

## Supplementary Information

### **A Quantum-based Molecular Dynamics Study of ICM-102/HNO<sub>3</sub> host-guest reaction at high temperatures**

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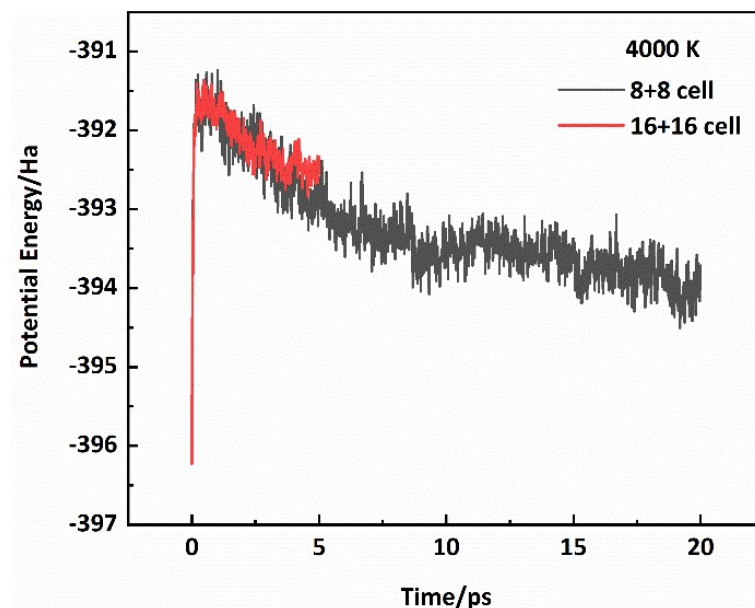
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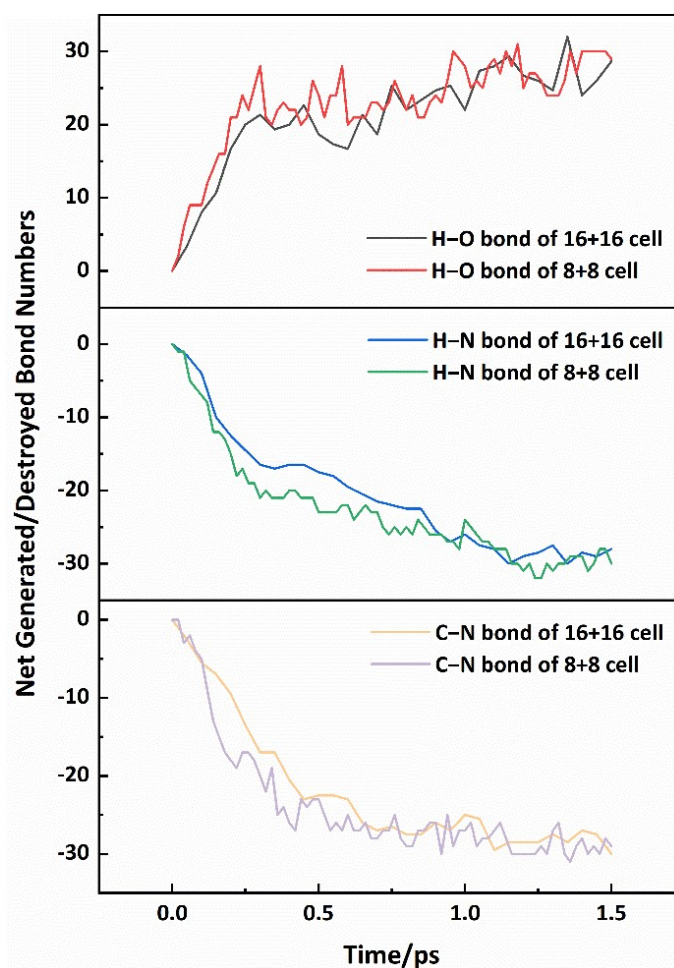
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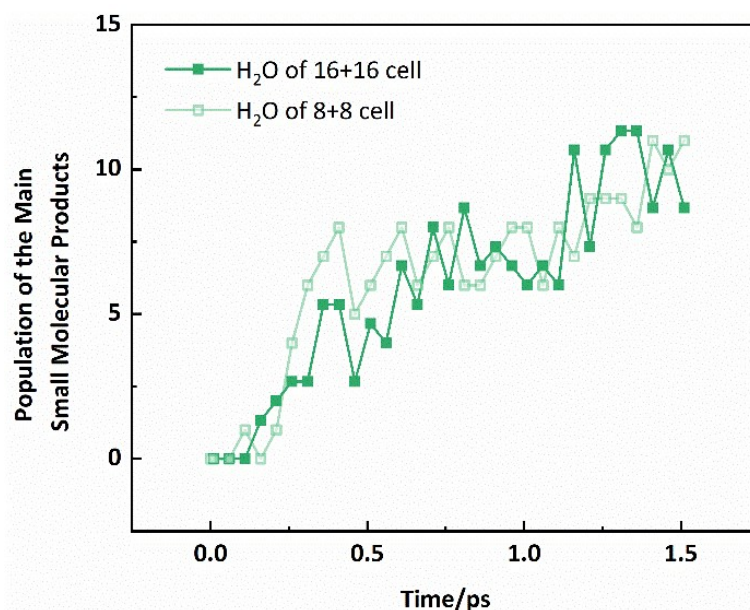
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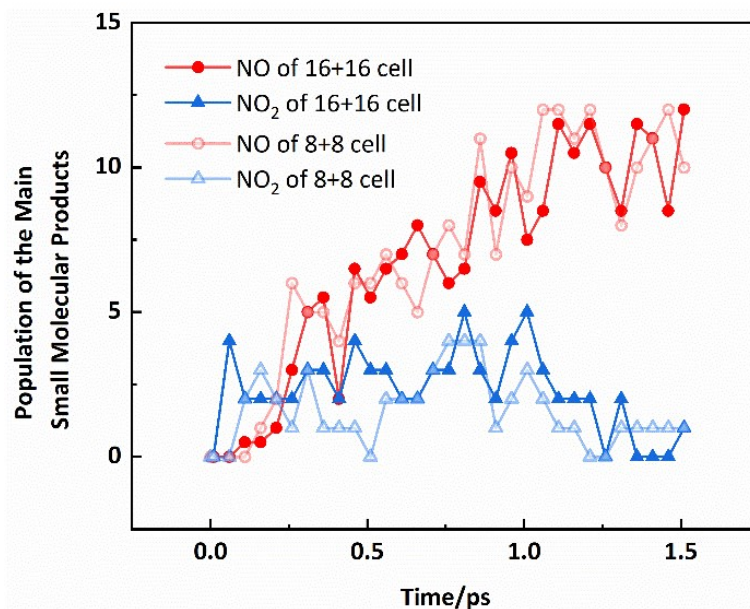
**Figure S1.** Comparison of PE of 8+8 cell and 16+16 cell at 4000 K. Since the calculation of 16+16 cell takes too long, we only calculated 5 ps.



**Figure S2.** Comparison of the cumulative sums of net generated/destroyed bonds in 8+8 cell and 16+16 cell.



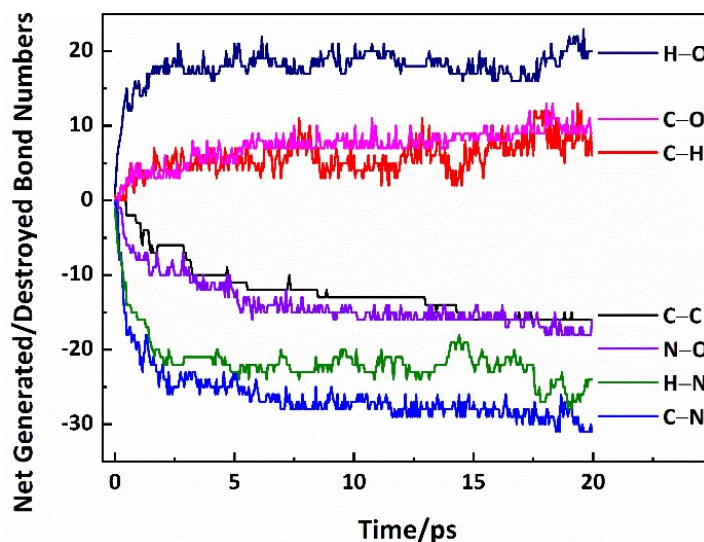
**Figure S3.** Comparison of the number of H<sub>2</sub>O in 8+8 cell and 16+16 cell.



**Figure S4.** Comparison of the number of NO and NO<sub>2</sub> in 8+8 cell and 16+16 cell.

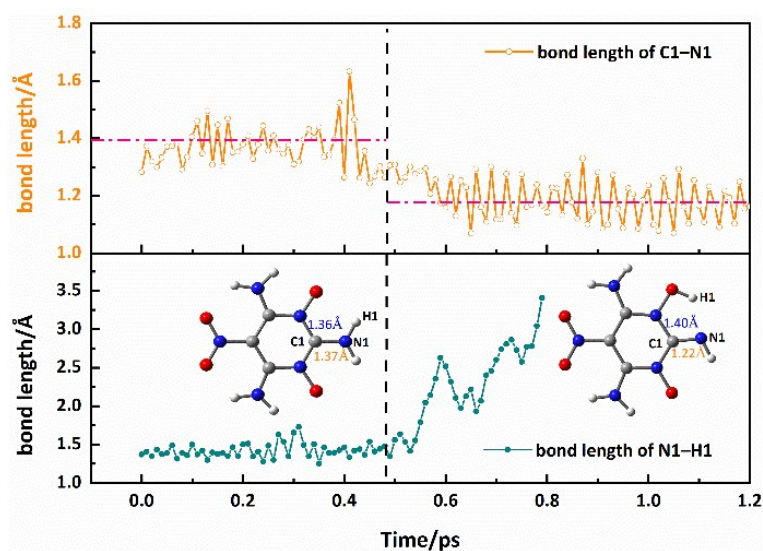
In order to test the reliability of our initial cell, we performed some simulations with an enlarged cell (a  $2 \times 1 \times 1$  supercell with 16 ICM-102 molecules and 16 HNO<sub>3</sub> molecules). We divided the calculated values in 16+16 cell by 2 to compare with the initial cell. We calculated the evolution of PE of two systems (**Figure S1**) to compare the law of energy release. And the change of net generated/destroyed bonds (**Figure S2**), the change of the main small molecular products numbers (**Figure S3** and **Figure S4**) also agreed with that of our initial cell. Thus, we believed that the calculation results of our initial cell are reliable.

The cumulative sums of the net generated/destroyed bonds in the pure ICM-102 system at 3000 K is shown in **Figure S5**. The H–O bonds are rapidly formed and the H–N bonds break at the beginning of the reaction, which corresponds to the first hydrogen transfer reaction step. The cleavage of a large number of C–N bonds means that the ring structure of ICM-102 is rapidly destroyed. As the reaction goes on, the other bonds are formed/broken in succession.

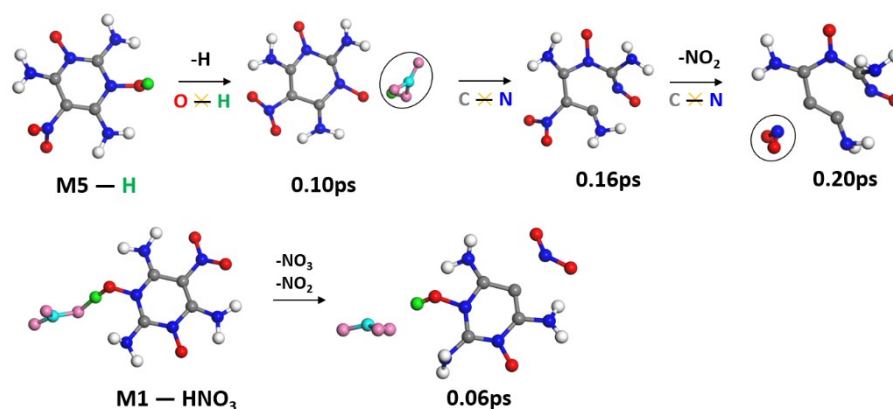


**Figure S5.** Cumulative sums of the net generated/destroyed bonds in the pure ICM-102 system at 3000 K.

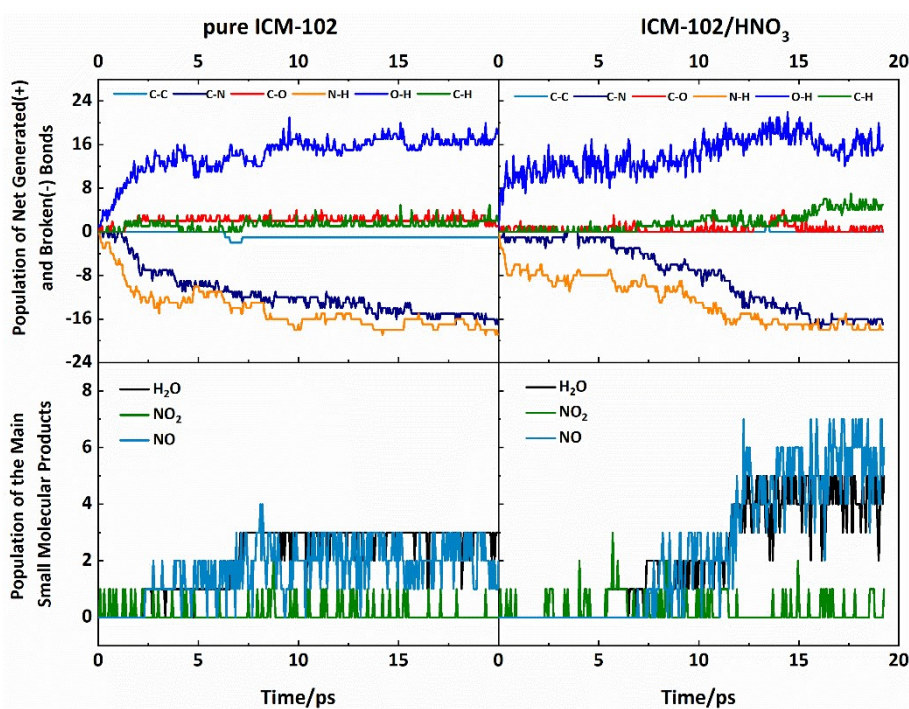
We traced the change of C–N and N–H bond length as a function of time, prior to, and after the hydrogen transfer reaction, as shown in **Figure S6**. We found that when the H atom associated with the amino group is transferred to a nearby O atom, the length of the C–NH<sub>2</sub> bond was significantly reduced, while the C–N bond in the ICM-102 ring was elongated. This provided an evidence that the C–N bond was more likely to break after intramolecular hydrogen transfer.



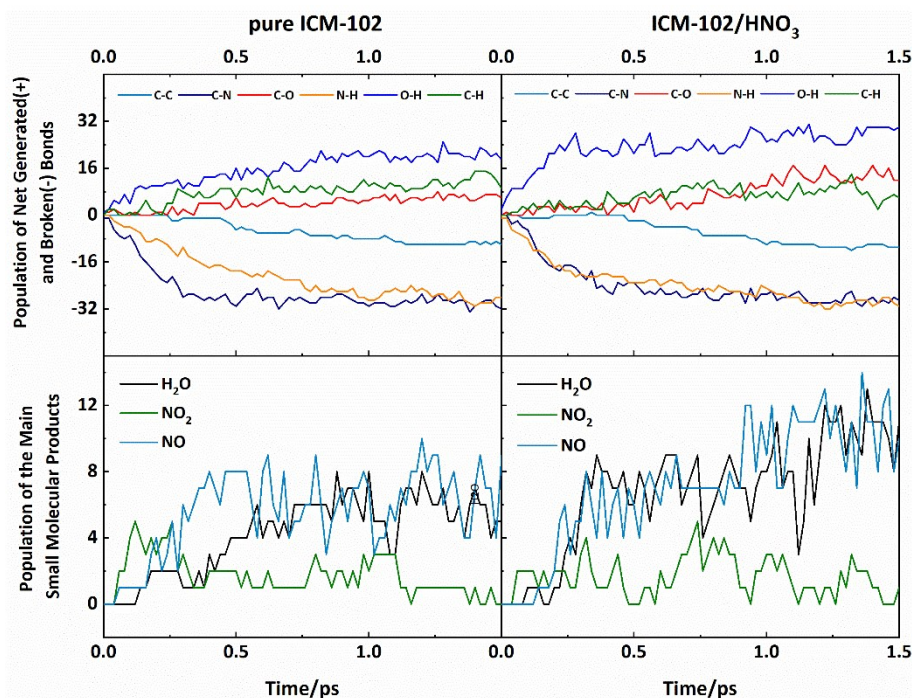
**Figure S6.** Change of C–N and H–N bond length as a function of time, prior to, and after the hydrogen transfer reaction of ICM-102.



**Figure S7.** Snapshots of the initial reaction of the M1 and M5 molecules in the ICM-102/HNO<sub>3</sub> system. The M1 molecule first dissociated the nitro group. The initial reaction of M5 molecule was C–N bond cleavage after (H) was removed by NO<sub>3</sub>.

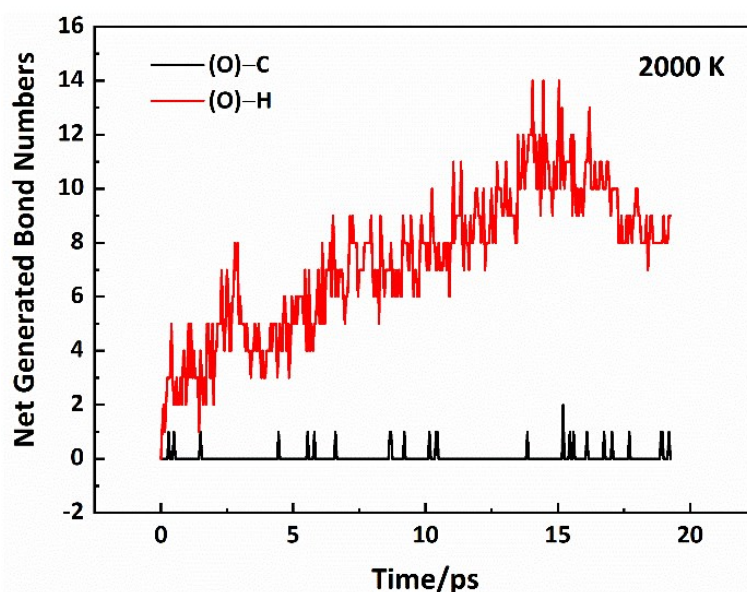


**Figure S8.** Comparison of the cumulative sums of net generated/broken bonds in the two systems, and major small molecular products, at 2000 K.

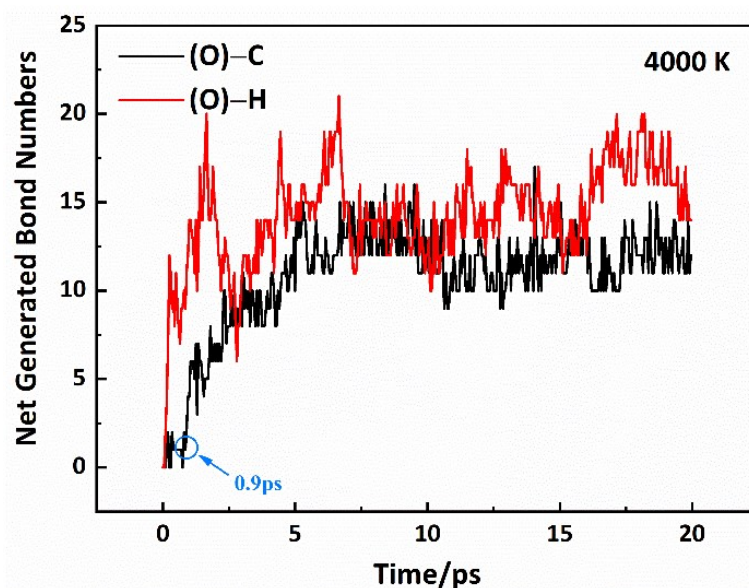


**Figure S9.** Comparison of the cumulative sums of net generated/broken bonds in the two systems, and major small molecular products, at 4000 K.

The comparison of the cumulative sums of net generated/broken bonds in the two systems, and major small molecular products at 2000 and 4000 K are shown in **Figure S8** and **Figure S9**, respectively. At 2000 K, the number of net generated/broken bonds and products in the ICM-102/HNO<sub>3</sub> system exceed that of pure ICM-102 until ~12 ps. However, at 4000 K, the number of net generated/broken bonds and products in the ICM-102/HNO<sub>3</sub> system exceed that of pure ICM-102 from the beginning of the reaction. Thus, we consider that the higher the temperature is, the weaker initial inhibition effect is.

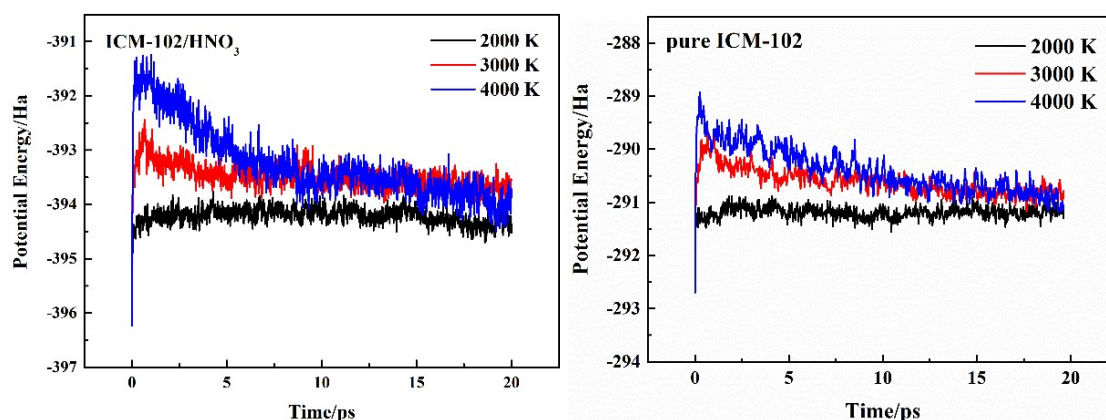


**Figure S10.** Cumulative sums of the net generated bond numbers at 2000 K.



**Figure S11.** Cumulative sums of the net generated bond numbers at 4000 K.

The cumulative sums of the net generated bond numbers between the (O) atoms and the C/H atoms at 2000 and 4000 K, are shown in **Figure S10** and **Figure S11**, respectively. It can be found that the number of (O)–H bonds increases gradually at time zero, indicating that from the beginning of the reaction, the (O) atoms in the system start to bond with the H atoms of the ICM-102 amino group. At 2000K, the number of generated (O)–C bonds are almost zero, indicating that ICM-102 molecules may maintain its basic ring structure, and molecules in the system did not decompose violently. However, a large number of (O)–C bonds generate from 0.9 ps at 4000 K. This indicates that the ICM-102 molecules in the system undergo a short delay followed by rapid decomposition.

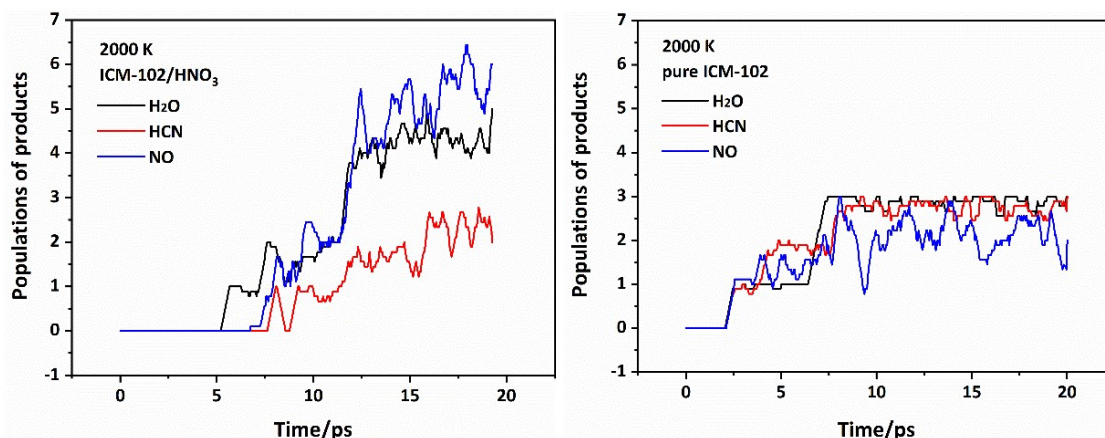


**Figure S12.** Evolution of absolute PE of the ICM-102/HNO<sub>3</sub> and pure ICM-102 systems.

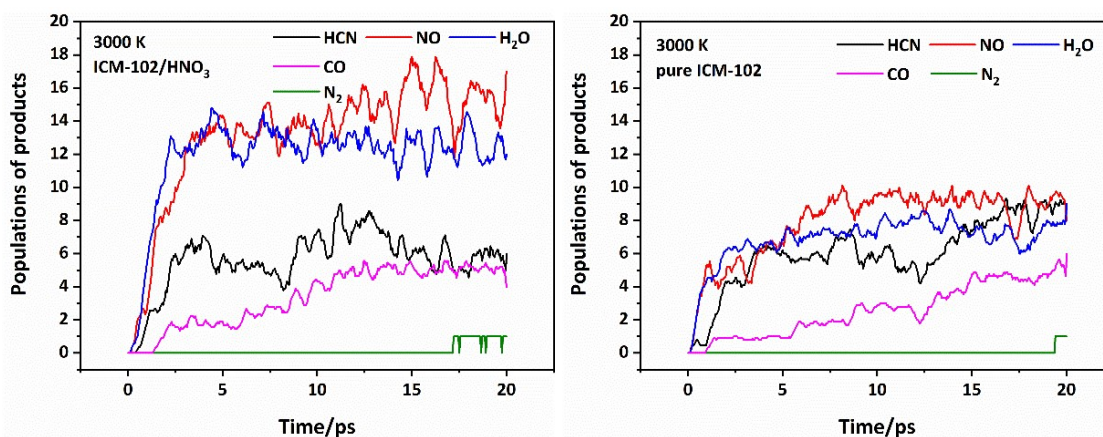
The evolution of absolute PE of the two systems is shown in **Figure S12**. The PE of two systems first increase to the maximum value then decreases, at 3000 and 4000 K. The PE curve is smooth at 2000 K, which means there is no obvious heat release occurs during the reaction. The heat release of ICM-102/HNO<sub>3</sub> system is more than that of pure ICM-102



at different temperatures.



**Figure S13.** Evolution of the population of main final products with time in the ICM-102/HNO<sub>3</sub> and pure ICM-102 systems at 2000 K.



**Figure S14.** Evolution of the population of main final products with time in the ICM-102/HNO<sub>3</sub> and pure ICM-102 systems at 3000 K.

The evolution of the number of main products as a function of time in the two systems at 2000 K and 3000 K, are shown in **Figure S13** and **Figure S14**, respectively. The incorporation of HNO<sub>3</sub> does not significantly change the final main product type. But it is obvious that the number of main final products in ICM-102/HNO<sub>3</sub> system is higher than that of pure ICM-102 system.