ADVANCED THEORY AND SIMULATIONS

Supporting Information

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Cocrystal Growth in Organic Semiconductor Thin Films: Simulation of Pentacene, Perfluoropentacene, and Their 1:1 Blend Deposited On Graphite

*Emilio Lorini, Lorenzo Soprani and Luca Muccioli**

Supporting Information

Co-crystal growth in organic semiconductor thin films: simulation of pentacene, perfluoropentacene, and their 1:1 blend deposited on graphite

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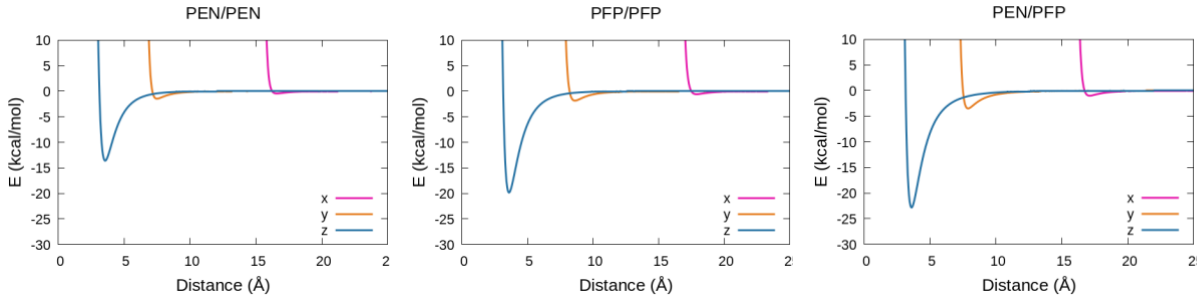

Figure S1: To quantify the intermolecular interactions, both electrostatic and Lennard-Jones potentials were calculated for the three possible couples of parallel molecules (PEN/PEN, PFP/PFP and PEN/PFP) along three different directions, corresponding to principal inertia axes.

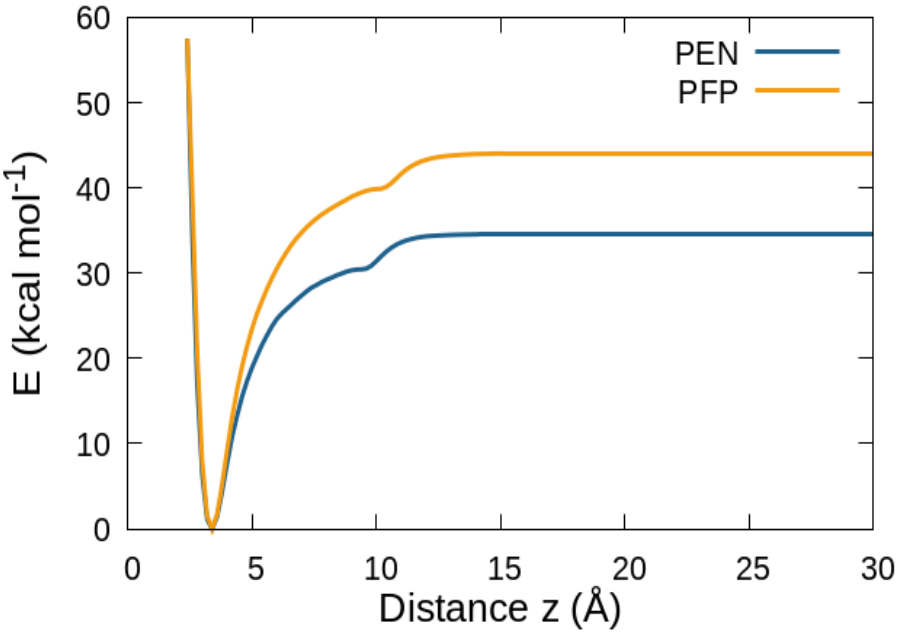

Figure S2: Adsorption free energy profile obtained moving vertically one molecule on the graphite surface (4 layers). The adsorption energy reported in the text was calculated as the difference between the value at the minimum (~3.5 Å) and the value at 30 Å.

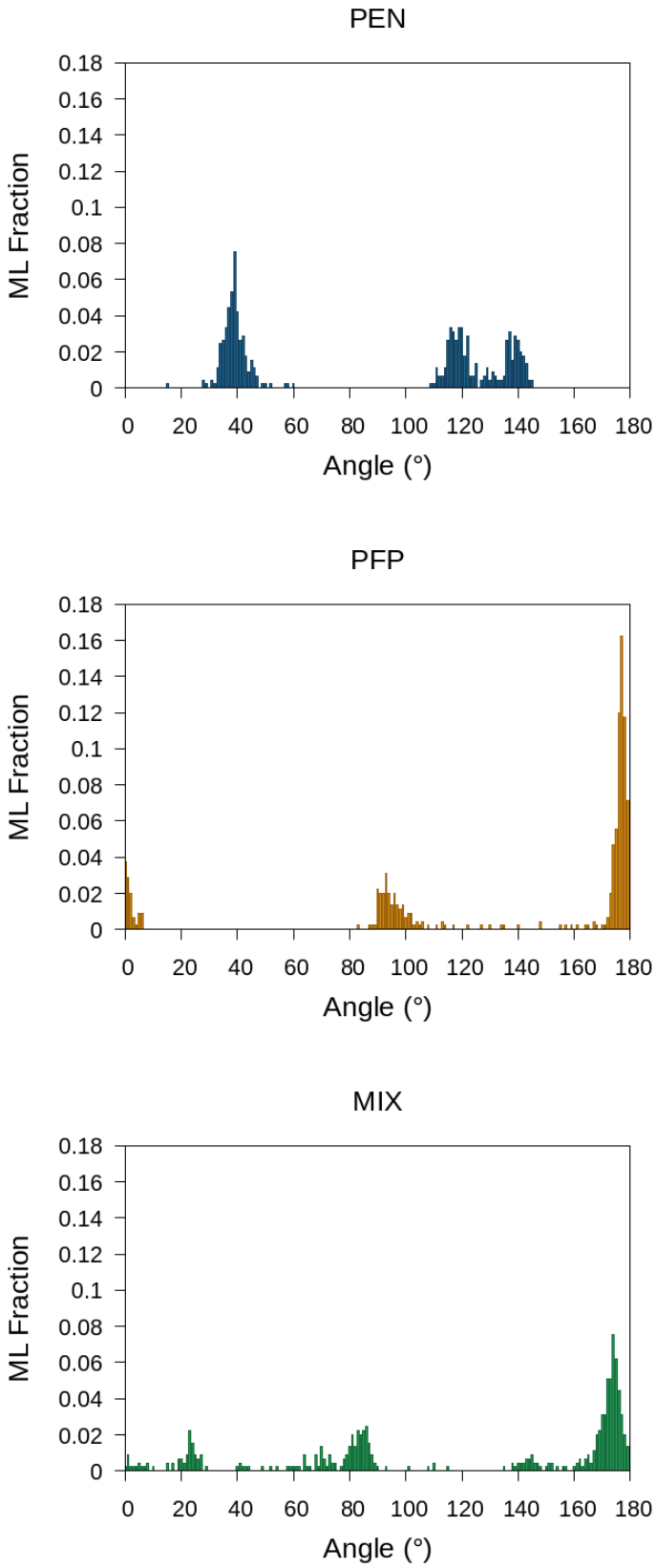

Figure S3: Distribution of the angle between the long molecular axis and the <100> graphite axis (the x side of the simulation box) for PEN, PFP and MIX system sat the final step of the deposition.

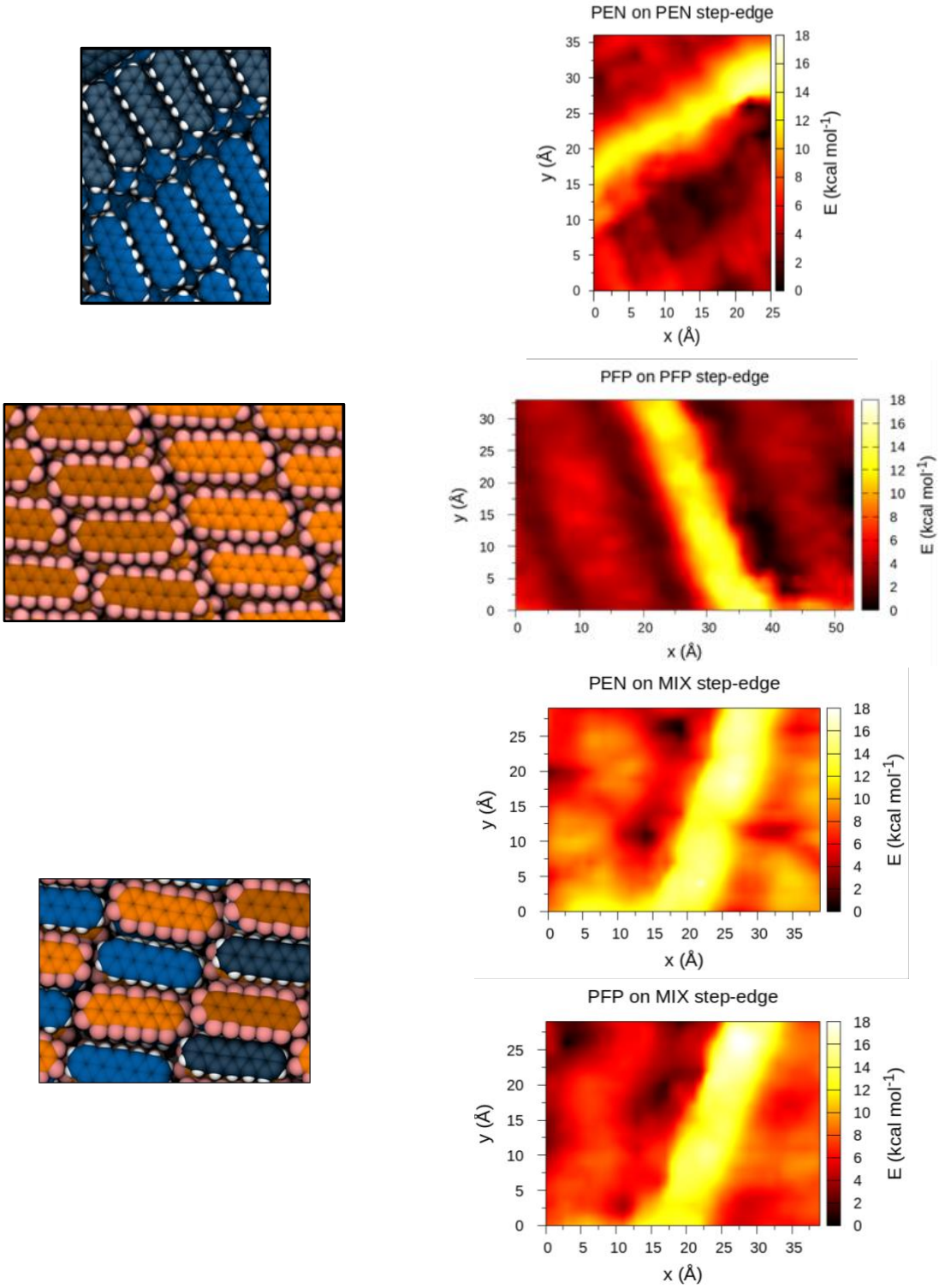

Figure S4. Right: free energy maps for moving one molecule across a short-side step edge, highlighting the orthogonal barriers to diffusion. Maps were calculated through the ABF method for PFP, PEN and MIX system, in the regions of the samples displayed in the snapshots on the left.

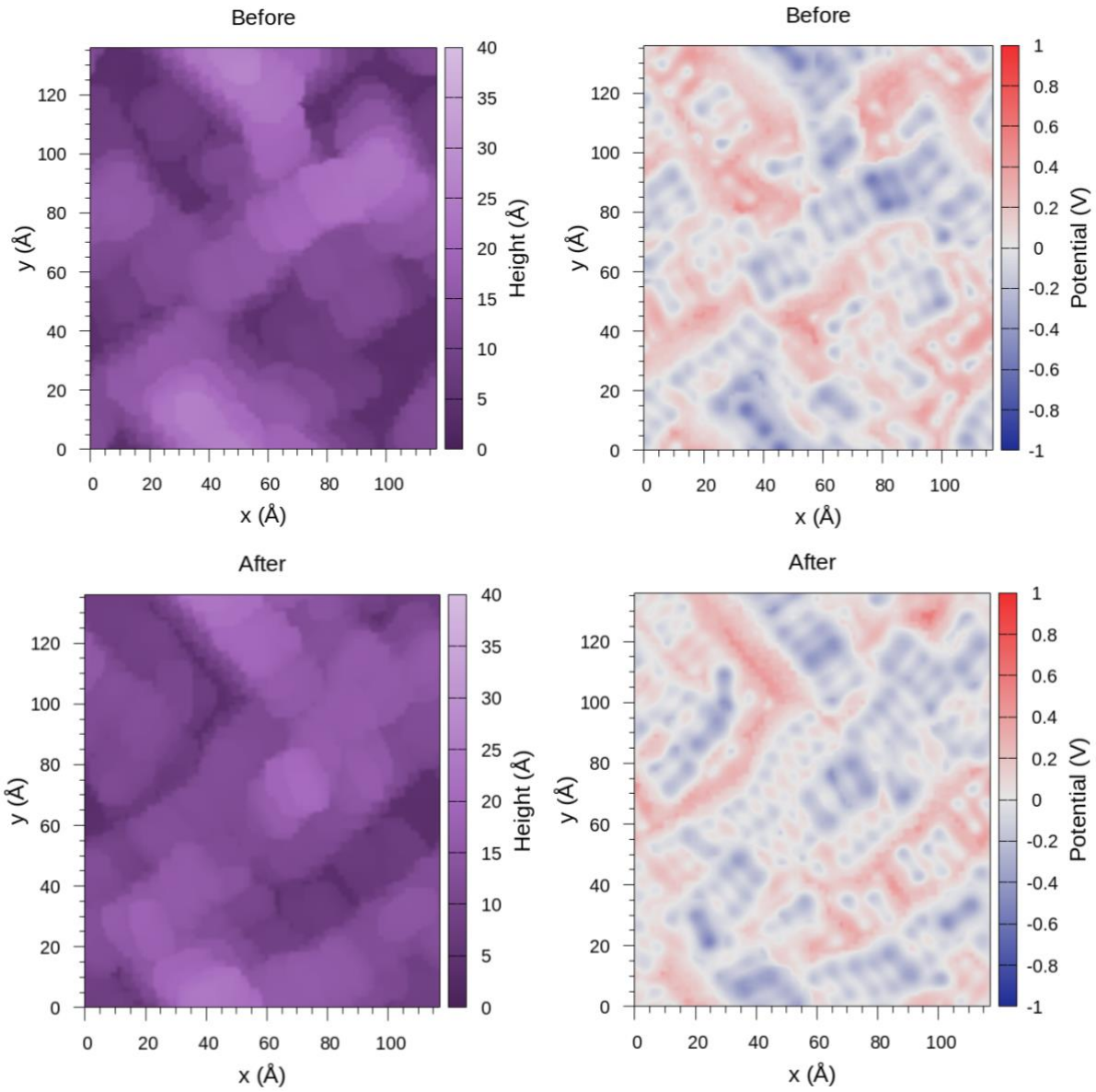

Figure S5: Electrostatic potential maps (right) and relative topography maps (left) of the morphologies of PEN system, before (top) and after annealing for 5 ns at 500 K (bottom).

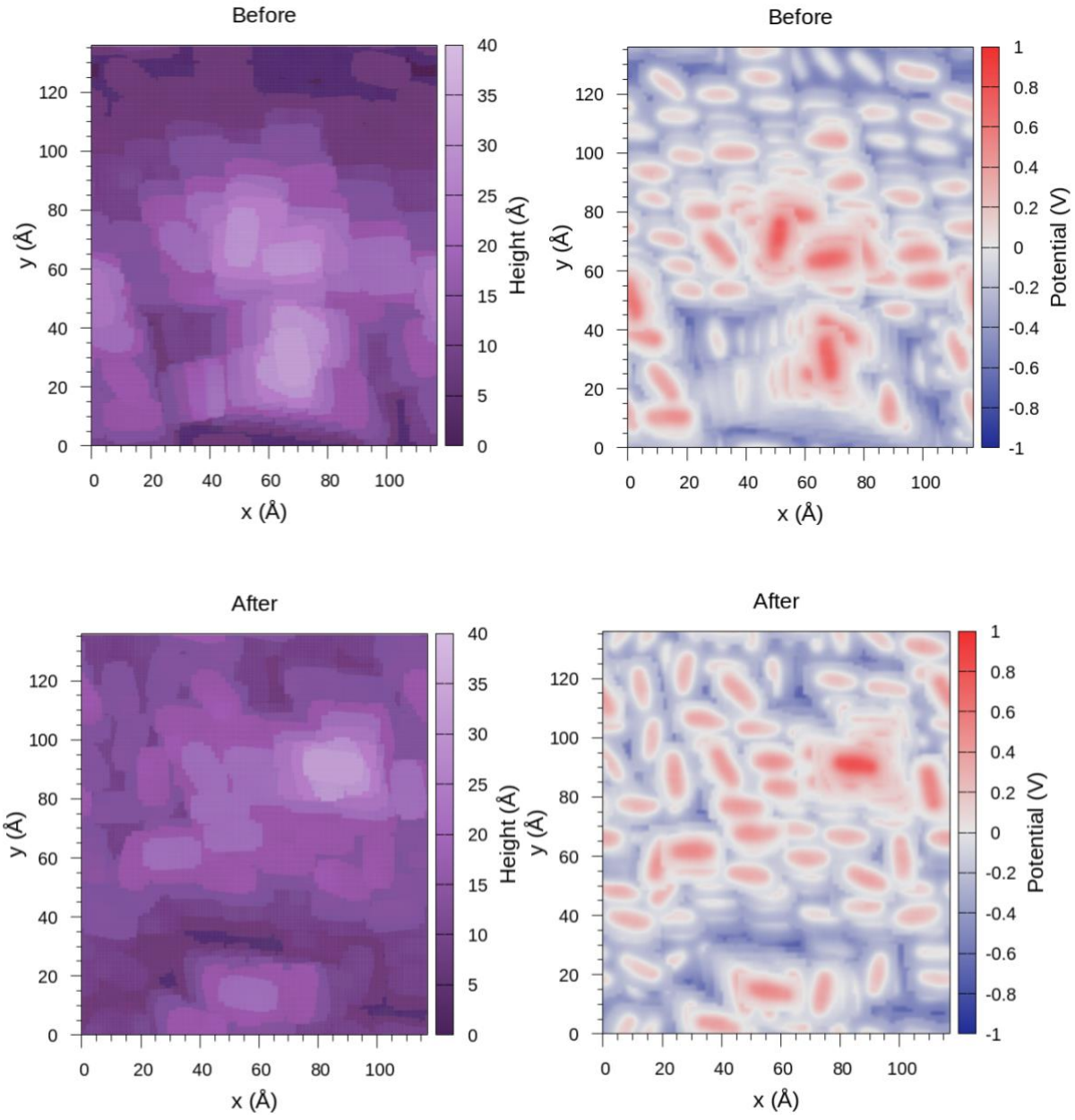

Figure S6: Electrostatic potential maps (right) and relative topography maps (left) of the morphologies of PFP system, before (top) and after annealing for 5 ns at 500 K (bottom).

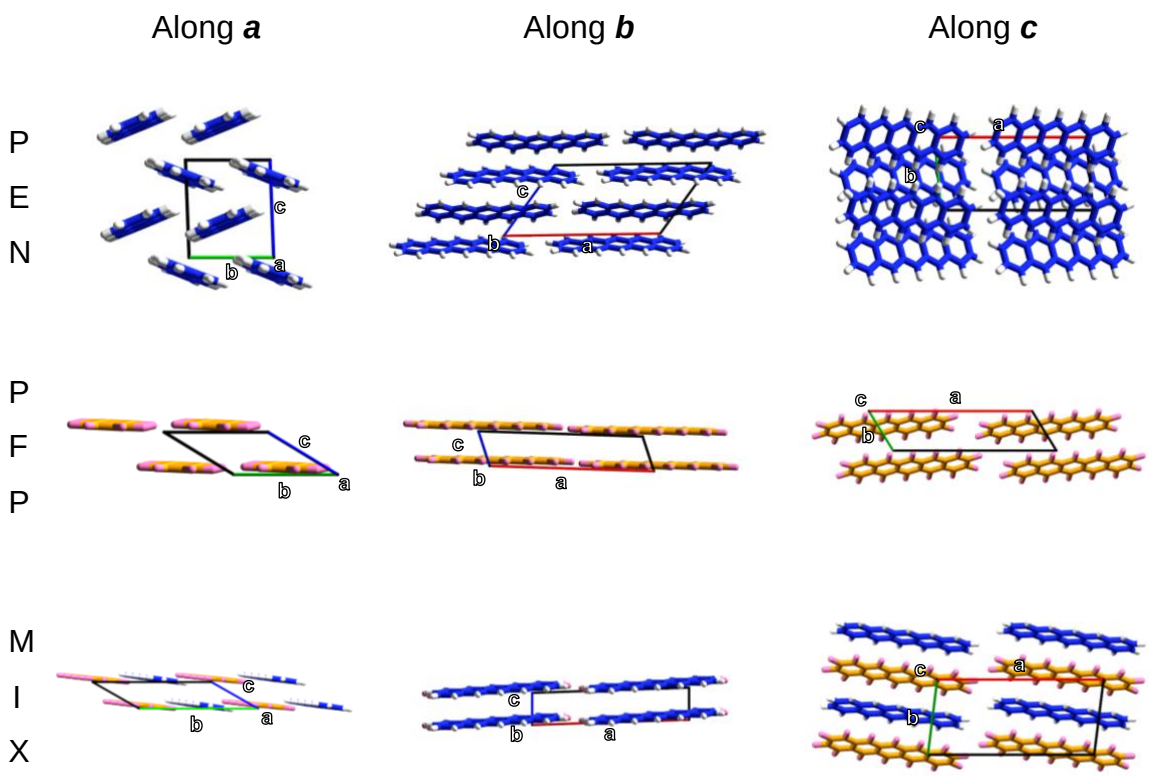

Figure S7: Views along each cell axis of 2x2x2 replicated unit cells obtained from deposition simulations on graphite for PEN, PFP and MIX crystals.

Table S1. Averaged short-side step edge energy barriers (kcal mol^{-1}) for PFP, PEN and MIX crystal terraces. For MIX we report the barriers relative to the heterogeneous (HE) channel.

System	PEN molecule		PFP molecule	
	downward	upward	downward	upward
PEN	8.0	10.0	-	-
PFP	-	-	10.0	10.5
MIX	8.5	11.0	8.0	12.0

Table S2. PEN tentative crystal cell dimensions and atomic coordinates as obtained from the analysis of deposition simulations, given in pdb format. No attempts were made for determining the symmetry group and optimizing atomic coordinates.

```
CRYST1   16.077    6.217    8.885  83.45  52.72  81.97
REMARK CELL AXIS    16.077    0.000    0.000
REMARK CELL AXIS     0.868    6.156    0.000
REMARK CELL AXIS     5.382    0.264    7.065
ATOM      1  C1  PEN    01       3.241  -3.078  -1.232  1.00  1.00       PEN
ATOM      2  C2  PEN    01       4.494  -2.474  -1.434  1.00  1.00       PEN
ATOM      3  C3  PEN    01       4.571  -1.164  -1.939  1.00  1.00       PEN
ATOM      4  C4  PEN    01       3.396  -0.456  -2.247  1.00  1.00       PEN
ATOM      5  C5  PEN    01       2.141  -1.058  -2.045  1.00  1.00       PEN
ATOM      6  C6  PEN    01       2.063  -2.373  -1.530  1.00  1.00       PEN
ATOM      7  C7  PEN    01       0.966  -0.352  -2.355  1.00  1.00       PEN
ATOM      8  C8  PEN    01      -0.287  -0.953  -2.141  1.00  1.00       PEN
ATOM      9  C9  PEN    01      -0.365  -2.264  -1.610  1.00  1.00       PEN
ATOM     10  C10 PEN    01       0.811  -2.973  -1.309  1.00  1.00       PEN
ATOM     11  C11 PEN    01      -1.461  -0.236  -2.432  1.00  1.00       PEN
ATOM     12  C12 PEN    01      -2.714  -0.809  -2.149  1.00  1.00       PEN
ATOM     13  C13 PEN    01      -2.793  -2.117  -1.610  1.00  1.00       PEN
ATOM     14  C14 PEN    01      -4.044  -2.670  -1.282  1.00  1.00       PEN
ATOM     15  C15 PEN    01      -5.211  -1.906  -1.462  1.00  1.00       PEN
ATOM     16  C16 PEN    01      -6.461  -2.434  -1.091  1.00  1.00       PEN
ATOM     17  C17 PEN    01      -7.625  -1.662  -1.254  1.00  1.00       PEN
ATOM     18  C18 PEN    01      -7.545  -0.364  -1.792  1.00  1.00       PEN
ATOM     19  C19 PEN    01      -6.298   0.166  -2.169  1.00  1.00       PEN
ATOM     20  C20 PEN    01      -5.131  -0.600  -2.002  1.00  1.00       PEN
ATOM     21  C21 PEN    01      -3.884  -0.060  -2.363  1.00  1.00       PEN
ATOM     22  C22 PEN    01      -1.619  -2.849  -1.356  1.00  1.00       PEN
ATOM     23  H23 PEN    01       3.187  -4.084  -0.847  1.00  1.00       PEN
ATOM     24  H24 PEN    01       5.394  -3.026  -1.200  1.00  1.00       PEN
ATOM     25  H25 PEN    01       5.533  -0.700  -2.099  1.00  1.00       PEN
ATOM     26  H26 PEN    01       3.458   0.547  -2.644  1.00  1.00       PEN
ATOM     27  H27 PEN    01       1.032   0.649  -2.753  1.00  1.00       PEN
ATOM     28  H28 PEN    01       0.757  -3.971  -0.901  1.00  1.00       PEN
ATOM     29  H29 PEN    01      -1.403   0.764  -2.834  1.00  1.00       PEN
ATOM     30  H30 PEN    01      -3.828   0.937  -2.775  1.00  1.00       PEN
ATOM     31  H31 PEN    01      -6.239   1.163  -2.581  1.00  1.00       PEN
ATOM     32  H32 PEN    01      -8.437   0.235  -1.912  1.00  1.00       PEN
ATOM     33  H33 PEN    01      -8.582  -2.068  -0.961  1.00  1.00       PEN
ATOM     34  H34 PEN    01      -6.524  -3.430  -0.676  1.00  1.00       PEN
ATOM     35  H35 PEN    01      -4.108  -3.659  -0.852  1.00  1.00       PEN
ATOM     36  H36 PEN    01      -1.679  -3.838  -0.927  1.00  1.00       PEN
ATOM      1  C1  PEN    02      -3.407   2.499   2.196  1.00  1.00       PEN
ATOM      2  C2  PEN    02      -4.578   1.775   1.912  1.00  1.00       PEN
ATOM      3  C3  PEN    02      -4.494   0.454   1.435  1.00  1.00       PEN
ATOM      4  C4  PEN    02      -3.237  -0.144   1.243  1.00  1.00       PEN
ATOM      5  C5  PEN    02      -2.063   0.579   1.511  1.00  1.00       PEN
ATOM      6  C6  PEN    02      -2.148   1.905   1.997  1.00  1.00       PEN
ATOM      7  C7  PEN    02      -0.808  -0.017   1.297  1.00  1.00       PEN
ATOM      8  C8  PEN    02       0.364   0.708   1.573  1.00  1.00       PEN
ATOM      9  C9  PEN    02       0.280   2.028   2.078  1.00  1.00       PEN
ATOM     10  C10 PEN    02      -0.976   2.624   2.284  1.00  1.00       PEN
ATOM     11  C11 PEN    02       1.620   0.123   1.334  1.00  1.00       PEN
ATOM     12  C12 PEN    02       2.792   0.857   1.589  1.00  1.00       PEN
ATOM     13  C13 PEN    02       2.709   2.172   2.108  1.00  1.00       PEN
ATOM     14  C14 PEN    02       3.880   2.912   2.346  1.00  1.00       PEN
ATOM     15  C15 PEN    02       5.132   2.354   2.029  1.00  1.00       PEN
ATOM     16  C16 PEN    02       6.302   3.113   2.209  1.00  1.00       PEN
ATOM     17  C17 PEN    02       7.552   2.573   1.860  1.00  1.00       PEN
ATOM     18  C18 PEN    02       7.634   1.270   1.337  1.00  1.00       PEN
ATOM     19  C19 PEN    02       6.468   0.501   1.167  1.00  1.00       PEN
ATOM     20  C20 PEN    02       5.215   1.042   1.507  1.00  1.00       PEN
ATOM     21  C21 PEN    02       4.045   0.289   1.301  1.00  1.00       PEN
ATOM     22  C22 PEN    02       1.453   2.752   2.359  1.00  1.00       PEN
ATOM     23  H23 PEN    02      -3.477   3.511   2.566  1.00  1.00       PEN
ATOM     24  H24 PEN    02      -5.542   2.233   2.070  1.00  1.00       PEN
ATOM     25  H25 PEN    02      -5.391  -0.112   1.222  1.00  1.00       PEN
ATOM     26  H26 PEN    02      -3.179  -1.162   0.892  1.00  1.00       PEN
ATOM     27  H27 PEN    02      -0.748  -1.024   0.916  1.00  1.00       PEN
ATOM     28  H28 PEN    02      -1.044   3.631   2.667  1.00  1.00       PEN
ATOM     29  H29 PEN    02       1.685  -0.876   0.929  1.00  1.00       PEN
ATOM     30  H30 PEN    02       4.105  -0.706   0.887  1.00  1.00       PEN
ATOM     31  H31 PEN    02       6.533  -0.500   0.767  1.00  1.00       PEN
ATOM     32  H32 PEN    02       8.593   0.857   1.059  1.00  1.00       PEN
ATOM     33  H33 PEN    02       8.443   3.170   1.991  1.00  1.00       PEN
ATOM     34  H34 PEN    02       6.241   4.116   2.603  1.00  1.00       PEN
ATOM     35  H35 PEN    02       3.825   3.913   2.746  1.00  1.00       PEN
ATOM     36  H36 PEN    02       1.388   3.757   2.746  1.00  1.00       PEN
END
```

Table S3. PFP tentative crystal cell dimensions and atomic coordinates as obtained from the analysis of deposition simulations, given in pdb format. No attempts were made for determining the symmetry group and optimizing atomic coordinates.

```
CRYST1  17.6880   9.0700   6.4130  32.19  75.37  60.98
REMARK CELL AXIS   -14.199   -6.201    0.022
REMARK CELL AXIS    -3.375    8.416   -0.0124
REMARK CELL AXIS     1.465    2.620   -6.423
ATOM      1  F1  PFP     1      -7.218   1.943  -0.060  1.00  0.00       PFP
ATOM      2  F2  PFP     1      -7.429  -0.785  -0.185  1.00  0.00       PFP
ATOM      3  F3  PFP     1      -5.238  -2.335  -0.205  1.00  0.00       PFP
ATOM      4  F4  PFP     1      -2.706  -2.539  -0.170  1.00  0.00       PFP
ATOM      5  F5  PFP     1       0.216   2.734   0.124  1.00  0.00       PFP
ATOM      6  F6  PFP     1      -2.276   2.938   0.069  1.00  0.00       PFP
ATOM      7  F7  PFP     1      -4.808   3.135   0.029  1.00  0.00       PFP
ATOM      8  C8  PFP     1      -4.837   1.790  -0.027  1.00  0.00       PFP
ATOM      9  C9  PFP     1      -6.104   1.186  -0.081  1.00  0.00       PFP
ATOM     10  C10 PFP     1      -6.212  -0.207  -0.149  1.00  0.00       PFP
ATOM     11  C11 PFP     1      -5.055  -1.002  -0.163  1.00  0.00       PFP
ATOM     12  C12 PFP     1      -3.761  -0.412  -0.107  1.00  0.00       PFP
ATOM     13  C13 PFP     1      -2.582  -1.201  -0.121  1.00  0.00       PFP
ATOM     14  C14 PFP     1      -1.291  -0.607  -0.060  1.00  0.00       PFP
ATOM     15  C15 PFP     1       0.110   1.395   0.074  1.00  0.00       PFP
ATOM     16  C16 PFP     1      -1.181   0.805   0.014  1.00  0.00       PFP
ATOM     17  C17 PFP     1      -2.364   1.597   0.025  1.00  0.00       PFP
ATOM     18  C18 PFP     1      -3.651   1.003  -0.036  1.00  0.00       PFP
ATOM     19  F19 PFP     1       7.218  -1.944   0.062  1.00  0.00       PFP
ATOM     20  F20 PFP     1       7.430   0.784   0.185  1.00  0.00       PFP
ATOM     21  F21 PFP     1       5.240   2.334   0.203  1.00  0.00       PFP
ATOM     22  F22 PFP     1       2.707   2.538   0.169  1.00  0.00       PFP
ATOM     23  F23 PFP     1      -0.215  -2.734  -0.124  1.00  0.00       PFP
ATOM     24  F24 PFP     1       2.276  -2.939  -0.069  1.00  0.00       PFP
ATOM     25  F25 PFP     1       4.808  -3.136  -0.026  1.00  0.00       PFP
ATOM     26  C26 PFP     1       4.838  -1.791   0.029  1.00  0.00       PFP
ATOM     27  C27 PFP     1       6.105  -1.187   0.082  1.00  0.00       PFP
ATOM     28  C28 PFP     1       6.213   0.206   0.149  1.00  0.00       PFP
ATOM     29  C29 PFP     1       5.056   1.001   0.162  1.00  0.00       PFP
ATOM     30  C30 PFP     1       3.762   0.411   0.107  1.00  0.00       PFP
ATOM     31  C31 PFP     1       2.584   1.201   0.120  1.00  0.00       PFP
ATOM     32  C32 PFP     1       1.292   0.607   0.060  1.00  0.00       PFP
ATOM     33  C33 PFP     1      -0.109  -1.395  -0.074  1.00  0.00       PFP
ATOM     34  C34 PFP     1       1.182  -0.806  -0.014  1.00  0.00       PFP
ATOM     35  C35 PFP     1       2.364  -1.597  -0.025  1.00  0.00       PFP
ATOM     36  C36 PFP     1       3.651  -1.004   0.037  1.00  0.00       PFP
END
```

Table S4. MIX tentative crystal cell dimensions and atomic coordinates as obtained from the analysis of deposition simulations, given in pdb format. No attempts were made for determining the symmetry group and optimizing atomic coordinates.

```
CRYST1   16.604   15.342    6.823  29.09  98.84 101.18
REMARK CELL AXIS    16.604    0.000    0.000
REMARK CELL AXIS    -2.975   15.051    0.000
REMARK CELL AXIS    -1.046    5.870    3.315
ATOM      1  C1  PEN    01       4.759  -0.696   0.414  1.00  1.00       PEN
ATOM      2  C2  PEN    01       6.149  -0.901   0.356  1.00  1.00       PEN
ATOM      3  C3  PEN    01       6.664  -2.193   0.145  1.00  1.00       PEN
ATOM      4  C4  PEN    01       5.791  -3.286  -0.005  1.00  1.00       PEN
ATOM      5  C5  PEN    01       4.400  -3.086   0.051  1.00  1.00       PEN
ATOM      6  C6  PEN    01       3.882  -1.785   0.261  1.00  1.00       PEN
ATOM      7  C7  PEN    01       3.525  -4.177  -0.105  1.00  1.00       PEN
ATOM      8  C8  PEN    01       2.135  -3.972  -0.052  1.00  1.00       PEN
ATOM      9  C9  PEN    01       1.617  -2.670   0.158  1.00  1.00       PEN
ATOM     10  C10 PEN    01       2.491  -1.580   0.315  1.00  1.00       PEN
ATOM     11  C11 PEN    01       1.260  -5.062  -0.210  1.00  1.00       PEN
ATOM     12  C12 PEN    01      -0.130  -4.856  -0.159  1.00  1.00       PEN
ATOM     13  C13 PEN    01      -0.648  -3.555   0.051  1.00  1.00       PEN
ATOM     14  C14 PEN    01      -2.038  -3.350   0.103  1.00  1.00       PEN
ATOM     15  C15 PEN    01      -2.913  -4.441  -0.053  1.00  1.00       PEN
ATOM     16  C16 PEN    01      -4.304  -4.241   0.002  1.00  1.00       PEN
ATOM     17  C17 PEN    01      -5.177  -5.334  -0.148  1.00  1.00       PEN
ATOM     18  C18 PEN    01      -4.662  -6.626  -0.359  1.00  1.00       PEN
ATOM     19  C19 PEN    01      -3.272  -6.831  -0.417  1.00  1.00       PEN
ATOM     20  C20 PEN    01      -2.395  -5.742  -0.263  1.00  1.00       PEN
ATOM     21  C21 PEN    01      -1.004  -5.947  -0.316  1.00  1.00       PEN
ATOM     22  C22 PEN    01       0.227  -2.465   0.209  1.00  1.00       PEN
ATOM     23  H23 PEN    01       4.372   0.299   0.576  1.00  1.00       PEN
ATOM     24  H24 PEN    01       6.824  -0.063   0.470  1.00  1.00       PEN
ATOM     25  H25 PEN    01       7.734  -2.342   0.094  1.00  1.00       PEN
ATOM     26  H26 PEN    01       6.193  -4.275  -0.172  1.00  1.00       PEN
ATOM     27  H27 PEN    01       3.925  -5.166  -0.267  1.00  1.00       PEN
ATOM     28  H28 PEN    01       2.101  -0.587   0.475  1.00  1.00       PEN
ATOM     29  H29 PEN    01       1.655  -6.053  -0.371  1.00  1.00       PEN
ATOM     30  H30 PEN    01      -0.614  -6.940  -0.477  1.00  1.00       PEN
ATOM     31  H31 PEN    01      -2.886  -7.826  -0.580  1.00  1.00       PEN
ATOM     32  H32 PEN    01      -5.338  -7.463  -0.474  1.00  1.00       PEN
ATOM     33  H33 PEN    01      -6.247  -5.184  -0.098  1.00  1.00       PEN
ATOM     34  H34 PEN    01      -4.706  -3.252   0.170  1.00  1.00       PEN
ATOM     35  H35 PEN    01      -2.438  -2.360   0.266  1.00  1.00       PEN
ATOM     36  H36 PEN    01      -0.168  -1.473   0.370  1.00  1.00       PEN
ATOM      1  F1  PFP    02      -7.081  -0.171  -0.414  1.00  1.00       PFP
ATOM      2  F2  PFP    02      -8.084   2.365  -0.171  1.00  1.00       PFP
ATOM      3  F3  PFP    02      -6.440   4.485   0.034  1.00  1.00       PFP
ATOM      4  F4  PFP    02      -4.070   5.412   0.113  1.00  1.00       PFP
ATOM      5  F5  PFP    02       0.255   1.213  -0.209  1.00  1.00       PFP
ATOM      6  F6  PFP    02      -2.068   0.306  -0.321  1.00  1.00       PFP
ATOM      7  F7  PFP    02      -4.433  -0.609  -0.433  1.00  1.00       PFP
ATOM      8  C8  PFP    02      -4.851   0.666  -0.323  1.00  1.00       PFP
ATOM      9  C9  PFP    02      -6.239   0.877  -0.314  1.00  1.00       PFP
ATOM     10  C10 PFP    02      -6.750   2.173  -0.190  1.00  1.00       PFP
ATOM     11  C11 PFP    02      -5.876   3.267  -0.082  1.00  1.00       PFP
ATOM     12  C12 PFP    02      -4.465   3.077  -0.093  1.00  1.00       PFP
ATOM     13  C13 PFP    02      -3.566   4.169   0.013  1.00  1.00       PFP
ATOM     14  C14 PFP    02      -2.157   3.972   0.008  1.00  1.00       PFP
ATOM     15  C15 PFP    02      -0.233   2.462  -0.111  1.00  1.00       PFP
ATOM     16  C16 PFP    02      -1.640   2.656  -0.109  1.00  1.00       PFP
ATOM     17  C17 PFP    02      -2.542   1.562  -0.218  1.00  1.00       PFP
ATOM     18  C18 PFP    02      -3.946   1.759  -0.214  1.00  1.00       PFP
ATOM     19  F19 PFP    02       5.594   7.697   0.413  1.00  1.00       PFP
ATOM     20  F20 PFP    02       6.597   5.162   0.169  1.00  1.00       PFP
ATOM     21  F21 PFP    02       4.953   3.042  -0.033  1.00  1.00       PFP
ATOM     22  F22 PFP    02       2.583   2.115  -0.110  1.00  1.00       PFP
ATOM     23  F23 PFP    02      -1.743   6.313   0.213  1.00  1.00       PFP
ATOM     24  F24 PFP    02       0.580   7.220   0.324  1.00  1.00       PFP
ATOM     25  F25 PFP    02       2.945   8.136   0.435  1.00  1.00       PFP
ATOM     26  C26 PFP    02       3.363   6.861   0.325  1.00  1.00       PFP
ATOM     27  C27 PFP    02       4.751   6.650   0.314  1.00  1.00       PFP
ATOM     28  C28 PFP    02       5.263   5.354   0.190  1.00  1.00       PFP
ATOM     29  C29 PFP    02       4.389   4.260   0.084  1.00  1.00       PFP
ATOM     30  C30 PFP    02       2.977   4.450   0.096  1.00  1.00       PFP
ATOM     31  C31 PFP    02       2.079   3.358  -0.009  1.00  1.00       PFP
ATOM     32  C32 PFP    02       0.670   3.554  -0.004  1.00  1.00       PFP
ATOM     33  C33 PFP    02      -1.254   5.064   0.115  1.00  1.00       PFP
ATOM     34  C34 PFP    02       0.153   4.870   0.112  1.00  1.00       PFP
ATOM     35  C35 PFP    02       1.054   5.965   0.222  1.00  1.00       PFP
ATOM     36  C36 PFP    02       2.458   5.768   0.217  1.00  1.00       PFP
END
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