3)4 with Ar, Kr, and Xe. *Int. J. Thermophys.* **2004**, *25*, 1775–1798.

(S16) Mayo, S. L.; Olafson, B. D.; Goddard, W. A. DREIDING: A Generic Force Field for Molecular Simulations. *J. Phys. Chem.* **1990**, *94*, 8897–8909.

(S17) Porezag, D.; Frauenheim, Th.; Köhler, Th.; Seifert, G.; Kaschner, R. Construction of Tight-Binding-like Potentials on the Basis of Density-Functional Theory: Application to Carbon. *Phys. Rev. B* **1995**, *51*, 12947–12957.

(S18) Seifert, G.; Porezag, D.; Frauenheim, T. Calculations of Molecules, Clusters, and Solids with a Simplified LCAO-DFT-LDA Scheme. *Int. J. Quantum Chem.* **1996**, *58*, 185–192.

(S19) Goyal, P.; Elstner, M.; Cui, Q. Application of the SCC-DFTB Method to Neutral and Protonated Water Clusters and Bulk Water. *J. Phys. Chem. B* **2011**, *115*, 6790–6805.

(S20) Riccardi, D.; Yang, S.; Cui, Q. Proton Transfer Function of Carbonic Anhydrase: Insights from QM/MM Simulations. *Biochim. Biophys. Acta* **2010**, *1804*, 342–351.

(S21) Elstner, M.; Porezag, D.; Jungnickel, G.; Elsner, J.; Haugk, M.; Frauenheim, Th.; Suhai, S.; Seifert, G. Self-Consistent-Charge Density-Functional Tight-Binding Method for Simulations of Complex Materials Properties. *Phys. Rev. B* **1998**, *58*, 7260–7268.
(S22) Zobelli, A.; Gloter, A.; Ewels, C. P.; Seifert, G.; Colliex, C. Electron Knock-on Cross Section of Carbon and Boron Nitride Nanotubes. *Phys. Rev. B* 2007, 75, 245402.

(S23) Lehtinen, O.; Kurasch, S.; Krasheninnikov, A. V.; Kaiser, U. Atomic Scale Study of the Life Cycle of a Dislocation in Graphene from Birth to Annihilation. *Nat Commun* 2013, 4, 1–7.

(S24) Gruden, M.; Andjeklović, L.; Kuriappan, J. A.; Stepanović, S.; Zlatar, M.; Cui, Q.; Elstner, M. Benchmarking Density Functional Tight Binding Models for Barrier Heights and Reaction Energetics of Organic Molecules. *J Comput Chem* 2017, 38, 2171–2185.

(S25) Grimme, S. Semiempirical GGA-Type Density Functional Constructed with a Long-Range Dispersion Correction. *J. Comput. Chem* 2006, 27, 1787–1799.

(S26) Grimme, S. Accurate Description of van Der Waals Complexes by Density Functional Theory Including Empirical Corrections. *J Comput Chem* 2004, 25, 1463–1473.

(S27) Lukose, B.; Kuc, A.; Frenzel, J.; Heine, T. On the Reticular Construction Concept of Covalent Organic Frameworks. *Beilstein J. Nanotechnol.* 2010, 1, 60–70.

(S28) Gemming, S.; Enyashin, A. N.; Frenzel, J.; Seifert, G. Adsorption of Nucleotides on the Rutile (110) Surface. *IJMR* 2010, 101, 758–764.

(S29) Kubillus, M.; Kubař, T.; Gaus, M.; Řezáč, J.; Elstner, M. Parameterization of the DFTB3 Method for Br, Ca, Cl, F, I, K, and Na in Organic and Biological Systems. *J. Chem. Theory Comput.* 2015, 11, 332–342.

(S30) Ensing, B.; Laio, A.; Gervasio, F. L.; Parrinello, M.; Klein, M. L. A Minimum Free Energy Reaction Path for the E2 Reaction between Fluoro Ethane and a Fluoride Ion. *J. Am. Chem. Soc.* 2004, 126, 9492–9493.

(S31) Laio, A.; Gervasio, F. L. Metadynamics: A Method to Simulate Rare Events and Reconstruct the Free Energy in Biophysics, Chemistry and Material Science. *Rep. Prog. Phys.* 2008, 71, 126601.

(S32) Nair, N. N.; Schreiner, E.; Marx, D. Peptide Synthesis in Aqueous Environments: The Role of Extreme Conditions on Amino Acid Activation. *J. Am. Chem. Soc.* 2008, 130, 14148–14160.

(S33) Mulliken, R. S. Electronic Population Analysis on LCAO–MO Molecular Wave Functions. I. *J. Chem. Phys.* 1955, 23, 1833–1840.