Supporting Information

Hydrogen-bonding Interactions Between [BMIM][BF_4] and Acetonitrile

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1. Method:

Quantum Chemical Calculations

All computations were performed with the Gaussian 03 program.[1] The molecular energies, geometries, vibrational frequencies, vibrational intensities and ^{1}H NMR of the isolated CH_3CN, $[BMIM]^+$–$[BF_4]^-$ complexes, $[BMIM]^+$–CH_3CN complexes, $[BMIM]^+$–$[BF_4]^-$–CH_3CN complexes and $2[BMIM]^+$–$2[BF_4]^-$–CH_3CN complexes have been calculated using the B3LYP method in conjunction with the 6–31++G** basis set. The optimized geometries at local energy minimum were ensured by the absence of imaginary vibrational frequency. Meanwhile, the basis set superposition error (BSSE) correction was estimated for obtaining accurate interaction energies. The sum of van der Waals atomic radii of hydrogen and nitrogen (2.6 Å) and that of hydrogen and fluorine (2.45 Å) are used as critical values for judging the existence of hydrogen-bonds between hydrogen and nitrogen/fluorine.[2]

2. Results

The optimized geometries and respective interaction energies of $[BMIM]^+$–$[BF_4]^-$ complexes are shown in Figure S1. The absolute value of the interaction energy of the first conformer is much greater than the other three conformers, meaning it is the most stable one.

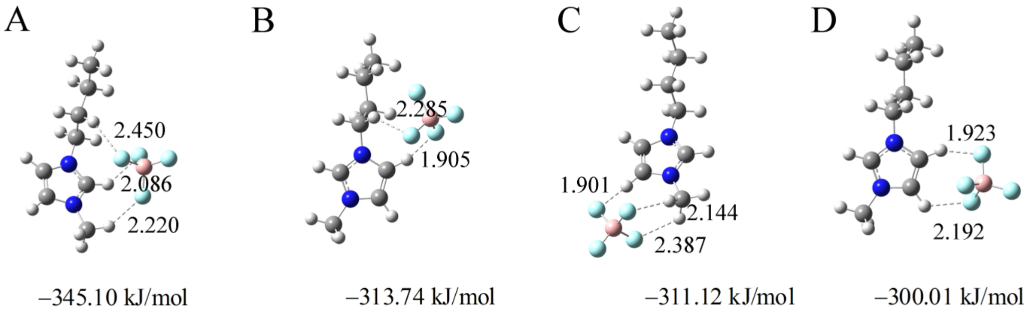


Figure S1. Optimized geometries and corresponding interaction energies of $[BMIM]^+$–$[BF_4]^-$ complexes. Hydrogen-bonds are denoted by dashed lines, and the corresponding H···F distances are labeled. The corresponding interaction energies are shown below the complexes.

The optimized geometries and respective interaction energies of $[BMIM][BF_4]$–CH_3CN complexes are shown in Figure S2(A–D), They give the interaction modes in the presence of both the anion, the cation, and CH_3CN. The methyl group and the N atom of CH_3CN are found to interact with the ionic liquid simultaneously. The methyl group of CH_3CN locates above the imidazolium ring in Figure S2A and S2B as can be seen more clearly in Figure S2E and S2F. The results are in general agreement with the ^{1}H NMR result. All the most stable conformers in Figure S2 demonstrate that CH_3CN molecule cannot insert into the cation $[BMIM]^+$ and anion $[BF_4]^-$. It illuminates that it is not easy for a neutral molecule like acetonitrile to break apart the strong Coulombic interaction between $[BMIM]^+$ and $[BF_4]^-$ by simple insertion between them when the concentration of acetonitrile is low.

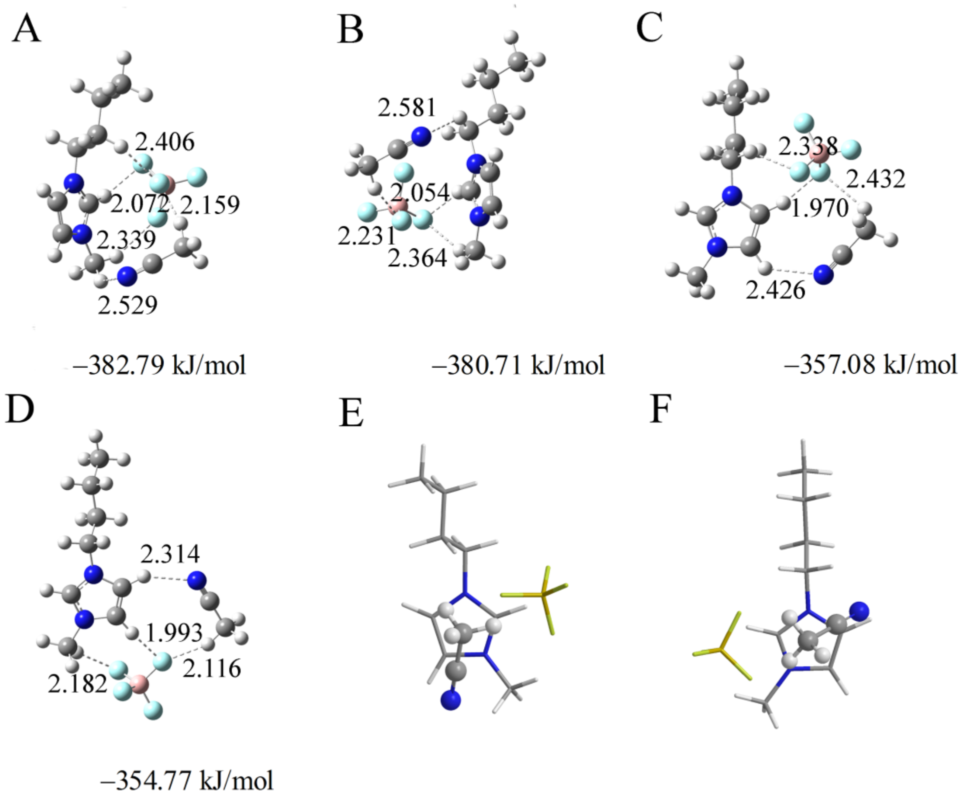
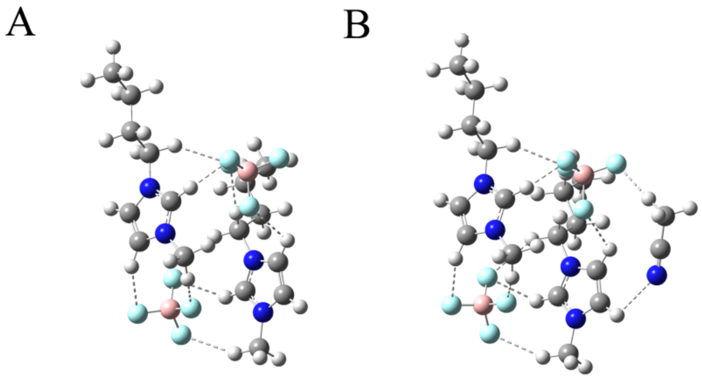


Figure S2. Optimized geometries and corresponding interaction energies of four $[BMIM][BF_4]$–CH_3CN complexes (A, B, C, and D). Hydrogen-bonds are denoted by dashed lines, and the corresponding H···N and H···F distances are labeled. The corresponding interaction energies are shown below the complexes. E and F are the printscreen captures of the top view of the complexes A and B in respect to the imidazolium ring.

[BMIM][BF_4] are presented in the form of sticks to show more clearly that the methyl group of CH_3CN locates right above the imidazolium ring.

The optimized geometry of an ionic cluster containing two cations and two anions is presented in Figure S3A. The [BF_4]$^-$ anions are situated between the two [BMIM]$^+$ cations and interact with them at the same time. The optimized geometry of the complex between the ionic cluster and an acetonitrile molecule is presented in Figure S3B. For clarity, the corresponding distances of the hydrogen-bonds in Figure S3 are not displayed. As seen in the figure, the CH_3CN molecule stays on the outer skirt of the cluster with its N and the methyl group interacting with the ionic liquid simultaneously.



−775.88 kJ/mol   −808.21 kJ/mol

Figure S3. Optimized geometries and corresponding interaction energies of an ion cluster and an ion cluster–CH_3CN complex. Hydrogen-bonds are denoted by dashed lines. The corresponding interaction energies are shown below the complexes.

3. References

(1) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheesman, V. G. Zakrzewski, J. A., Jr. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, A. Petersson, P. Y. G. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian 03, Revision B. 03, Gaussian Inc., Pittsburgh, PA, 2003.

(2) L. Pauling, *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: New York, 1960.