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

Supporting Information

Controlled hydrophilization of black phosphorene: A reactive molecular dynamics simulation approach

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In this file, at first, some figures have been given. Then, the force field parameter values have been mentioned for the used atoms.[1]

Figure S1 illustrates the side-view snapshots of the MD simulations of a water droplet on the pristine phosphorene surface along the armchair and zigzag directions after equilibration, wherein the number of molecules are 500.

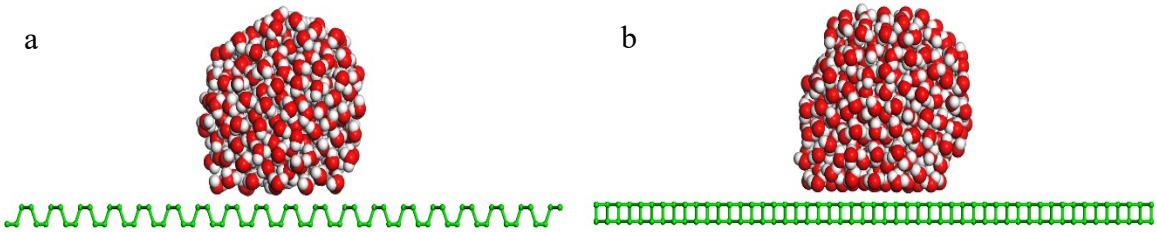

Figure S1. Equilibrium configuration simulation of a water droplet with 500 water molecules on the pristine phosphorene surface along (a) armchair and (b) zigzag directions. Red, white and green represent the oxygen, hydrogen, and phosphorus atoms, respectively.

Figures S2-S4 show the contour maps of the equilibrium states of the systems with 1000, 1200, and 1500 water molecules, respectively on the pristine phosphorene surface for both armchair and zigzag directions.

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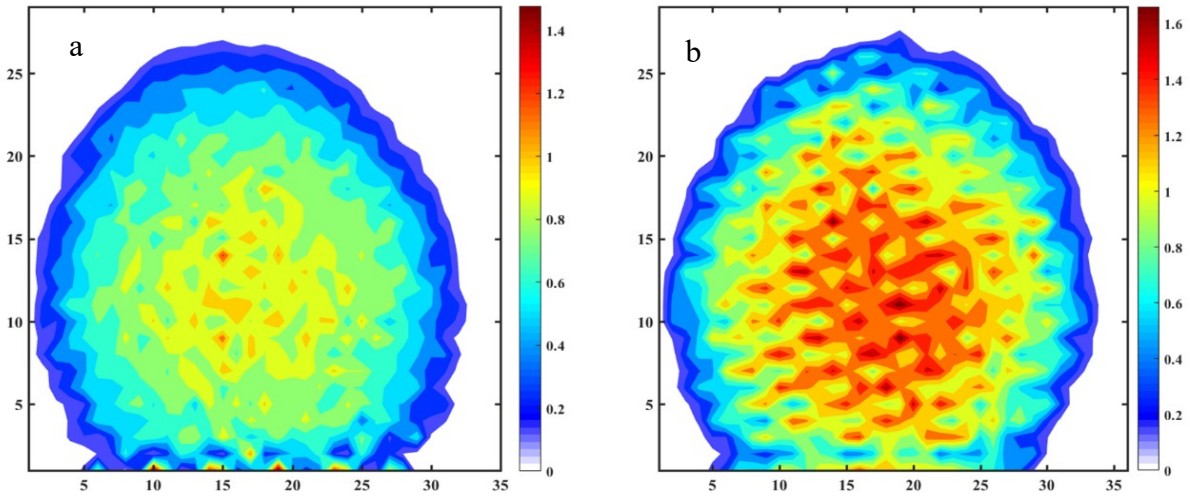

Figure S2. Contour map of water droplet with 1000 water molecules on the phosphorene surface along (a) the armchair and (b) the zigzag directions.

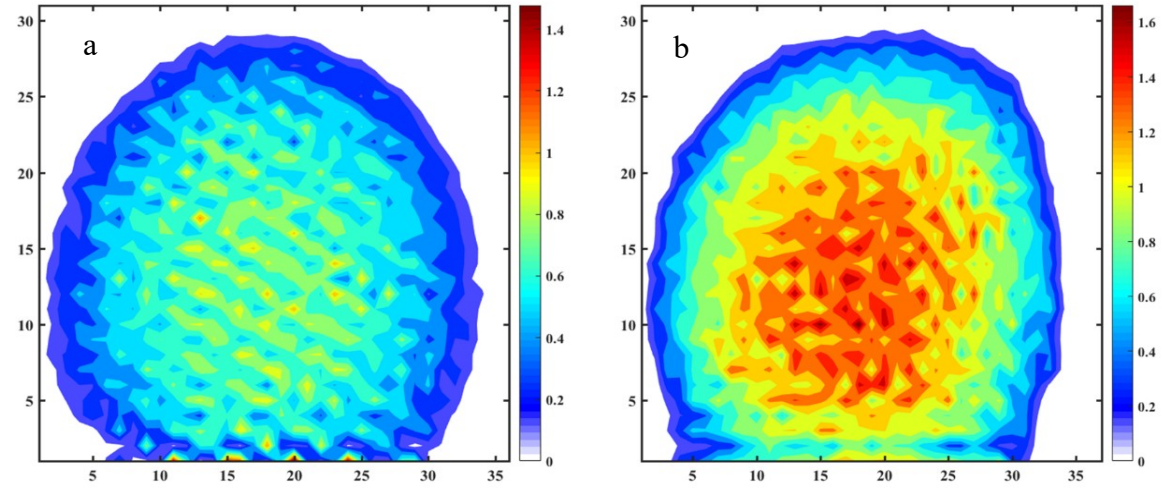

Figure S3. Contour map of water droplet with 1200 water molecules on the phosphorene surface along (a) the armchair and (b) the zigzag directions.

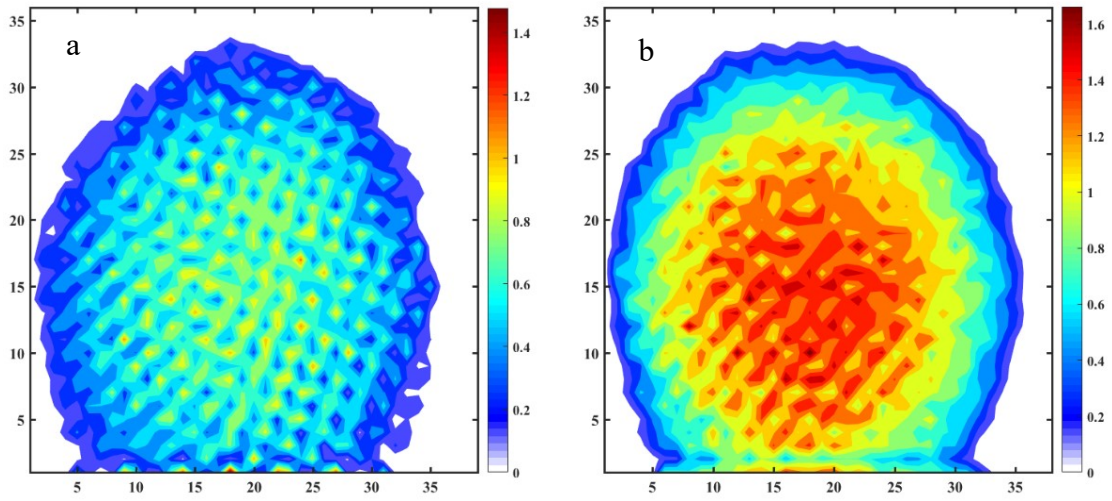

Figure S4. Contour map of water droplet with 1500 water molecules on the phosphorene surface along (a) the armchair and (b) the zigzag directions.

Figure S5 shows the initial and equilibrium configurations of the two water molecules on the pristine phosphorene surface in three different directions.

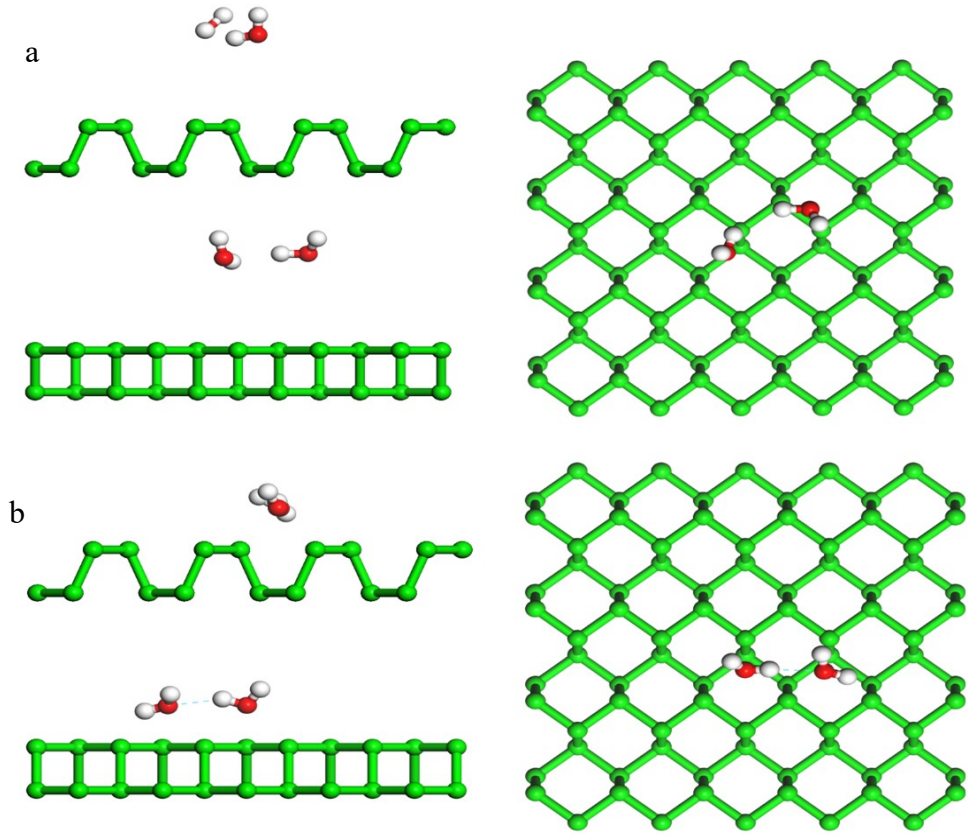

Figure S5. (a) Initial and (b) equilibrium configurations of two water molecules on the pristine phosphorene surface from the side and top view. Red, white and green represent the oxygen, hydrogen, and phosphorus atoms, respectively.

In the next step, five water molecules were placed on the phosphorene surface in order to further investigate the formation of the hydrogen chain. Figure S6 shows the initial and equilibrium configurations of the five water molecules on the pristine phosphorene surface from the top and side views.

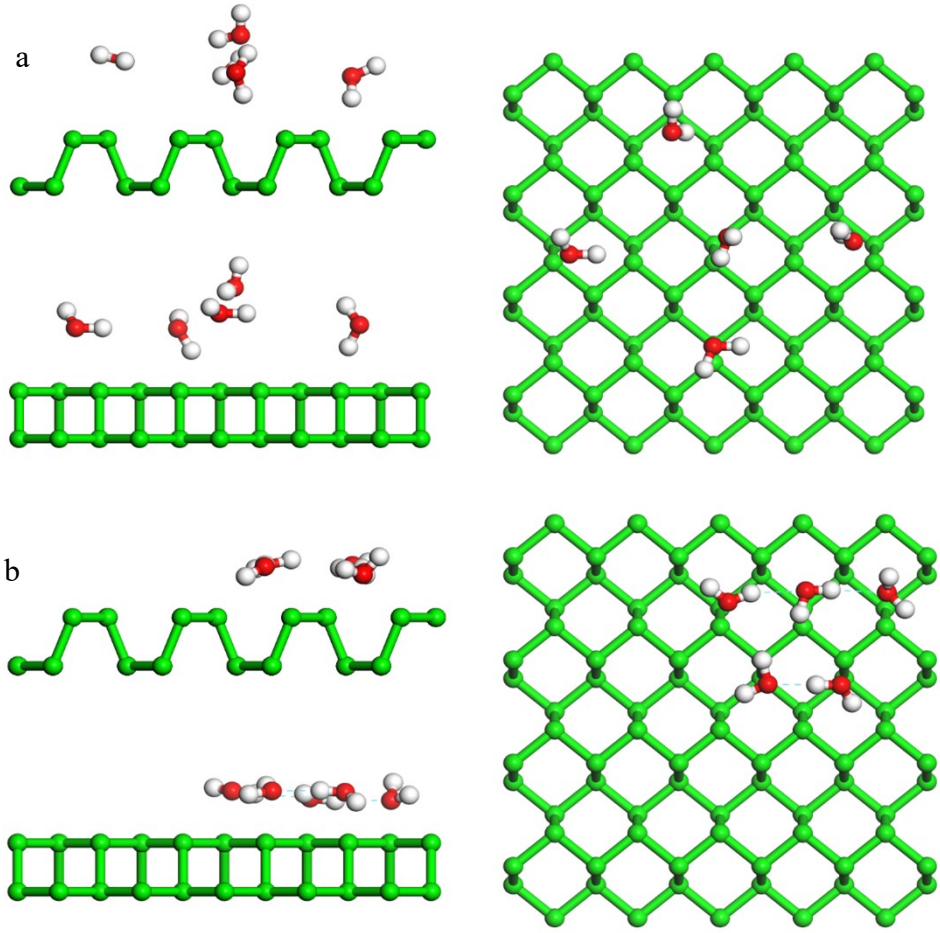

Figure S6. (a) Initial and (b) equilibrium configurations of five water molecules on the pristine phosphorene surface from the side and top view. Red, white and green represent the oxygen, hydrogen, and phosphorus atoms, respectively.

By comparing the initial and equilibrium configurations of Figure S6, a binary chain and a ternary chain were formed in the zigzag direction of the surface between the phosphorene surface grooves, respectively.

Figure S7 shows the initial and equilibrium configurations of two water molecules on the phosphorene oxide surface in three different directions.

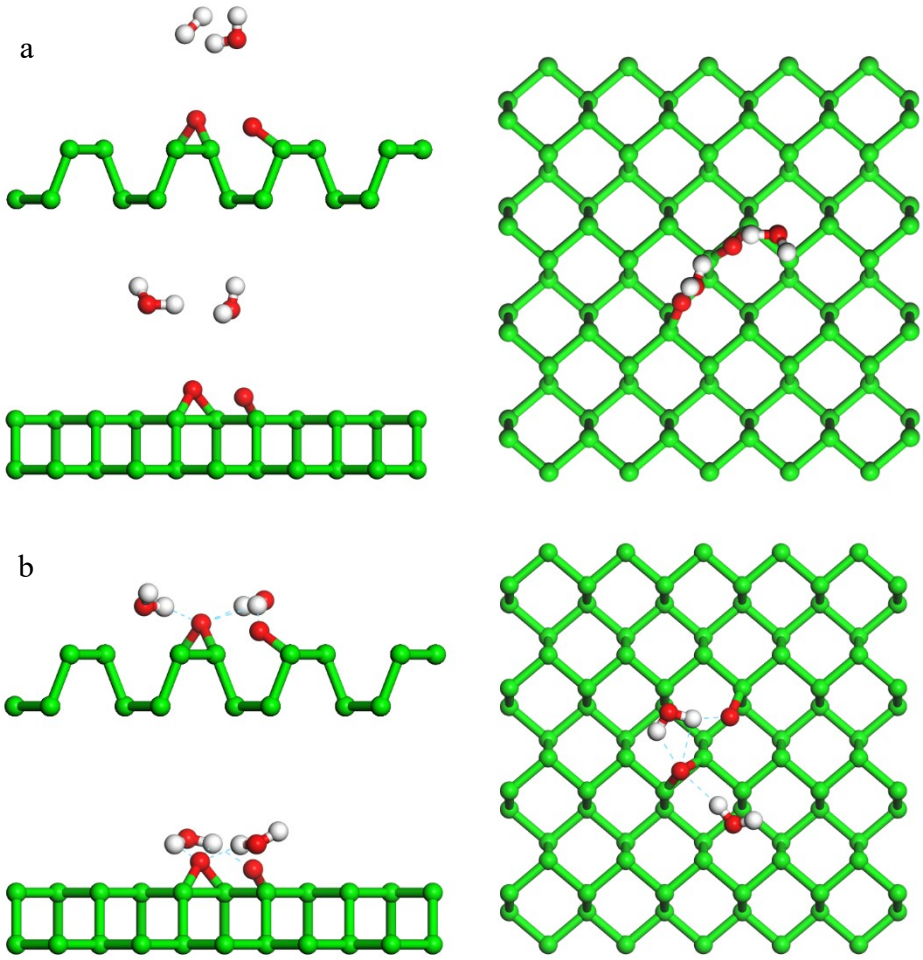

Figure S7. (a) Initial and (b) equilibrium configurations of two water molecules on the phosphorene oxide surface from the side and the top views. Red, white and green represent the oxygen, hydrogen, and phosphorus atoms, respectively.

According to the equilibrium configurations shown in Figure S7(b), the formation of hydrogen bonds with surface oxygen atoms restricts the movement of water molecules and prevents the formation of a chain of water molecules in the zigzag direction.

Figure S8 shows the initial and equilibrium configurations for placing five water molecules on phosphorene oxide in three different directions. According to Figure S8, the primary water molecules form hydrogen bonds around the surface of oxygen.

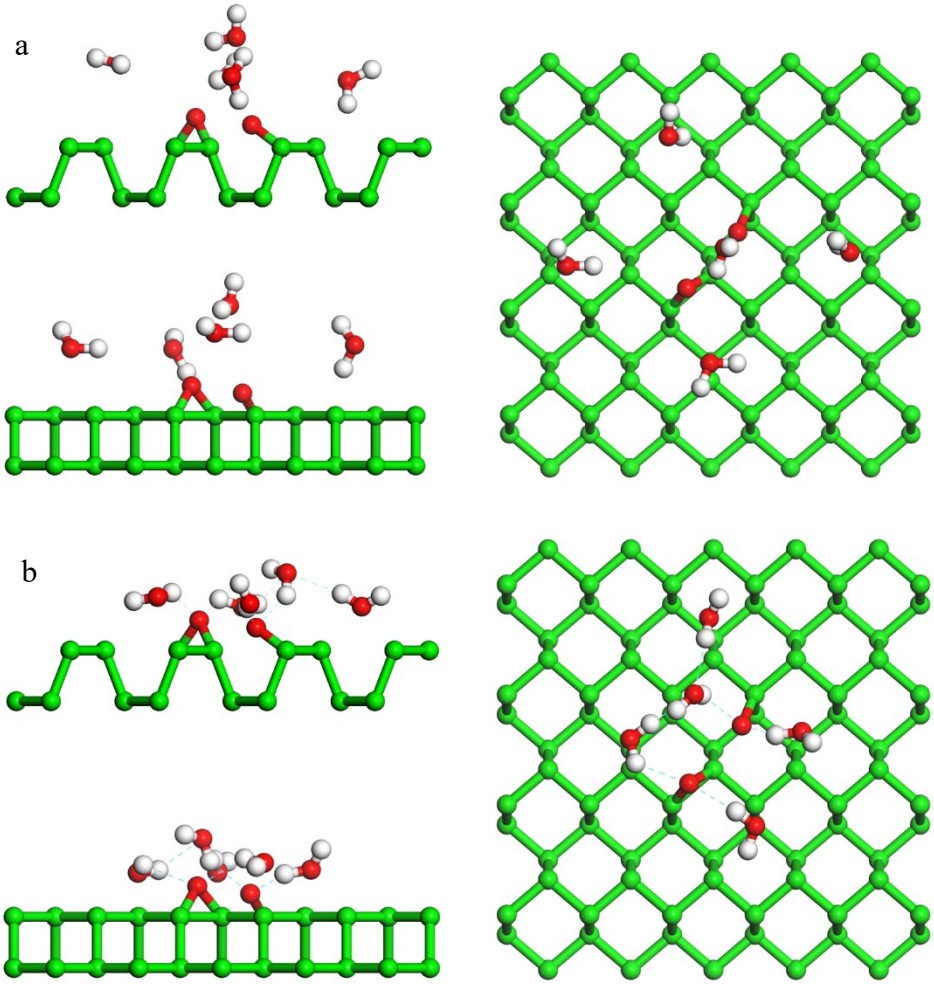

Figure S8. (a) Initial and (b) equilibrium configurations of five water molecules on the phosphorene oxide from the side and top views. Red, white and green represent the oxygen, hydrogen, and phosphorus atoms, respectively.

Table S1 represents the maximum number of hydrogen bonds for placement of 1, 2, 5, 10, and 500 water molecules on the pristine and phosphorene oxide surfaces.

Table S1. Maximum number of hydrogen bonds for placement of 1, 2, 5, 10, and 500 water molecules on the pristine and the phosphorene oxide surfaces

Surface	Number of water molecules on the surface	Number of oxygen atoms on the surface	Number of hydrogen bonds water molecules with oxygen atoms on the surface	Number of Hydrogen bonds between water molecules	Total hydrogen bonds on the surface
Pristine phosphorene	1	2	0	0	0
Phosphorene oxide	1	2	2	0	2
Pristine phosphorene	2	2	0	1	1
Phosphorene oxide	2	2	2	1	3
Pristine phosphorene	5	2	0	3	3
Phosphorene oxide	5	2	4	1	5
Pristine phosphorene	10	2	0	8	8
Phosphorene oxide	10	2	7	4	11
Pristine phosphorene	500	100	0	806	806
Phosphorene oxide	500	100	552	385	937

As shown in the above table, phosphorene surface oxidation has increased the number of hydrogen bonds. The phosphorene hydrophobic surface has converted to the hydrophilic

surface by increasing the number of hydrogen bonds. These results are under Huang and his colleagues' empirical results.[2] So, in the following, we have brought the calculation diagram of each system available in the above table.

Figure S9 indicates diagram of the number of hydrogen bonds relative to the time on the pristine phosphorene and the phosphorene oxide surfaces for 10 water molecules.

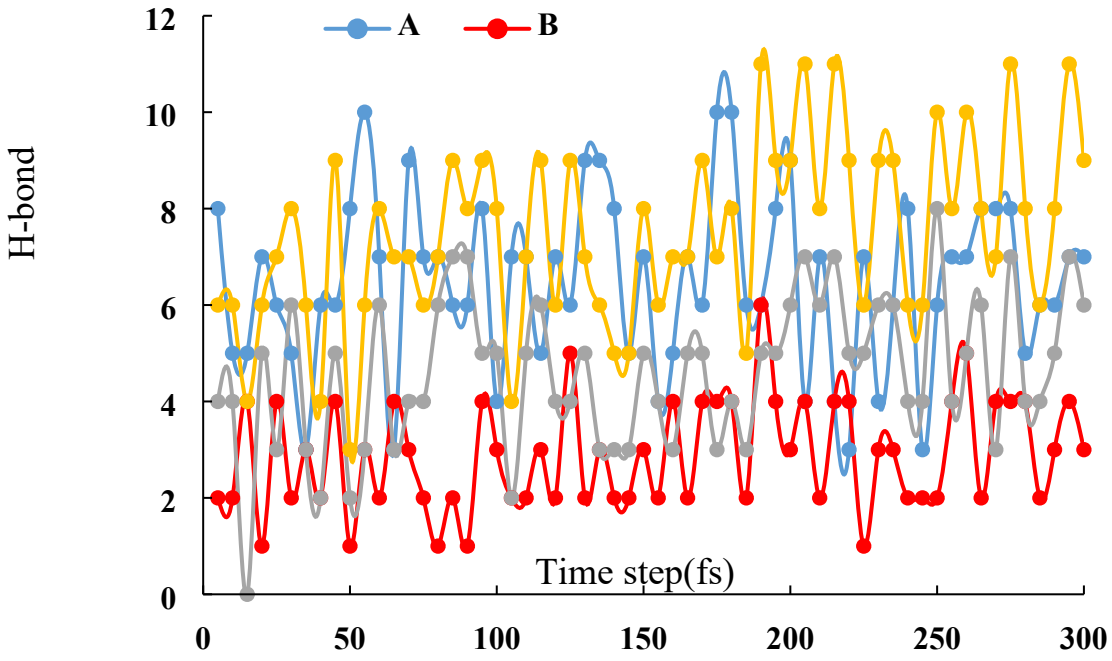

Figure S9. Diagram of the number of hydrogen bonds relative to the time for the simulation of the 300 last frames for ten water molecules on the pristine and oxidized surfaces. Mode A related to the pristine surface has been shown in blue. Modes B, C, and D are relative to the phosphorene oxide surface. Red colors show the number of hydrogen bonds between water molecules, gray color is regarding the number of hydrogen bonds with oxygen available on the surface, and yellow color indicates total hydrogen bonds on the oxidized surface, respectively.

As seen in the above diagram, due to the low number of simulation molecules, the number of hydrogen bonds has no fixed trend and has different changes at divergent times. According to the above diagram, total hydrogen bonds on the oxidized surface (yellow diagram) have increased toward the pristine surface (blue chart). According to the chart, it can be viewed that on the phosphorene oxide surface, the number of hydrogen bonds with surface oxygen atoms (gray diagram) has increased and the number of hydrogen bonds between water molecules has dropped on the oxidized surface (red chart).

Also, the diagram of the number of hydrogen bonds relative to the time in the presence and absence of the surface oxidation for 1 and 2 water molecules has been calculated in the following.

Figure S10 indicates diagram of the number of hydrogen bonds relative to the time on the pristine phosphorene and the phosphorene oxide surfaces for two water molecules.

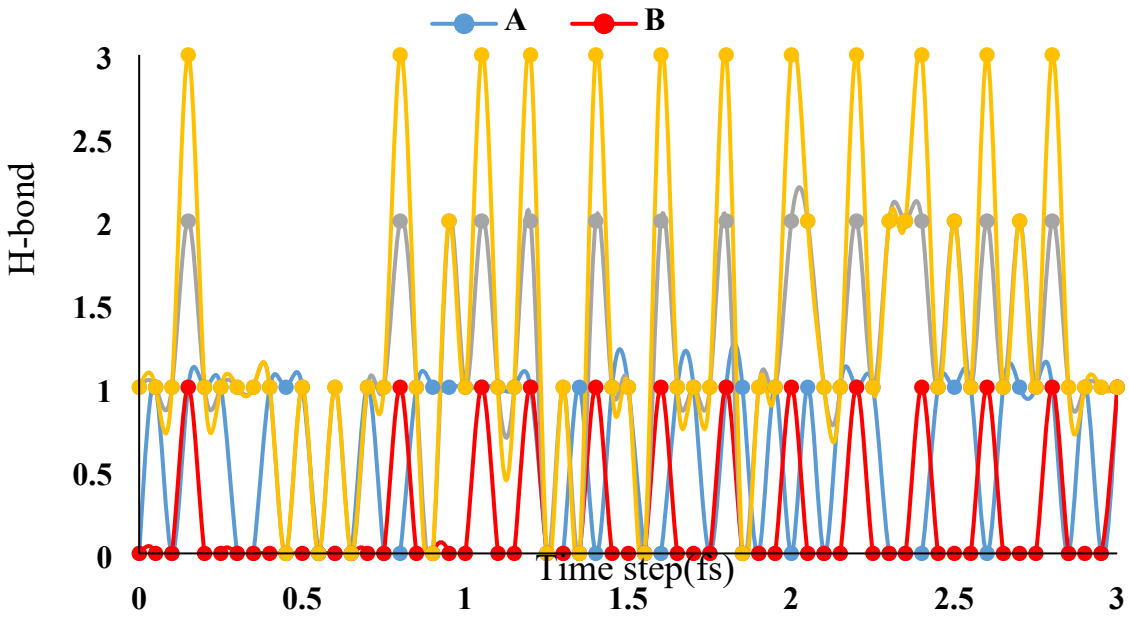

Figure S10. Diagram of the number of hydrogen bonds relative to the time for two water molecules on the pristine phosphorene and phosphorene oxide surfaces

As seen in the above diagram, the total number of hydrogen bonds (yellow chart) has increased with the oxidation of the phosphorene surface toward the pristine surface (the blue diagram). According to the changes in the gray and red charts, it concludes that the number of hydrogen bonds between water molecules and surface oxygen atoms (gray diagram) has increased by oxidation of the surface. The number of hydrogen bonds between water molecules has dropped too (the red chart). The phosphorene hydrophobic surface is converted to a hydrophilic surface by oxidation.

Figure S11 indicates diagram of the number of hydrogen bonds relative to the time on the pristine phosphorene and phosphorene oxide surfaces for one water molecule.

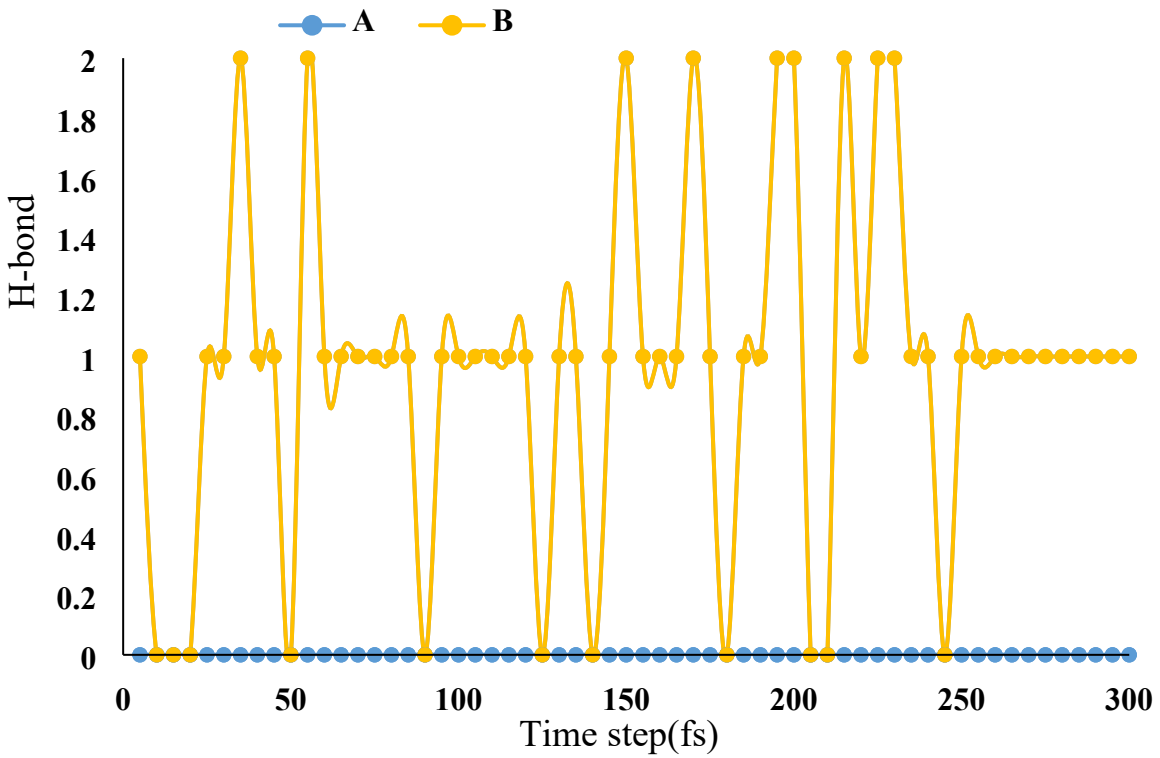

Figure S11. Number of hydrogen bonds relative to the time in the absence (diagram A) and presence (diagram B) of the surface oxidation for one water molecule

According to the above diagram, hydrogen bonds are created by the oxidation of the phosphorene surface (diagram B). Water molecule monomer establishes hydrogen bonds on the oxidized surface, and its mobility decreases. These results are matching to the experimental and quantum results in references [3] and [2]. Also, our results show that the phosphorene hydrophobic surface has been turned into a hydrophilic surface by its oxidation. These are according to the experimental results of reference [2].

Figure S12 shows the equilibrium configurations of a water droplet on the oxidized surface with a radius of 10 angstroms in the armchair and zigzag directions.

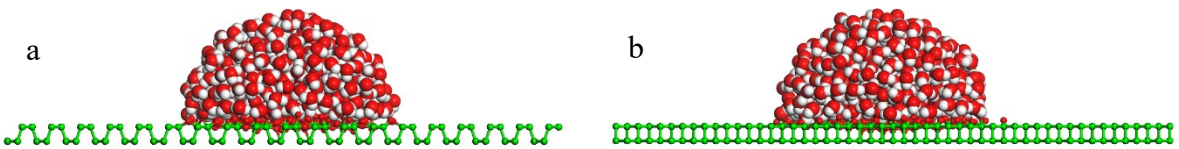

Figure S12. The equilibrium configuration of a water droplet on the oxidized surface with a

radius of 10 angstroms in the (a) armchair and (b) zigzag directions. Red, white and green represent the oxygen, hydrogen, and phosphorus atoms, respectively.

Figure S13 shows different configurations of measuring the contact angle for time-dependent stationary drop for water in contact with phosphorene oxide.

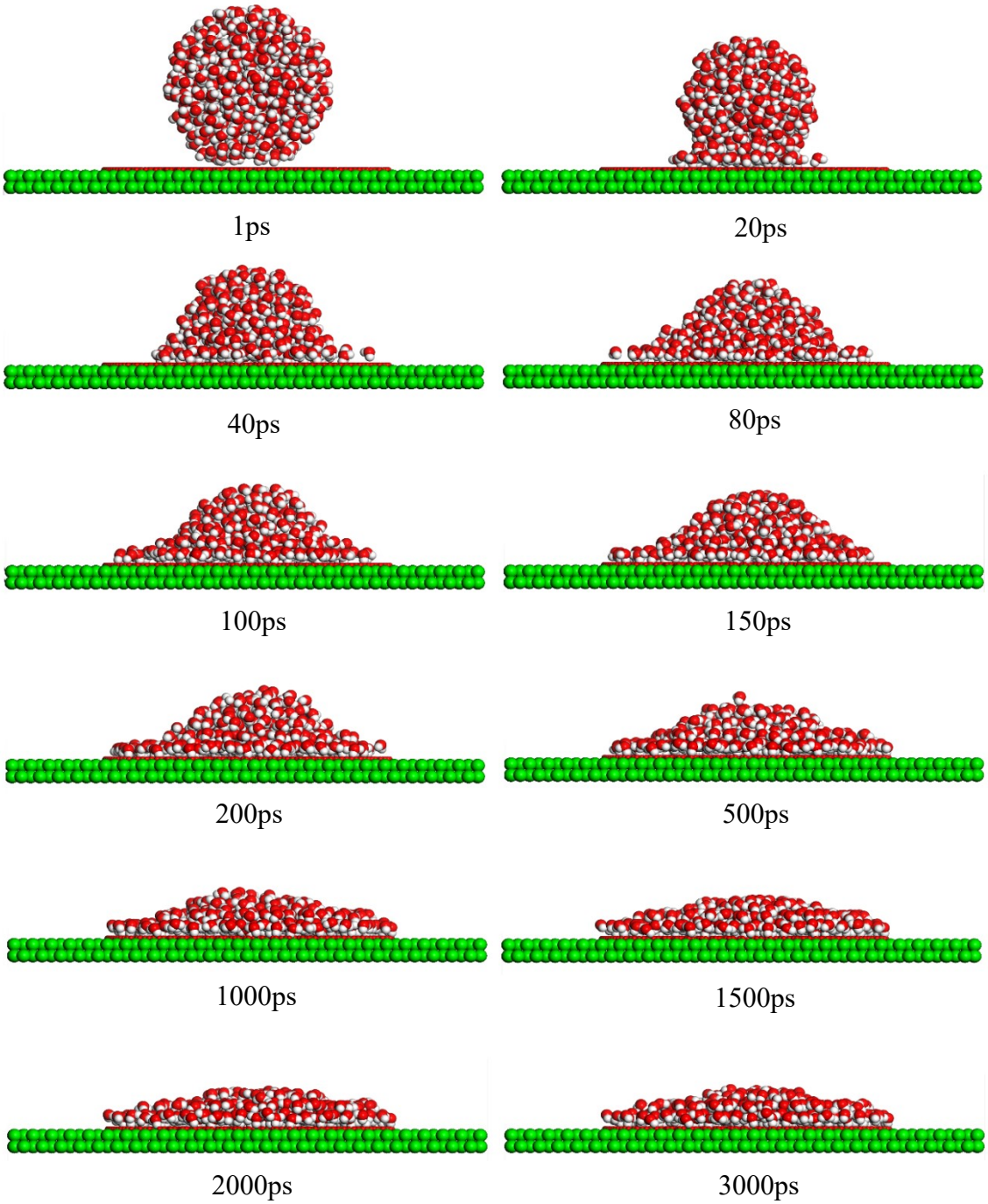

Figure S13. Different configurations of measuring the contact angle for time-dependent stationary drop for water in contact with phosphorene oxide. Red, white and green represent the oxygen, hydrogen, and phosphorus atoms, respectively.

The force field values for the utilized atoms in the paper from reference [1] have been listed below.

Reactive MD-force field c/h/o/p

39 ! Number of general parameters

50.0000 !Comment here

9.5469 !Comment here

26.5405 !Comment here

1.5105 !p(trip4)

6.6630 !p(trip3)

70.0000 !kc2

1.0588 !Comment here

4.6000 !Comment here

12.1176 !Comment here

13.3056 !Comment here

-70.1292 !p(trip1)

0.0000 !Comment here

10.0000 !Comment here

2.8793 !Comment here

33.8667 !Comment here

6.0891 !Comment here

1.0563 !Comment here

2.0384 !Comment here

6.1431 !Comment here

6.9290 !p(pen2)

0.3989 !p(pen3)

3.9954 !p(pen4)

-2.4837 !Comment here

9.6260 !Comment here

9.7452 !Comment here

4.1021 !Comment here

-1.2327 !Comment here

2.1645 !Comment here

1.5591 !Comment here

0.1000 !Comment here

2.1365 !Comment here

0.6991 !Comment here

50.0000 !Comment here

1.8512 !Comment here

0.5000 !Comment here

1.0000 !Comment here

5.0000 !Comment here

0.0000 !Comment here

2.6962 !Comment here

4 ! Nr of atoms; atomID;ro(sigma); Val;atom mass;Rvdw;Dij;gamma;ro(pi);Val(e)
alfa;gamma(w);Val(angle);p(ovun5);n.u.;chiEEM;etaEEM;n.u.
ro(pipi);p(lp2);Heat increment;p(boc4);p(boc3);p(boc5),n.u.;n.u.
p(ovun2);p(val3);n.u.;Val(boc);p(val5);n.u.;n.u.;n.u.

C 1.3825 4.0000 12.0000 1.9133 0.1853 0.9000 1.1359 4.0000
9.7602 2.1346 4.0000 33.2433 79.5548 5.8678 7.0000 0.0000
1.2104 0.0000 199.0303 8.6991 34.7289 13.3894 0.0000 1.9593
-2.8983 2.5000 1.0564 4.0000 2.9663 2.0000 0.0000 1.0000
0.0000 1.9593

```
H    0.7853   1.0000   1.0080   1.5904   0.0419   1.0206  -0.1000   1.0000
     9.3557   5.0518   1.0000   0.0000 121.1250   5.3200   7.4366   1.0000
    -0.1000   0.0000  62.4879   1.9771   3.3517   0.7571   101.0453   1.9593
   -15.7683   2.1488   1.0338   1.0000   2.8793   2.0000   0.0000   1.0000
101.0453   1.9593
O    1.2477   2.0000  15.9990   1.9236   0.0904   1.0503   1.0863   6.0000
    10.2127   7.7719   4.0000  36.9573 116.0768   8.5000   8.9989   2.0000
     0.9088   1.0003  60.8726  20.4140   3.3754   0.2702 949.7489     1.5509
    -3.6141   2.7025   1.0493   4.0000   2.9225   2.0000   0.0000   1.0000
          949.7489     1.5509
P    2.1199  3.0000  30.9738   2.3355   0.0887   0.4060   1.9507   5.0000
     9.5120   7.6148   3.0000   0.0000  82.517   6.3467   8.5658   0.0000
     1.8354   0.0000  120.0000  11.8556  15.5783   2.8491    5066.5788   2.1233
    -2.0858   4.8954   1.0338   3.0000   1.6350   2.6552   0.0743  15.5028
          5066.5788   2.1233
 10      ! Nr of bonds;
at1;at2;De(sigma);De(pi);De(pipi);p(be1);p(bo5);13corr;n.u.;p(bo6),p(ovun1)
                p(be2);p(bo3);p(bo4);n.u.;p(bo1);p(bo2)
 1  1 156.5953 100.0397  80.0000  -0.8157  -0.4591   1.0000  37.7369   0.4235
       0.4527  -0.1000   9.2605   1.0000  -0.0750   6.8316   1.0000   0.0000
 1  2 170.2316   0.0000   0.0000  -0.5931   0.0000   1.0000   6.0000   0.7140
       5.2267   1.0000   0.0000   1.0000  -0.0500   6.8315   0.0000   0.0000
 2  2 156.0973   0.0000   0.0000  -0.1377   0.0000   1.0000   6.0000   0.8240
       2.9907   1.0000   0.0000   1.0000  -0.0593   4.8358   0.0000   0.0000
 1  3 160.4802 105.1693  23.3059  -0.3873  -0.1613   1.0000  10.8851   1.0000
       0.5341  -0.3174   7.0303   1.0000  -0.1463   5.2913   0.0000   0.0000
```

```
3  3  60.1463 176.6202  51.1430  -0.2802  -0.1244   1.0000  29.6439   0.9114
      0.2441  -0.1239   7.6487   1.0000  -0.1302   6.2919   1.0000   0.0000
2  3 180.4373   0.0000   0.0000  -0.8074   0.0000   1.0000   6.0000   0.5514
      1.2490   1.0000   0.0000   1.0000  -0.0657   5.0451   0.0000   0.0000
4  4  52.2711  23.4911  20.0346   0.4917  -0.2395   1.0000  17.8190   0.7412
      1.4218  -0.2226  13.6705   1.0000  -0.2457   7.5884   1.0000   0.0000
2  4 124.0512   0.0000   0.0000  -0.3732   0.0000   1.0000   6.0000   0.5862
      5.9712   1.0000   0.0000   1.0000  -0.1003   5.6515   0.0000   0.0000
3  4  66.3159   163.0203    3.6587   0.5150   -0.3880   1.0000  27.5787   0.5448
      3.1520   -0.3536    6.8745   1.0000  -0.1236   6.8691   0.0000   0.0000
1  4 0.0000 0.0000  0.0000  -0.8157  -0.4591   1.0000  37.7369   0.0000
      0.4527  -0.1000   9.2605   1.0000  -0.0750   6.8316   0.0000   0.0000
6    ! Nr of off-diagonal terms. at1;at2;Dij;RvdW;alfa;ro(sigma);ro(pi);ro(pipi)
1  2   0.1219   1.4000   9.8442   1.1203  -1.0000  -1.0000
2  3   0.0344   1.6800  10.3247   0.9013  -1.0000  -1.0000
1  3   0.1131   1.8523   9.8442   1.2775   1.1342   1.0621
2  4   0.1064   1.5940  10.3773   1.4319  -1.0000  -1.0000
3  4   0.0935   1.5573  12.4155   1.7813   1.5141   1.3013
1  4   0.0497   1.9032  14.7287   1.2775   1.1342   1.0621
29    ! Nr of angles. at1;at2;at3;Thetao,o;p(val1);p(val2);p(coa1);p(val7);p(pen1);p(val4)
1  1  1  67.2326  22.0695   1.6286   0.0000   1.7959  15.4141   1.8089
1  1  2  65.2527  14.3185   6.2977   0.0000   0.5645   0.0000   1.1530
2  1  2  70.0840  25.3540   3.4508   0.0000   0.0050   0.0000   3.0000
1  2  2   0.0000   0.0000   6.0000   0.0000   0.0000   0.0000   1.0400
1  2  1   0.0000   3.4110   7.7350   0.0000   0.0000   0.0000   1.0400
2  2  2   0.0000  27.9213   5.8635   0.0000   0.0000   0.0000   1.0400
```

1 1 3 49.5561 7.3771 4.9568 0.0000 0.7533 15.9906 1.0010

3 1 3 77.1171 39.8746 2.5403 -24.3902 1.7740 -42.9758 2.1240

2 1 3 65.0000 14.2057 4.8649 0.0000 0.3504 0.0000 1.7185

1 3 1 74.3994 44.7500 0.7982 0.0000 3.0000 0.0000 1.0528

1 3 3 77.9854 36.6201 2.0201 0.0000 0.7434 67.0264 3.0000

3 3 3 80.7324 30.4554 0.9953 0.0000 1.6310 50.0000 1.0783

1 3 2 71.5018 21.7062 0.4735 0.0000 0.5186 0.0000 1.1793

2 3 3 84.9468 23.3540 1.5057 0.0000 2.6374 0.0000 1.3023

2 3 2 77.0645 10.4737 1.2895 0.0000 0.9924 0.0000 1.1043

1 2 3 0.0000 25.0000 3.0000 0.0000 1.0000 0.0000 1.0400

3 2 3 0.0000 0.0148 6.0000 0.0000 0.0000 0.0000 1.0400

2 2 3 0.0000 9.7025 6.0000 0.0000 0.0000 0.0000 1.0400

4 4 4 81.1291 81.4496 0.5055 0.0000 0.1993 0.000 1.0534

2 4 4 87.7897 48.0234 1.1576 0.0000 2.4234 0.0000 1.6028

2 4 2 91.5071 16.1001 2.6120 0.0000 0.5531 0.0000 1.0740

4 2 4 7.0790 0.0000 0.4358 0.0000 0.0000 0.1050 2.1684

2 2 4 0.0000 0.0000 6.0000 0.0000 0.0000 0.0000 1.0400

4 4 3 79.4673 20.2853 2.1889 0.0000 4.0310 0.000 1.0400

4 3 4 69.0819 5.8800 2.0083 0.0000 2.9124 0.000 2.8760

4 3 3 98.8001 6.2885 7.9680 0.0000 1.6053 0.000 2.1329

3 4 3 78.9719 10.1352 5.4789 0.0000 1.3632 0.000 2.6943

2 4 3 83.8172 18.8244 4.0039 0.0000 3.1936 0.0000 1.6946

2 3 4 79.3111 2.6567 4.7017 0.0000 2.6304 0.0000 2.4254

28 ! Nr of torsions. at1;at2;at3;at4;;V1;V2;V3;p(tor1);p(cot1);n.u;n.u.

1 1 1 1 -0.2500 11.5822 0.1879 -4.7057 -2.2047 0.0000 0.0000

1 1 1 2 -0.2500 31.2596 0.1709 -4.6391 -1.9002 0.0000 0.0000

2 1 1 2 -0.1770 30.0252 0.4340 -5.0019 -2.0697 0.0000 0.0000

1 1 1 3 -0.7098 22.2951 0.0060 -2.5000 -2.1688 0.0000 0.0000

2 1 1 3 -0.3568 22.6472 0.6045 -4.0088 -1.0000 0.0000 0.0000

3 1 1 3 -0.0528 6.8150 0.7498 -5.0913 -1.0000 0.0000 0.0000

1 1 3 1 2.0007 25.5641 -0.0608 -2.6456 -1.1766 0.0000 0.0000

1 1 3 2 -1.1953 42.1545 -1.0000 -8.0821 -1.0000 0.0000 0.0000

2 1 3 1 -0.9284 34.3952 0.7285 -2.5440 -2.4641 0.0000 0.0000

2 1 3 2 -2.5000 79.6980 1.0000 -3.5697 -2.7501 0.0000 0.0000

1 1 3 3 -0.0179 5.0603 -0.1894 -2.5000 -2.0399 0.0000 0.0000

2 1 3 3 -0.5583 80.0000 1.0000 -4.4000 -3.0000 0.0000 0.0000

3 1 3 1 -2.5000 76.0427 -0.0141 -3.7586 -2.9000 0.0000 0.0000

3 1 3 2 0.0345 78.9586 -0.6810 -4.1777 -3.0000 0.0000 0.0000

3 1 3 3 -2.5000 66.3525 0.3986 -3.0293 -3.0000 0.0000 0.0000

1 3 3 1 2.5000 -0.5332 1.0000 -3.5096 -2.9000 0.0000 0.0000

1 3 3 2 -2.5000 3.3219 0.7180 -5.2021 -2.9330 0.0000 0.0000

2 3 3 2 2.2500 -6.2288 1.0000 -2.6189 -1.0000 0.0000 0.0000

1 3 3 3 0.0531 -17.3983 1.0000 -2.5000 -2.1584 0.0000 0.0000

2 3 3 3 0.4723 -12.4144 -1.0000 -2.5000 -1.0000 0.0000 0.0000

3 3 3 3 -2.5000 -25.0000 1.0000 -2.5000 -1.0000 0.0000 0.0000

0 1 2 0 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000

0 2 2 0 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000

0 2 3 0 0.0000 0.1000 0.0200 -2.5415 0.0000 0.0000 0.0000

0 1 1 0 0.0000 50.0000 0.3000 -4.0000 -2.0000 0.0000 0.0000

0 3 3 0 0.5511 25.4150 1.1330 -5.1903 -1.0000 0.0000 0.0000

4 4 4 2 -0.0137 46.5023 0.7269 -3.2753 0.0000 0.0000 0.0000

2 4 4 2 -0.1595 49.6094 0.5875 -2.0714 0.0000 0.0000 0.0000

1 ! Nr of hydrogen bonds. at1;at2;at3;r(hb);p(hb1);p(hb2);p(hb3)

3 2 3 1.9682 -4.4628 1.7976 3.0000

References

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