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

Supporting information for

Thermal stability mechanism via energy absorption by chemical bonds bending and stretching in free space and the interlayer reaction of layered molecular structure explosives

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Detailed explanation of the applicability of several density functional (DFT) methods and basic sets to describe weak interactions

Figs. S1, S2

Tables S1

Detailed explanation of the applicability of several density functional (DFT) methods and basic sets to describe weak interactions

B3LYP[1, 2] has better comprehensive performance and is the most used density functional (DFT) method but B3LYP does not consider the weak interaction system when fitting the parameters and the long-range gradual progress of the correlation potential of B3LYP is obviously wrong. Although Sousa et al.[3] believe that B3LYP can barely calculate hydrogen bonds qualitatively, it is impossible to describe the π-π interaction, which is essentially dispersion effect. The most effective way to solve B3LYP's poor ability to describe the effect of dispersion is to introduce empirical dispersion correction terms such as B3LYP-D3[4]. The improvement of B3LYP-D3's description of the effect of dispersion over B3LYP is obvious. Tian Lu[5] verified that B3LYP-D3 has significantly improved calculation accuracy compared to B3LYP. Goerigk,L.[6] calculated the average error of several density functional (DFT) methods describing weak interaction, and also found that B3LYP-D3 is far superior to B3LYP. CAMB3LYP[7] is Handy and coworkers' long-range-corrected version of B3LYP using the Coulomb-attenuating method, which has advantages in the calculation of excitation energy, charge transfer, higher-order valence layers, vertical excitation of Rydberg, etc. , but is not satisfactory in describing weak interactions. M06-2X[8] introduced weak interactions when fitting the parameters, so the calculation of weak interaction is great and M06-2X is widely supported. Compared with M06-2X, M06-2X-D3 has a non-negligible improvement in calculating π-π interaction. Goerigk,L.[6] believes that M06-2X-D3 is the best hybrid functional in terms of calculating weak interactions. wB97X-D[9], added dispersion correction and re-parameterization to wB97X[10], has better ability to calculate the weak interactions. Since the dispersion correction is changed from DFT-D2 to DFT-D3, the accuracy of wB97XD3 is improved compared to wB97XD in terms of weak interaction, but wB97XD3 is not supported by Gaussian. In summary, M06-2X-D3 and wB97XD are basically enough to deal with various weak interaction systems. The performance of M06-2X is slightly better than wB97XD, and the accuracy of B3LYP-D3 (BJ) is slightly lower.

The initial basis set is 6-31G(d), which adds d orbital to heavy atoms on the basis of the split basis set 6-31G; 6-31+G(d) adds the diffuse basis set to the heavy atom based on 6-31G(d); The accuracy of 6-311+G(d) is slightly higher than that of 6-31+G(d); 6-311+G(d,p) adds p orbital to the hydrogen atom on the basis of the 6-311+G(d); 6-311G++(d,p) adds a dispersion function to the hydrogen atom based on 6-311+G(d, p), however, the dispersion function on hydrogen atoms is of little value and it takes a long time to calculate.

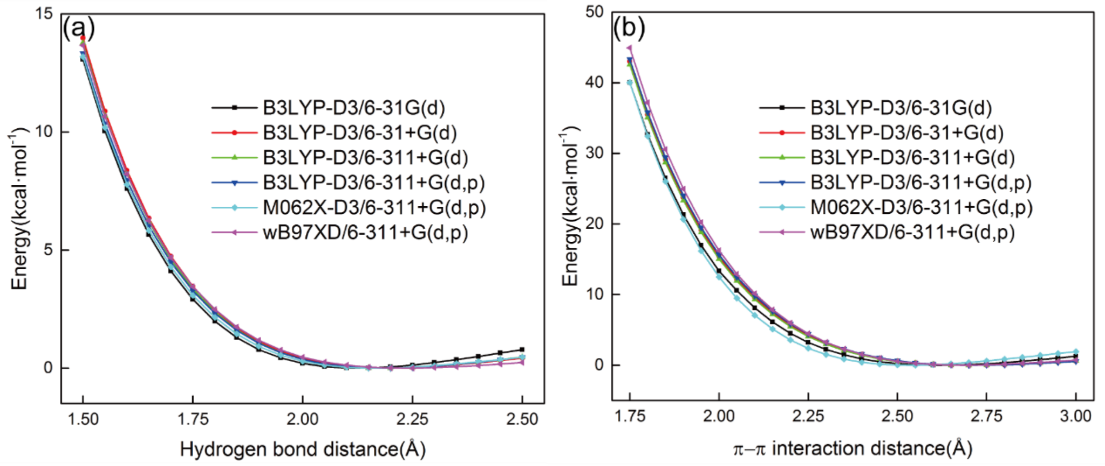

Fig. S1 (a) System energies with different hydrogen bond distances, (b) System energies with different π-π interaction distances calculated using several density functional (DFT) methods and basis set combinations of Gaussian16 program.

Fig. S1 (a) shows system energies with different hydrogen bond distances calculated using several density functional (DFT) methods and basis set combinations of Gaussian16 program. This Fig. S1 (a) shows that with respect to the intralayer hydrogen bond, the trends of the energies calculated by different density functional (DFT) methods and basis set combinations with distance are similar. The energy quickly decreases to the lowest point with the distance, and then slowly rises. The hydrogen bond distances corresponding to the minimum energies calculated by different density functional (DFT) methods and basis set combinations are all 2.2 Å. The energies corresponding to the same hydrogen bond distance calculated by different density functional (DFT) methods and basis set combinations are different. Within a hydrogen bond distance of less than 2.2 Å, the energy calculated by B3LYP-D3/6-31G(d) is less than that calculated by other combinations and the energy calculated by B3LYP-D3/6-31+G(d) and wB97XD/6-311+G(d,p) is greater than that calculated by other combinations. However, when the hydrogen bond distance is greater than 2.2 Å, the energy calculated by B3LYP-D3/6-31G(d) is greater than that calculated by other combinations and the energy calculated by wB97XD/6-311+G(d, p) is less than that calculated by other combinations. Although the energies calculated by density functional (DFT) methods and basis set combinations at the same hydrogen bond distance are different, the differences are all less than 1 Å, which shows that the density functional (DFT) methods and basis set combinations has very little effect on the energy at different hydrogen bond distances.

Fig. S1 (b) shows system energies with different π-π interaction distances calculated using several density functional (DFT) methods and basis set combinations of Gaussian16 program. It can be seen from Fig. 1(b) that the energies calculated by different combinations have the same trend with the π-π interaction distances, and decrease rapidly at first to reach a minimum at about 2.65 Å, and then slowly increase. However, for the same π-π interaction distance, the energies calculated by different combinations are different. For example, when π-π interaction distance is less than 2.65 Å, the energy calculated by M062X-D3/6-311+G(d,p) is greater than that calculated by other combinations for the same π-π interaction distance, but when it is greater than 2.65 Å, the energy calculated by M062X-D3/6-311+G(d,p) becomes the maximum value among the energies calculated by all combinations. Although there are differences, the difference between the energies calculated by different combinations is less than 10%, which also shows that density functional (DFT) methods and basis set combinations have little effect on the energies of different π-π interaction distances.

TableS1 Energy drift value at 0.01ps, 0.05ps and 0.1ps

Time step(ps)	0.01	0.05	0.1
Energy drift value	2.1×10^{-6}	1.0×10^{-5}	3.9×10^{-5}

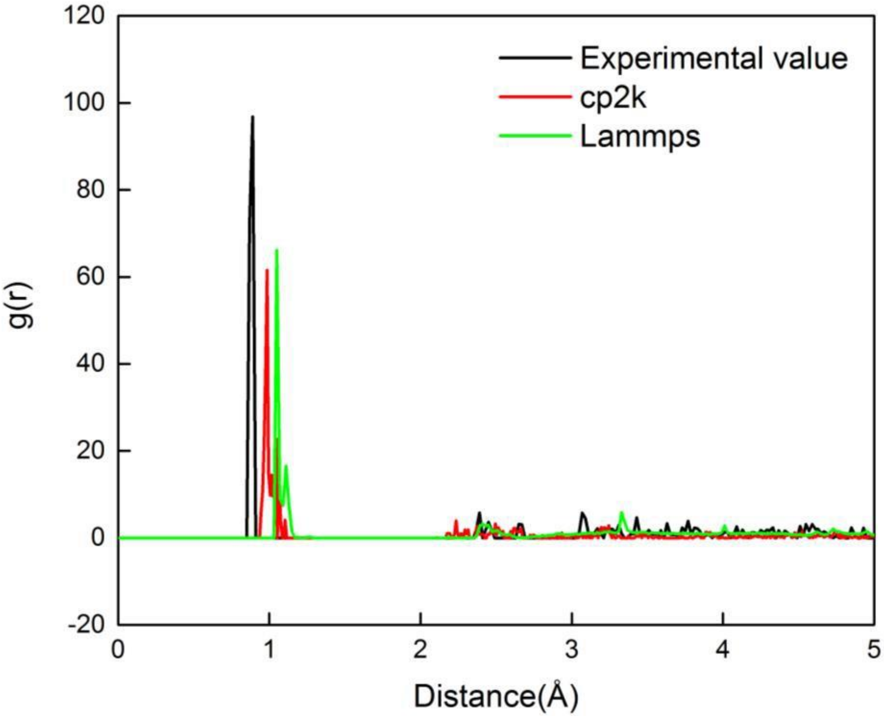

Fig S2. Comparison of the radial distribution functions of the ICM102 experimental structure at 298 K, the ICM102 structure obtained using cp2k and the ICM102 structure obtained using ReaxFF-lg.

Reference:

1. A. D. Becke, *Journal of Chemical Physics*, 1993, **98**, 5648-5652.
2. C. T. Lee, W. T. Yang and R. G. Parr, *Physical Review B*, 1988, **37**, 785-789.
3. S. F. Sousa, P. A. Fernandes and M. J. Ramos, *Journal of Physical Chemistry A*, 2007, **111**, 10439-10452.
4. S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *Journal of Chemical Physics*, 2010, **132**.
5. T. Lu and F. W. Chen, *Journal of Molecular Modeling*, 2013, **19**, 5387-5395.
6. L. Goerigk, A. Hansen, C. Bauer, S. Ehrlich, A. Najibi and S. Grimme, *Physical Chemistry Chemical Physics*, 2017, **19**, 32184-32215.
7. T. Yanai, D. P. Tew and N. C. Handy, *Chemical Physics Letters*, 2004, **393**, 51-57.
8. Y. Zhao and D. G. Truhlar, *Theoretical Chemistry Accounts*, 2008, **120**, 215-241.
9. J. D. Chai and M. Head-Gordon, *Physical Chemistry Chemical Physics*, 2008, **10**, 6615-6620.
10. J. D. Chai and M. Head-Gordon, *Journal of Chemical Physics*, 2008, **128**.