

**Excess Electron Interaction with Radiosensitive 5-Bromopyrimidine in Aqueous  
Solution: A Combined Ab Initio Molecular Dynamics and Time-Dependent  
Wave-Packet Study**

Changzhe Zhang, Yuxiang Bu\*

*Institute of Theoretical Chemistry, School of Chemistry and Chemical Engineering,  
Shandong University, Jinan, 250100, P. R. China*

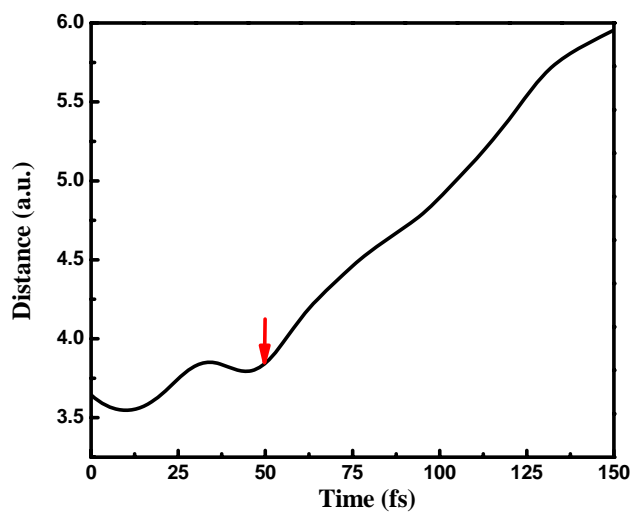
**The Corresponding Authors: [byx@sdu.edu.cn](mailto:byx@sdu.edu.cn)**

**Electronic Supplementary Materials**

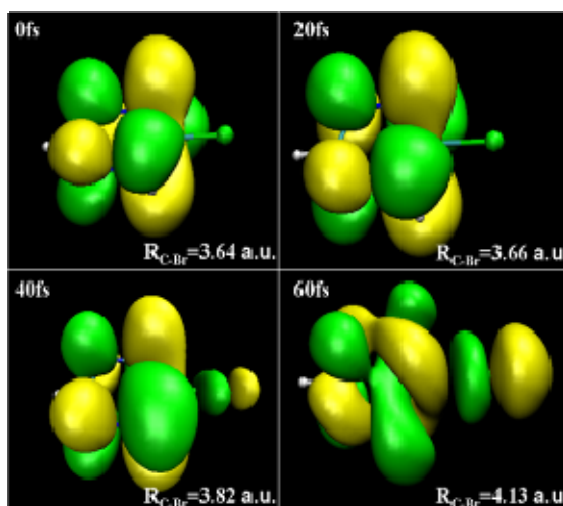
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## 1. AIMD Simulations of Excess Electron Attachment to the Gaseous 5-BrPy

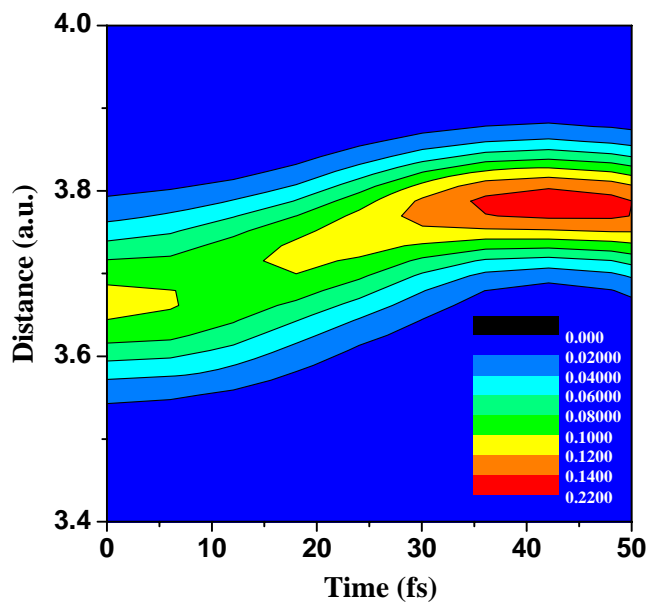


**Figure S1.** Time evolution of the C-Br bond length after an excess electron is vertically added to the gaseous 5-BrPy. The corresponding results are calculated with the Quickstep module of the CP2K package at the BLYP/TZV2P level.

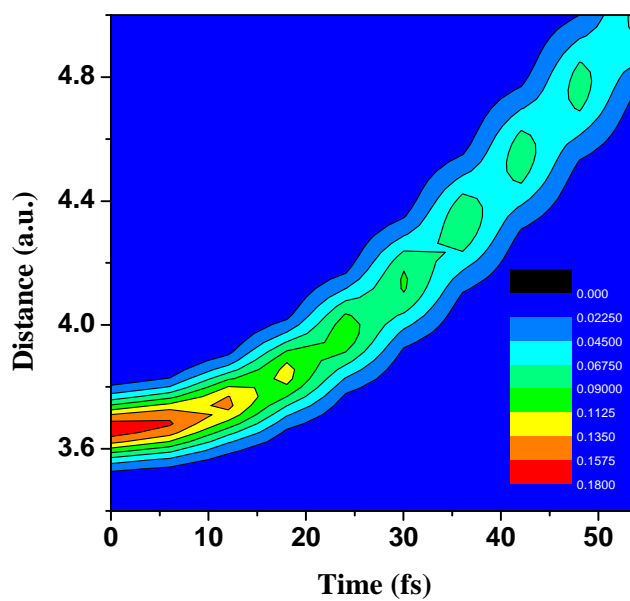


**Figure S2.** Snapshots extracted from trajectories after an excess electron is vertically added to the gaseous system. The green and yellow opaque shades are for positive and negative parts of the wave function (isovalue=0.02), respectively

## 2. Nuclear Wave Packet Dynamics along the Calculated Potential Energy Curves



**Figure S3.** Time evolution of wave packet along the vertical anionic potential energy surface.

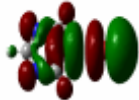
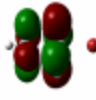
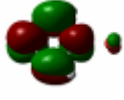
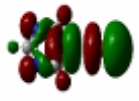
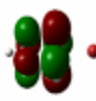


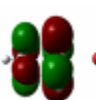

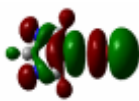

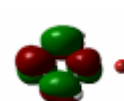


**Figure S4.** Time evolution of wave packet along the relaxed anionic potential energy surface.


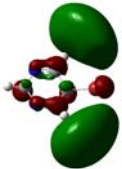
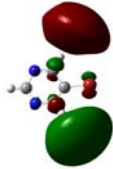
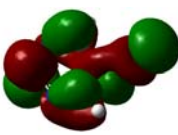
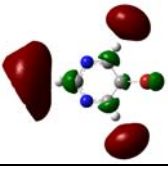
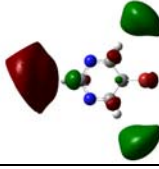
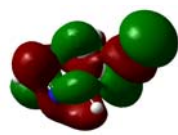
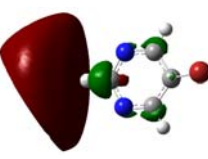
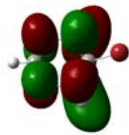
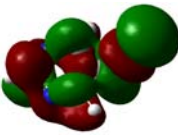
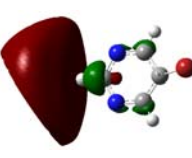

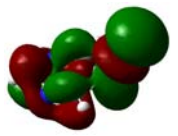
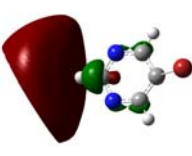
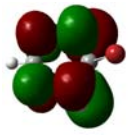
### 3. Characters of HOMO and a set of LUMOs for 5-BrPy in the Gas Phase

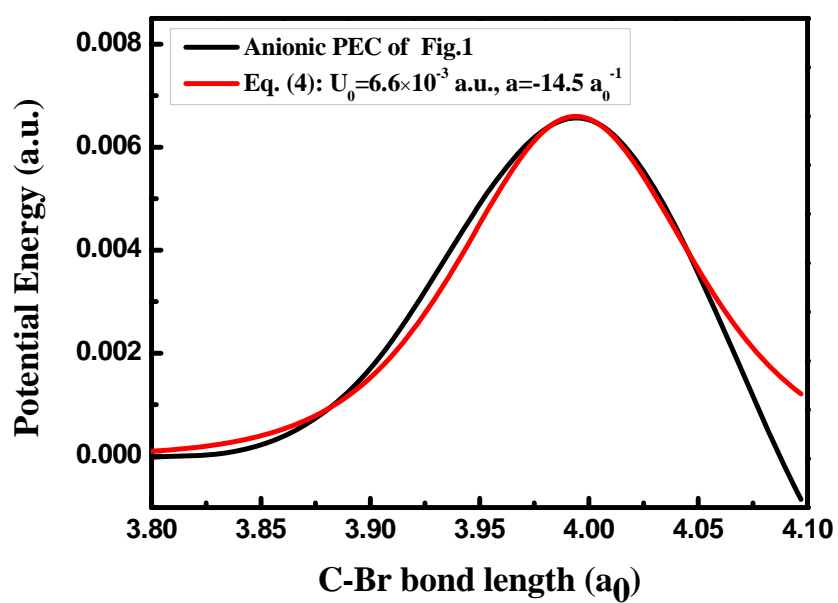
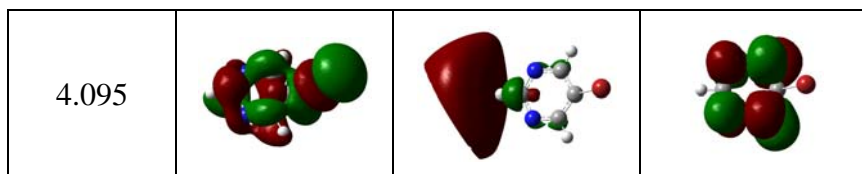
**Table S1.** Virtual orbitals for the optimized neutral 5-BrPy at different C-Br bond lengths, calculated at the B3LYP level of theory with a 6-311++G (d,p) basis set for C, H, and N atoms and the LANL2DZ basis set for Br atom.

| $R_{C-Br}$<br>(a.u.) | LUMO | LUMO+1 | LUMO+2 |
|----------------------|------|--------|--------|
| 3.057                |      |        |        |
| 3.246                |      |        |        |
| 3.434                |      |        |        |
| 3.623                |      |        |        |
| 3.717                |      |        |        |
| 3.812                |      |        |        |
| 3.906                |      |        |        |
| 4.000                |      |        |        |
| 4.095                |      |        |        |
| 4.189                |      |        |        |
| 4.378                |      |        |        |

|       |   |   |   |
|-------|---|---|---|
| 4.472 |  |  |  |
| 4.661 |  |  |  |
| 4.850 |  |  |  |
| 4.944 |  |  |  |

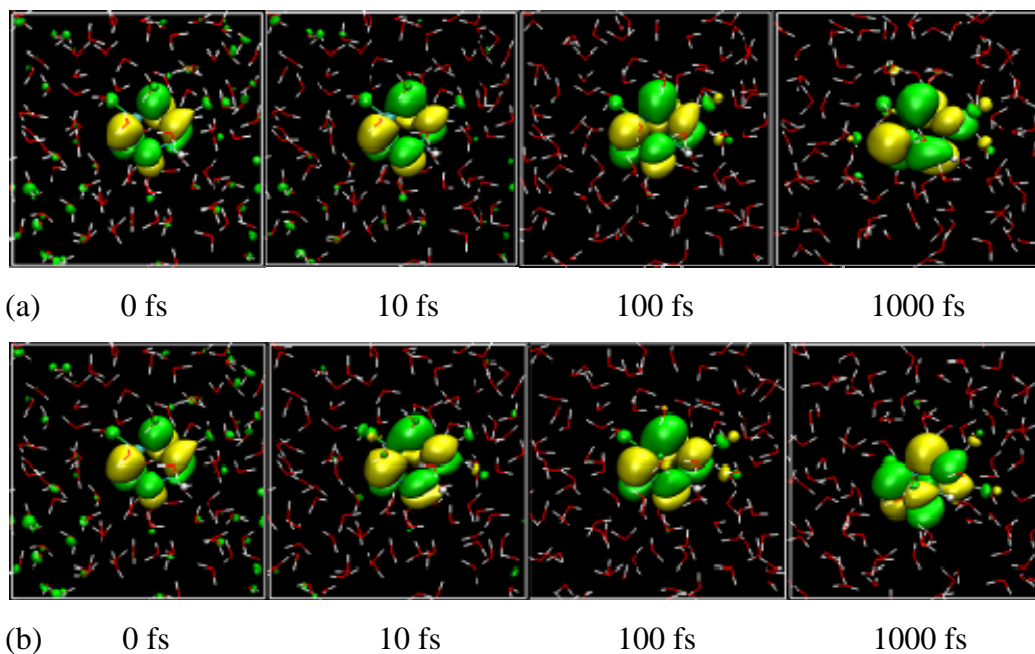
**Table S2.** HOMO and a set of LUMOs for the optimized anionic 5-BrPy at different C-Br bond lengths, calculated at the B3LYP level of theory with a 6-311++G (d,p) basis set for C, H, and N atoms and the LANL2DZ basis set for Br atom.

| $R_{C-Br}$<br>(a.u.) | HOMO  | LUMO  | LUMO+1  |
|----------------------|---|---|---|
| 3.434                |  |  |  |
| 3.623                |  |  |  |
| 3.812                |  |  |  |
| 3.906                |  |  |  |
| 4.000                |  |  |  |

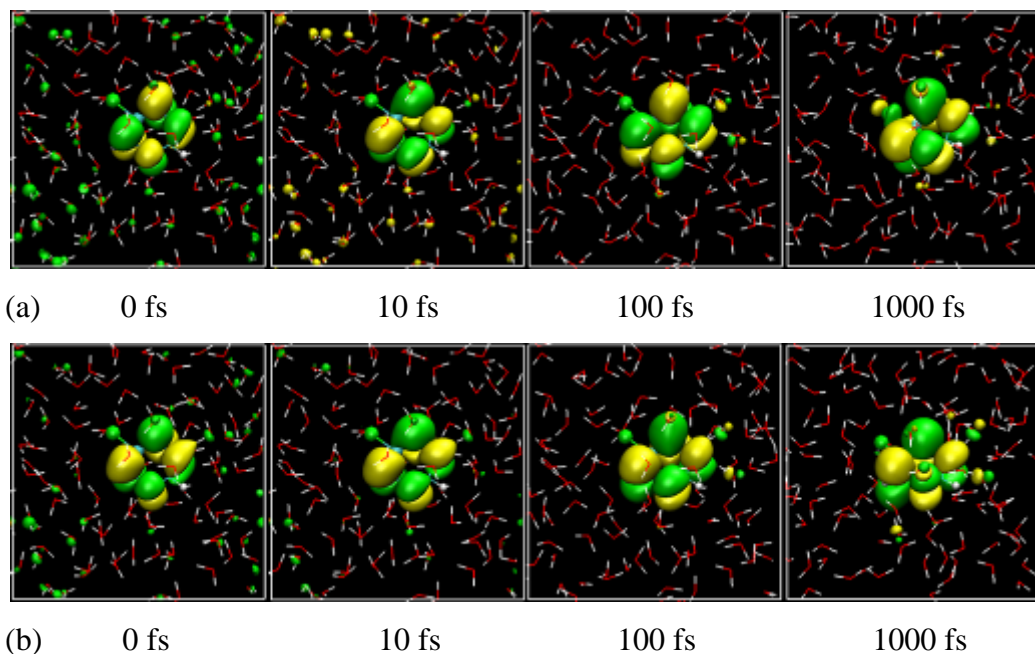


**Figure S5.** Comparison of analytical hyperbolic cosine curve fitted using Eq. (4) with the anionic potential energy curve in Figure 1.

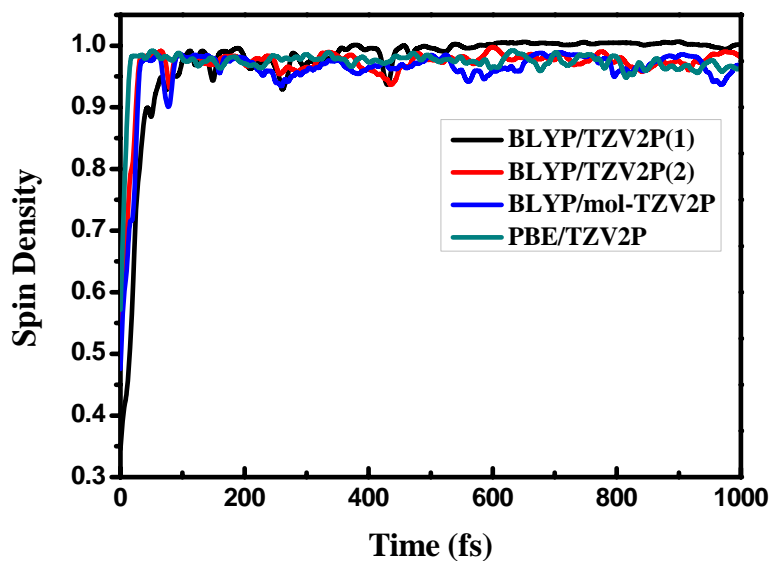
#### 4. AIMD Simulations of Excess Electron Attachment to the Solvated 5-BrPy



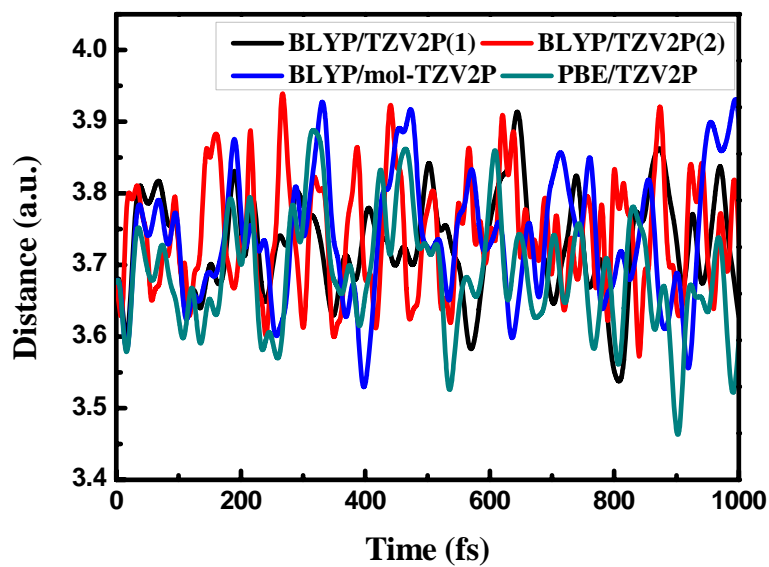
**Figure S6.** Snapshots from the AIMD trajectories after an excess electron is vertically injected to the aqueous 5-BrPy at the BLYP/TZV2P level. The green and yellow opaque shades are for positive and negative parts of the wave function (isovalue=0.02), respectively, and (a), (b) represent different initial configurations.



**Figure S7.** Snapshots from the AIMD trajectories after an excess electron is vertically injected to the aqueous 5-BrPy at the BLYP/mol-TZV2P (a) and PBE/TZV2P (b) levels.



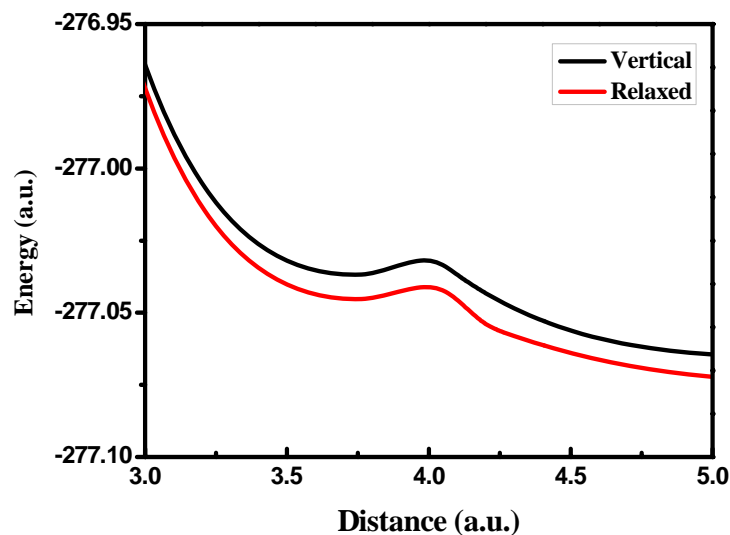
**Figure S8.** Time evolution of spin density on 5-BrPy calculated at the BLYP/TZV2P, BLYP/mol-TZV2P, and PBE/TZV2P levels.



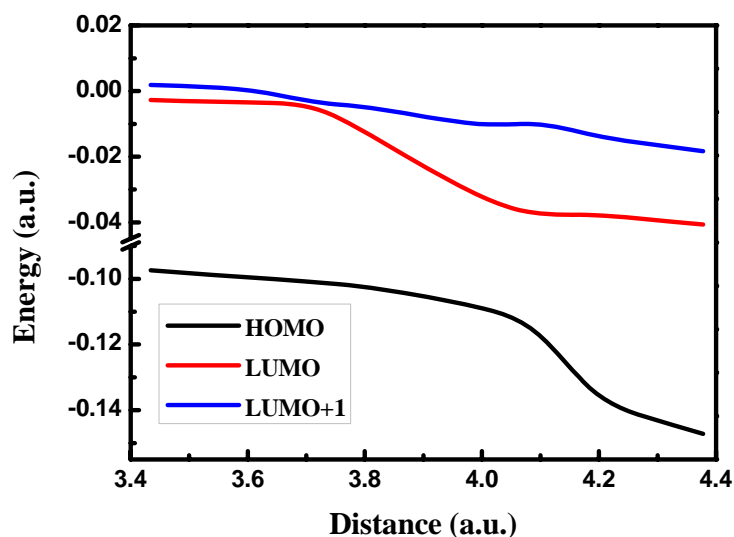
**Figure S9.** Time evolution of the C-Br bond length calculated at the BLYP/TZV2P, BLYP/mol-TZV2P, and PBE/TZV2P levels.



## 5. Potential Energy Surfaces and Corresponding Molecular Orbital Analyses in the PCM Solvent Model

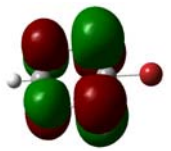
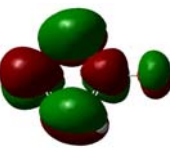
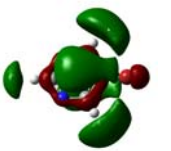
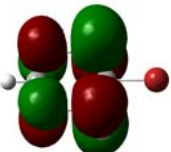

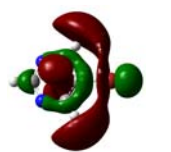
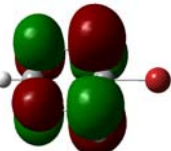
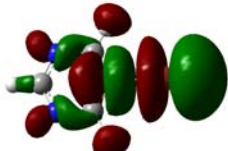
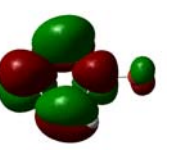
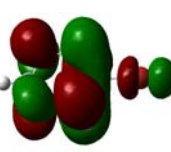
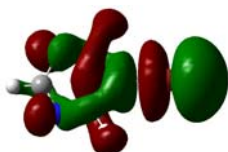
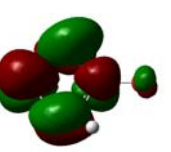
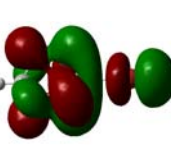
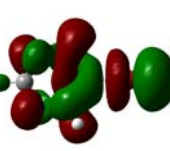
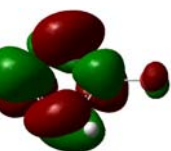
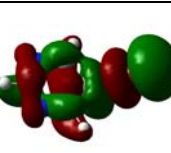
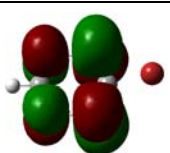
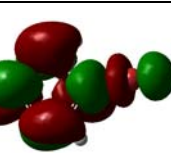


**Figure S10.** Potential energy curves along the C-Br stretching coordinate for the vertical and relaxed anionic 5-BrPy. The corresponding results are calculated in the PCM solvent model and at the B3LYP level of theory with a 6-311++G (d,p) basis set for C, H, and N atoms and the LANL2DZ basis set for Br atom.

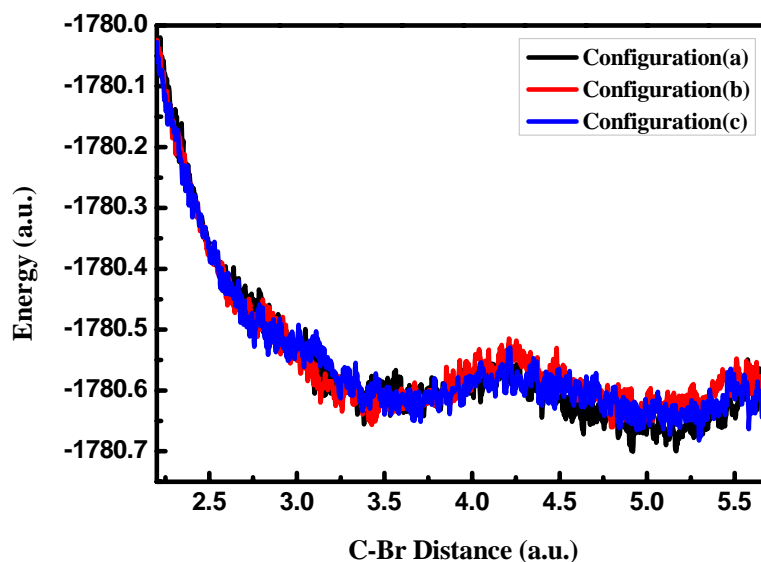


**Figure S11.** The molecular orbital energies for the optimized anionic 5-BrPy as a function of the C-Br distance. The corresponding results are calculated in the PCM solvent model and calculated at the B3LYP level of theory with a 6-311++G (d,p) basis set for C, H, and N atoms and the LANL2DZ basis set for Br atom.

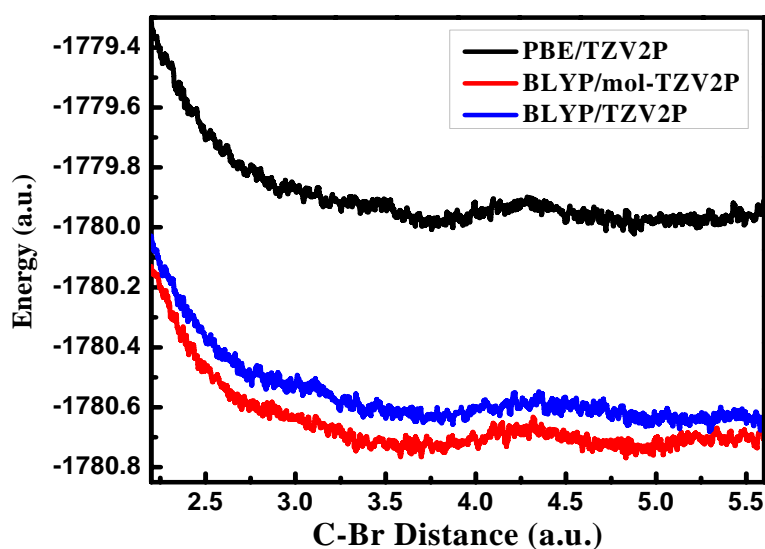
**Table S3.** HOMO and a set of LUMOs for the optimized anionic 5-BrPy at different C-Br bond lengths. The corresponding results are calculated in the PCM solvent model and at the B3LYP level of theory with a 6-311++G (d,p) basis set for C, H, and N atoms and the LANL2DZ basis set for Br atom.

| $R_{\text{C-Br}}$<br>(a.u.) | HOMO  | LUMO  | LUMO+1  |
|-----------------------------|---|---|---|
| 3.434                       |    |    |    |
| 3.623                       |    |    |    |
| 3.812                       |   |   |   |
| 4.000                       |  |  |  |
| 4.095                       |  |  |  |
| 4.283                       |  |  |  |

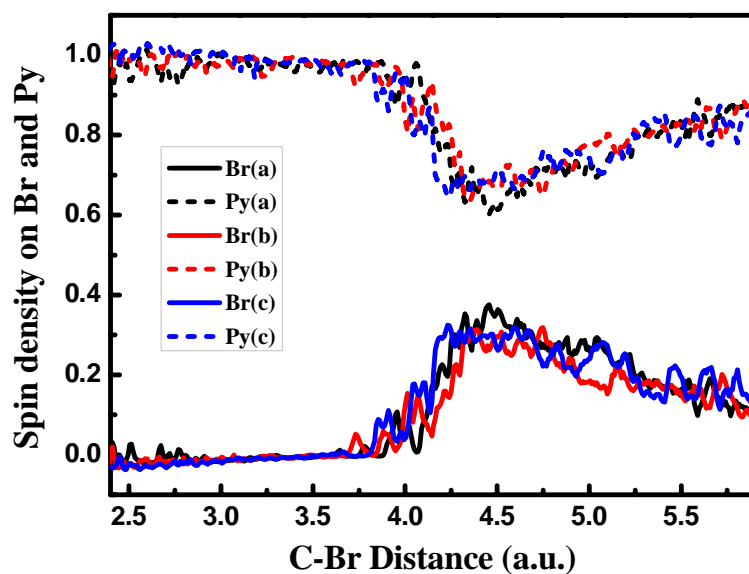
## 6. Potential Energy Surfaces and Corresponding Molecular Orbital Analyses in Realistic Aqueous Environment



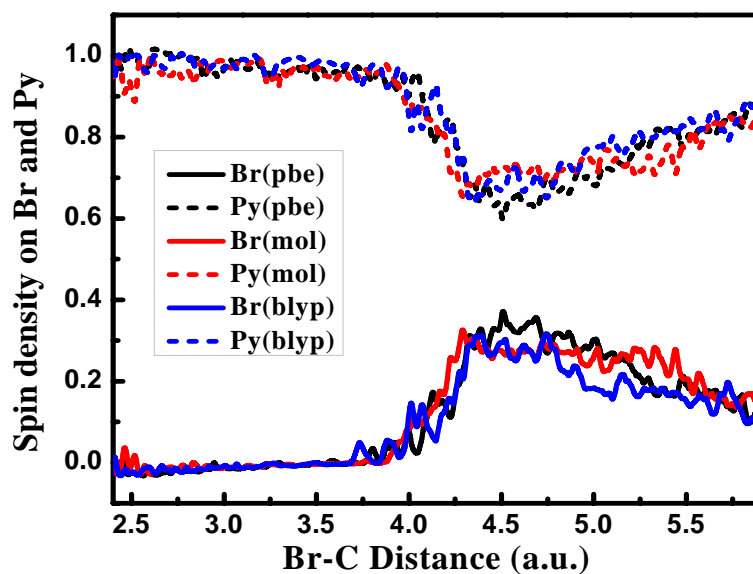
**Figure S12.** Potential energies in realistic aqueous environment varying with the C-Br bond length. AIMD simulations starting from three different initial configurations are carried out at the BLYP/TZV2P level and the C-Br bond is constrained with a increment of 0.001 Å per femtosecond.



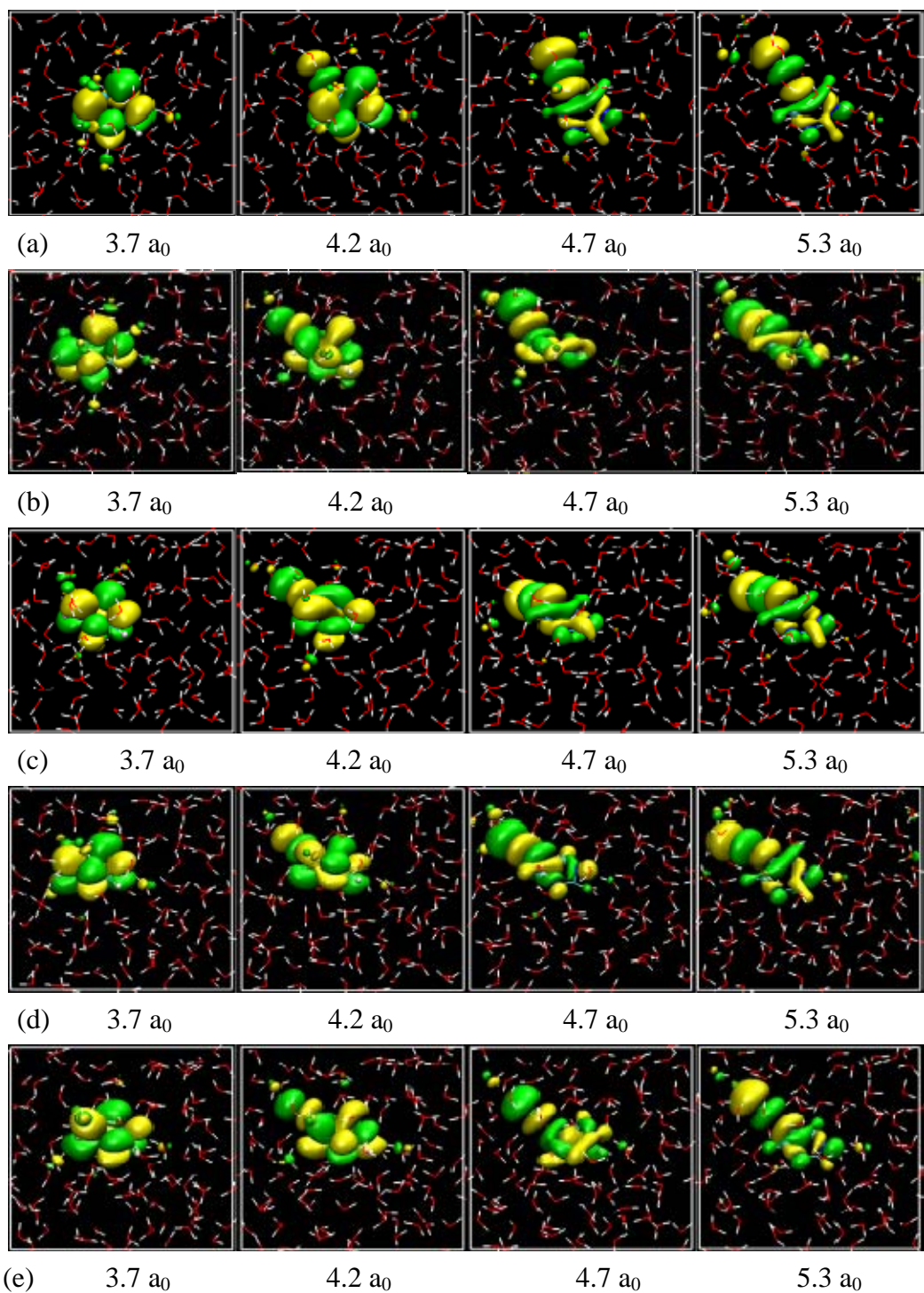
**Figure S13.** Potential energies in realistic aqueous environment varying with the C-Br bond length, and the corresponding results are calculated at the BLYP/TZV2P, BLYP/mol-TZV2P, and PBE/TZV2P levels, respectively.



**Figure S14.** Spin density on Br and pyrimidines varying with the C-Br bond length. AIMD simulations starting with three different initial configurations are carried out at the BLYP/TZV2P level and the C-Br bond is constrained with a increment of 0.001 Å per femtosecond.

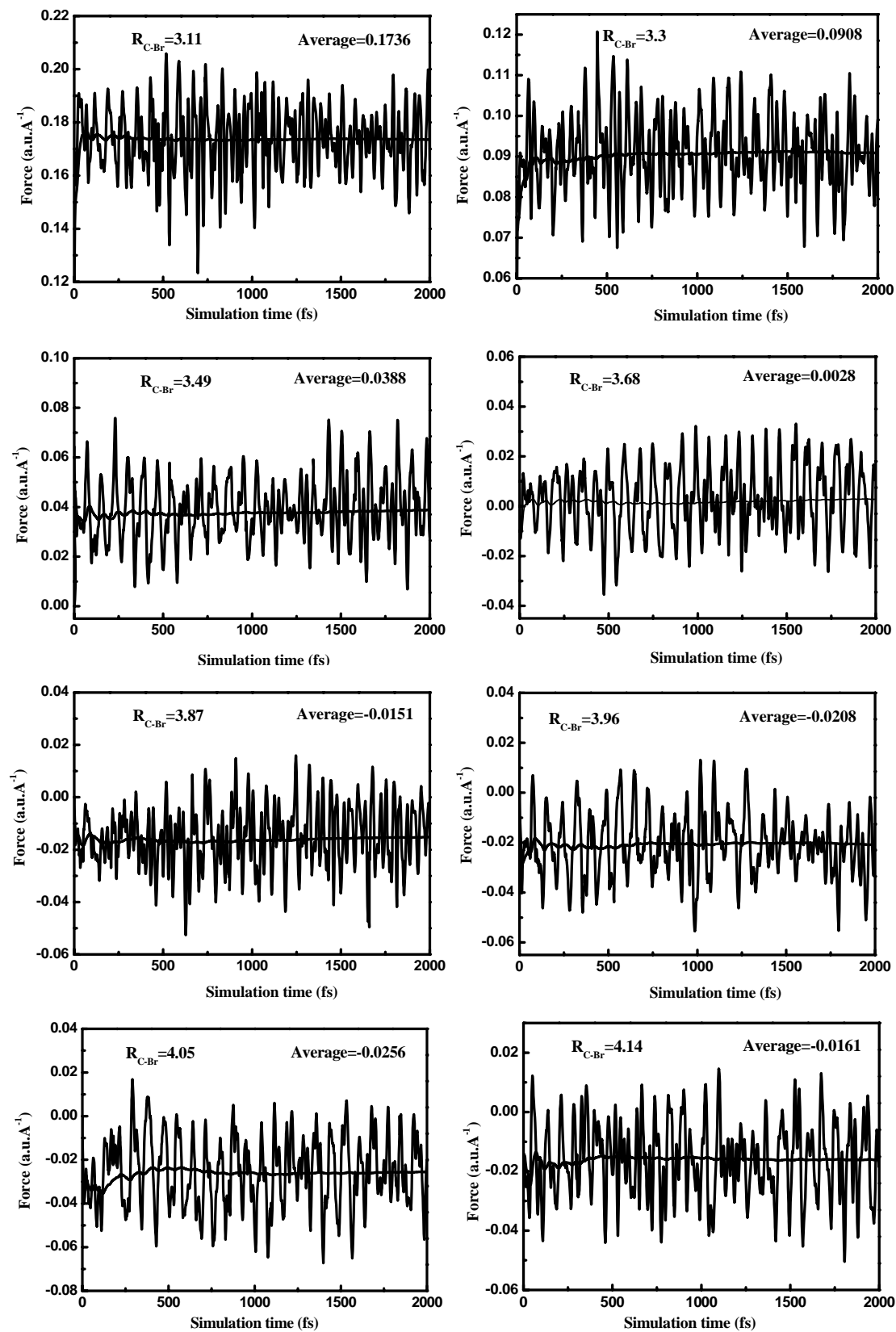


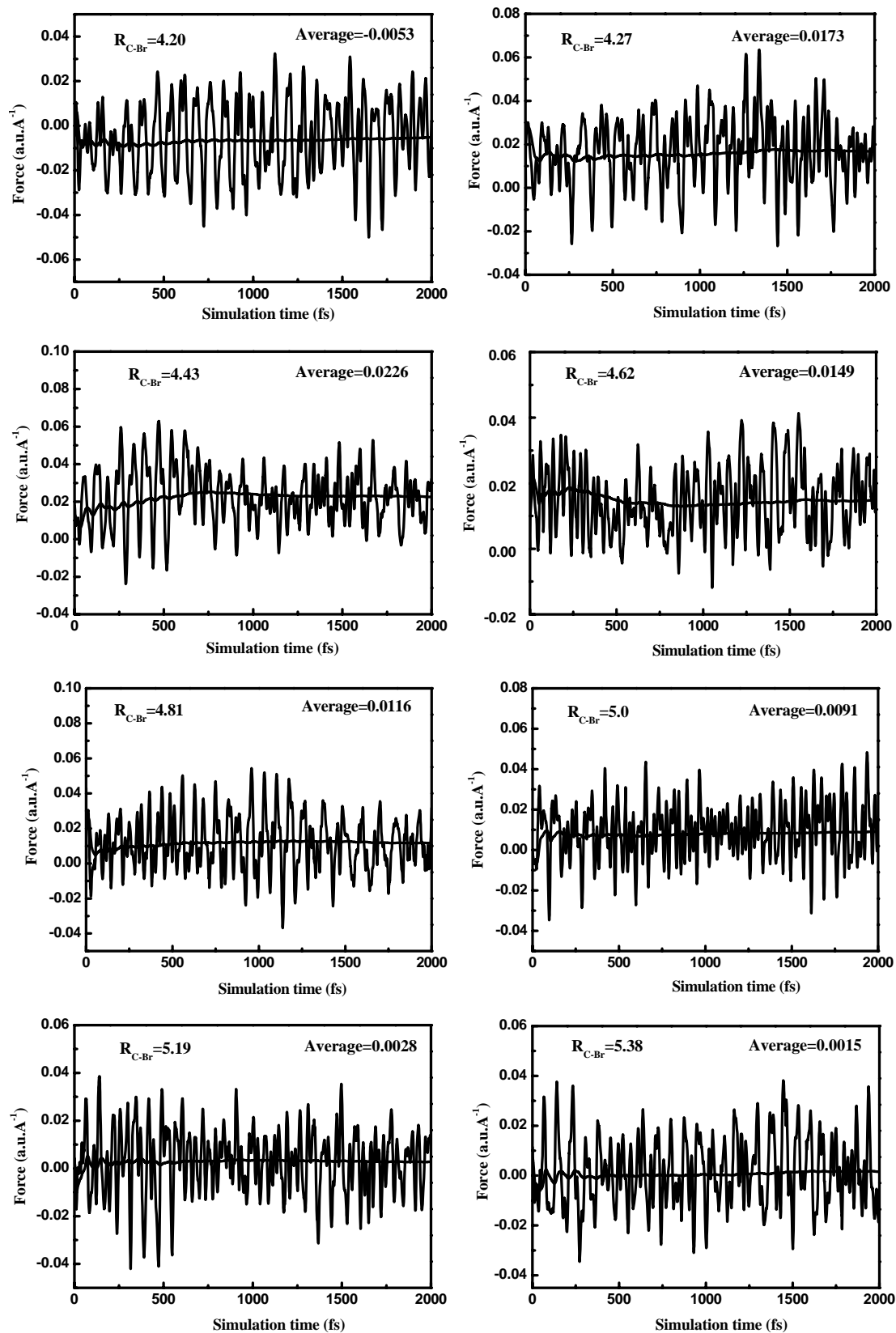
**Figure S15.** Spin density on Br and pyrimidines varying with the C-Br bond length, and the corresponding results are calculated at the BLYP/TZV2P, BLYP/mol-TZV2P, and PBE/TZV2P levels, respectively.

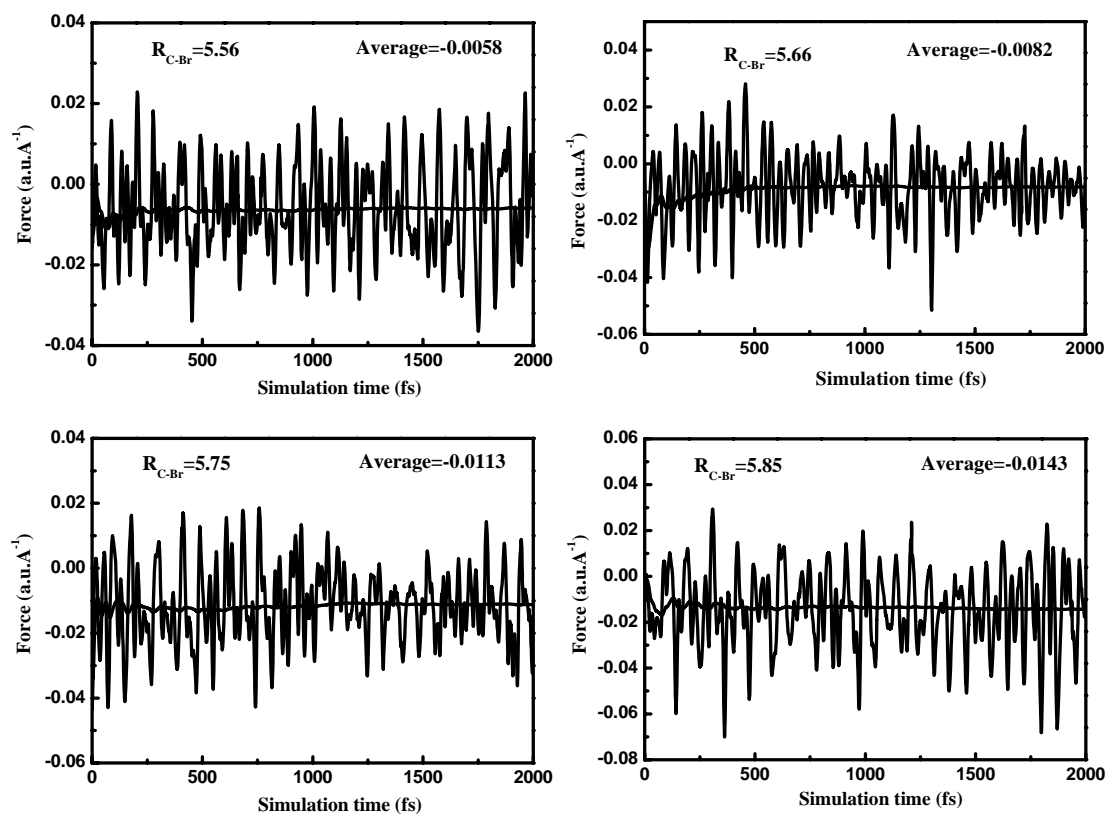


**Figure S16.** Snapshots from the constraint AIMD trajectories at different C-Br bond lengths. (a), (b), and (c) represent different initial configurations calculated at the BLYP/TZV2P level; (d), (e) are calculated at the PBE/TZV2P and BLYP/mol-TZV2P levels, respectively. The green and yellow opaque shades are for positive and negative parts of the wave function (isovalue=0.02), respectively.

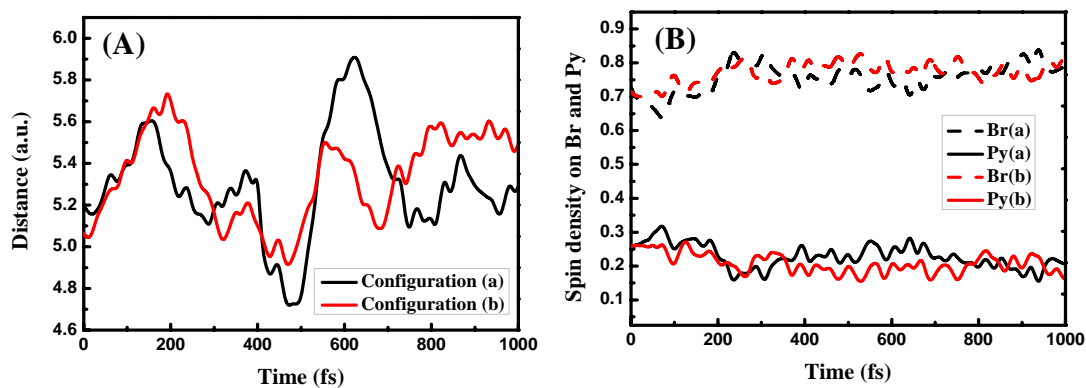
## 7. Free Energy Surface Calculations and Corresponding Analyses





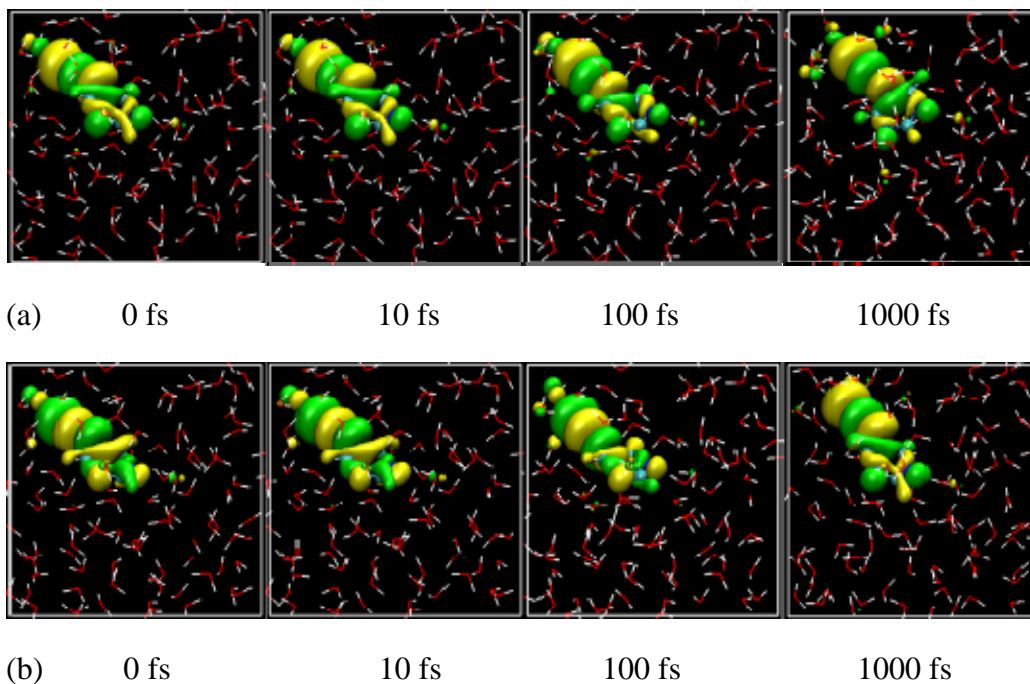


**Figure S17.** The average of constraint forces by constraining the C-Br distance at different values.



**Figure S18.** (A) Time evolution of the C-Br bond length for the anionic system with a large initial C-Br bond length; (B) Time evolution of spin densities on Br and pyrimidines. Two different initial configurations are examined and all corresponding results are calculated at the BLYP/TZV2P level.

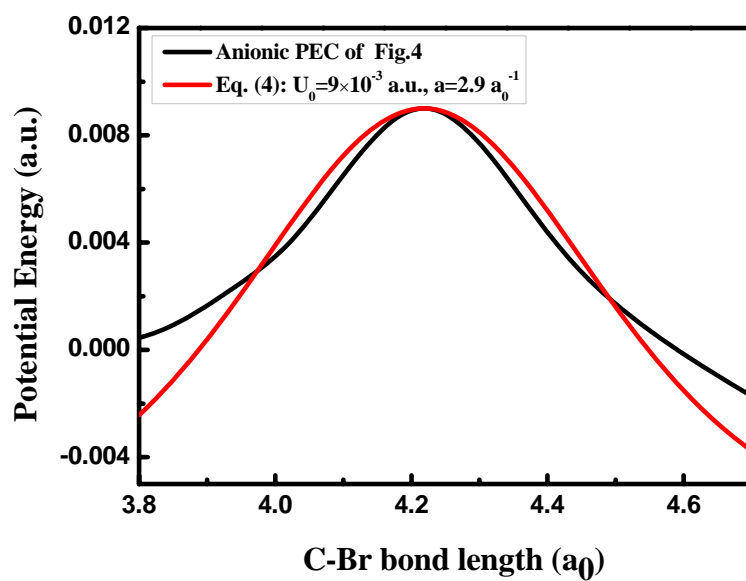




**Figure S19.** Time evolution of SOMOs for the anionic system with a large initial C-Br bond length and (a) and (b) represent different initial configurations.

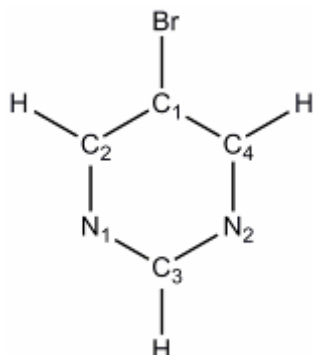
**Table S4.** The vertical electron affinity (VEA) and adiabatic electron affinity (AEA) of pyrimidine radical in the gas phase and PCM solvent, calculated at the B3LYP level of theory with a 6-311++G (d,p) basis set for C, H, and N atoms and the LANL2DZ basis set for Br atom.

| Py <sup>•</sup> | Gas phase | Aqueous phase |
|-----------------|-----------|---------------|
| VEA (eV)        | 1.414     | 3.853         |
| AEA (eV)        | 1.813     | 4.213         |

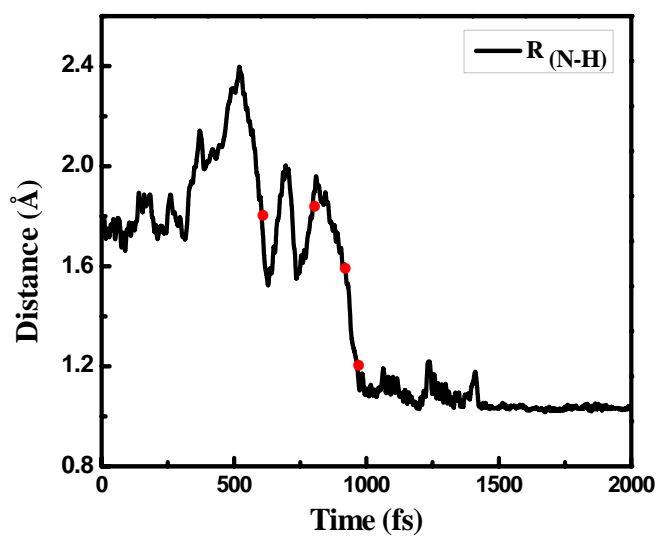


**Figure S20.** Comparison of analytical hyperbolic cosine curve fitted using Eq. (4) with the anionic potential energy curve in Figure 5.

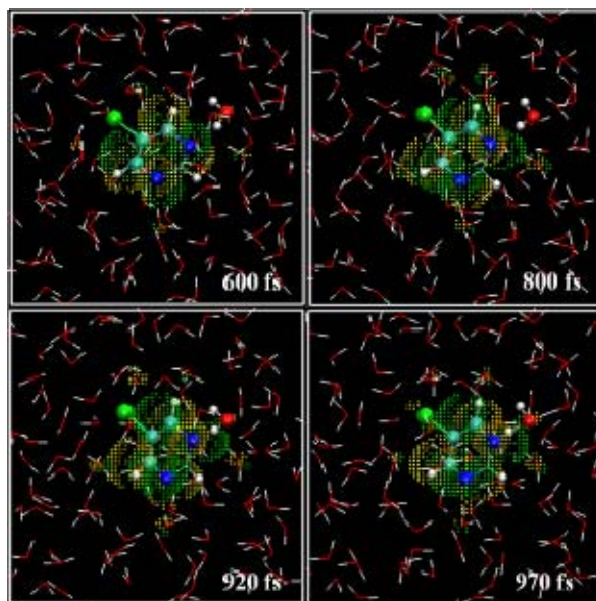
## 8. Proton Transfer Dynamics between Surrounding Water and A N Site of 5-BrPy



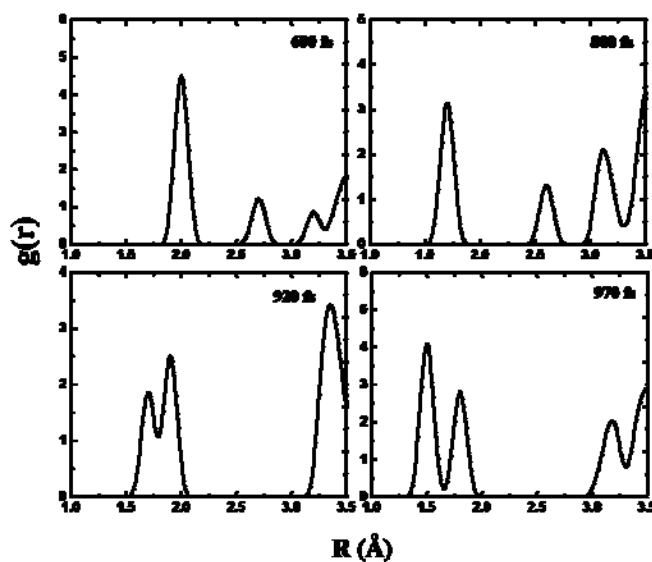
**Figure S21.** Schematic representation of 5-bromopyrimidine



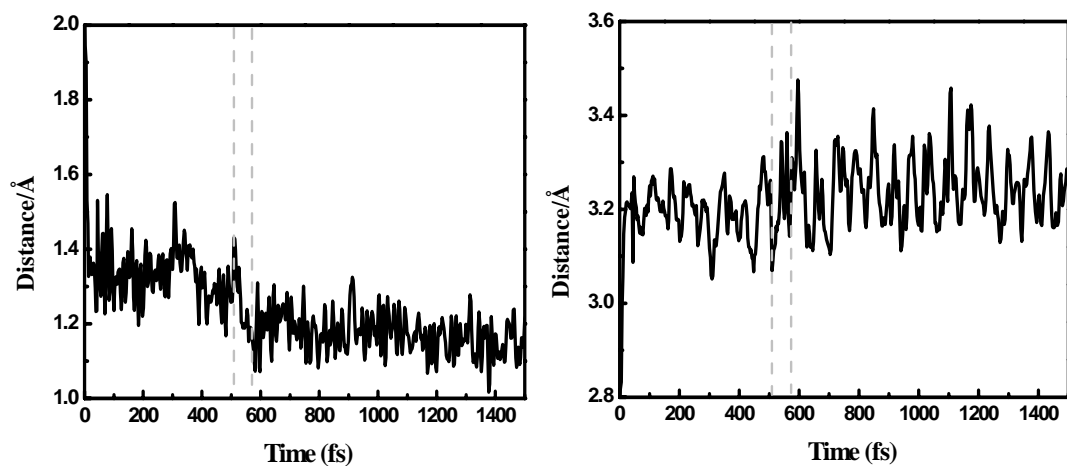
**Figure S22.** Time evolution of the distance between N<sub>2</sub> atom of 5-BrPy and a H atom of the reactive water.



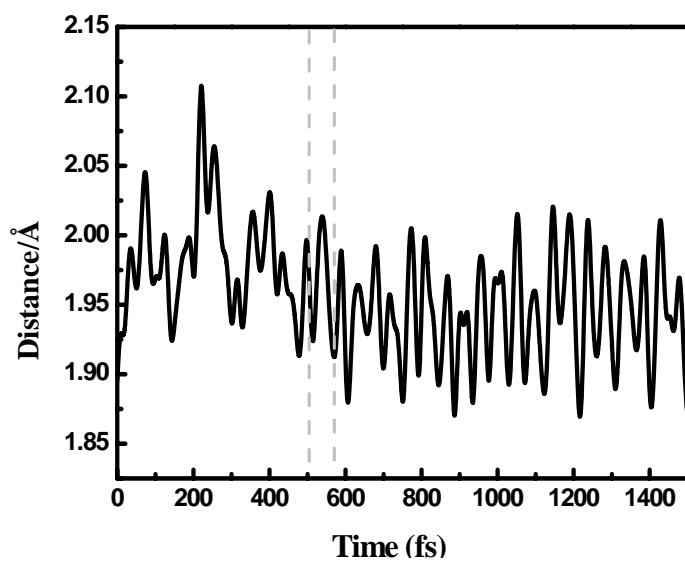
**Figure S23.** Snapshots from AIMD simulation trajectory of the proton transfer process (red dots in Figure S22), calculated at the BLYP/TZV2P level. The green and yellow shades are for positive and negative parts of the wave function (isovalue=0.02), respectively.



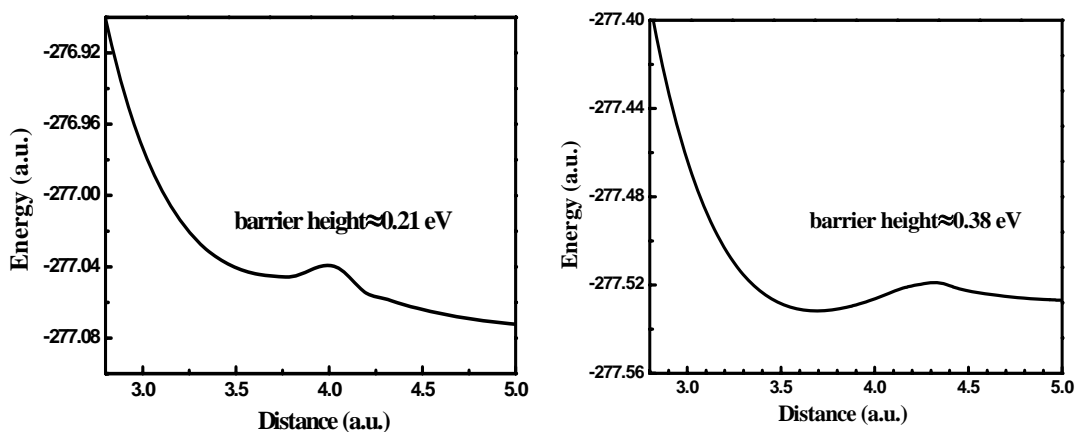
**Figure S24.** Radial distribution functions ( $g(r)$ ) between the oxygen atom of the reactive water and its surrounding water H atoms.



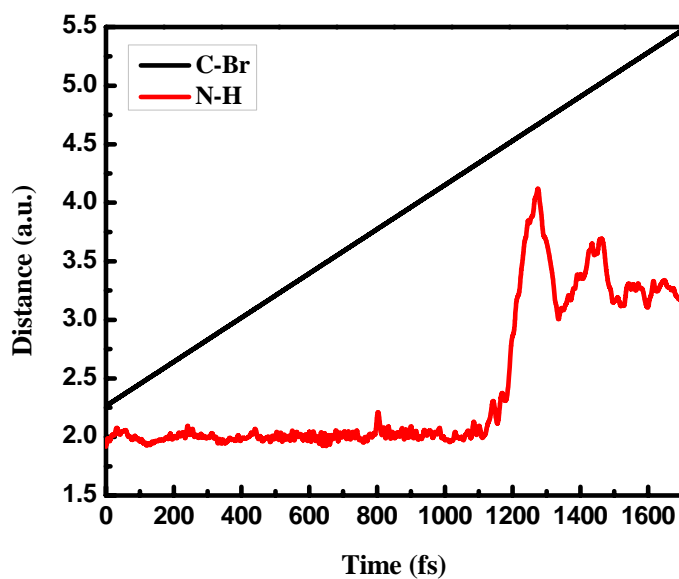
**Figure S25.** *Left panel*) Time evolution of the distance between the center of spin density and N atom during the AIMD simulation; *Right panel*) Time evolution of the distance between the center of spin density and Br atom during the AIMD simulation.



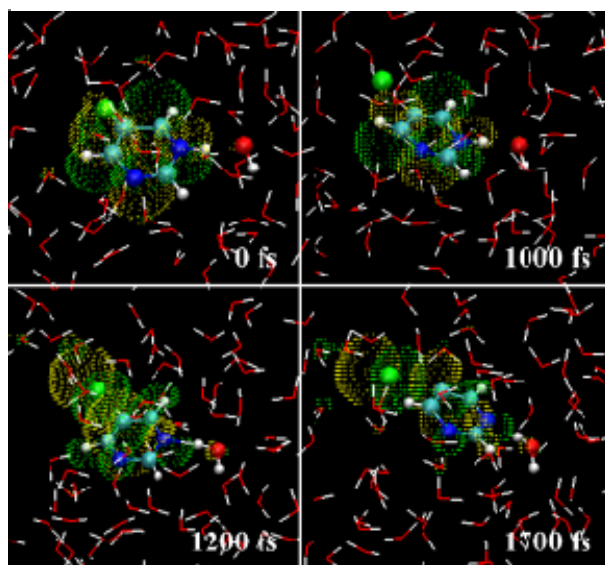
**Figure S26.** Time evolution of the C-Br bond length calculated at the BLYP/TZV2P level.



**Figure S27.** Potential energy curves along the C-Br stretching coordinate for the anion in the PCM solvent model: **(left)** unprotonated 5-BrPy and **(right)** protonated 5-BrPy, calculated at the B3LYP level of theory with a 6-311++G (d,p) basis set for C, H, and N atoms and the LANL2DZ basis set for Br atom.



**Figure S28.** Time evolution of the C-Br bond length and N-H bond length during the constrained AIMD simulation, and the corresponding results are calculated at the BLYP/TZV2P level.



**Figure S29.** Snapshots extracted from the trajectory of the constrained AIMD simulation at the BLYP/TZV2P level. The green and yellow shades are for positive and negative parts of the wave function (isovalue=0.02), respectively.