Electronic Supplementary Information

A triple helical structure supported solely by C–H···O hydrogen bond

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1. **X-ray crystallographic analysis**.....S2
2. **Computational method**.....S3
3. **Figure S1.** Molecular mechanics optimized structure for a nanomer.....S5
4. **Figure S2.** Molecular structure and crystal packing of **2**.....S6
5. **Crystal data for 1**.....S7
6. **References**.....S8

X-ray crystallographic analysis

Single-crystal X-ray diffraction data of 1 were collected by using a Bruker P4 diffractometer with a graphite monochromator using Mo-K radiation (λ = 0.71073 Å) in ω scan modes. All structures were solved by the direct method and refined (based on F^2 using all independent data) by full matrix least-squares methods (Bruker SHELXTL 97).[S1] The PF_6^- anion is found to be disordered with two independent orientations having occupancies of 0.5 and 0.5. Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were found in a difference map.

Computational method

The density functional theory (DFT) M06-2X/6-311++G** and *ab initio* MP2/6-311++G** calculations were used to evaluate the binding energies of the selected dimers and model complexes. The M06-2X functional developed by Truhlar and co-workers has been shown to bear considerably improved performance in describing diverse noncovalent weak interactions,[S2] which are a familiar drawback for other popular functionals, and thus is a suitable choice for the purpose of the present study. The coordinates for the selected dimers and the model complexes were extracted from the crystal structure; for the model complexes, hydrogen atoms were added to complete the valence. The geometry optimizations and frequency analyses for the hexamer in acetonitrile and water were carried out at M06-2X/6-31G level under the consideration of solvent effect. The reported association free energies for the hexamer in water and acetonitrile have been corrected for the standard state of 1 M in solution instead of 1 atm in gas phase, which is the default implementation in most quantum chemistry packages. The inclusion of the solvent effect was achieved by using the integral equation formalism version of the polarization continuum model. Natural population analysis was applied to obtain the atomic charge distribution for the hexamer. All the DFT and *ab initio* calculations were performed by Gaussian 09 program.[S3] For the molecular mechanics (MM) calculation of the nanomer, we used

the OPLS force field supplemented by the M06-2X/6-311++G** derived atomic charges. The triple helix of the nanomer was placed in a 45 Å × 45 Å × 45 Å periodic box of 3010 TIP3P water molecules.[S4] The truncation of nonbonded potential energy was treated by a potential switching function turned on at a distance of 11 Å and turned off at a distance of 15 Å. The MM calculation was achieved by HyperChem package.[S5]

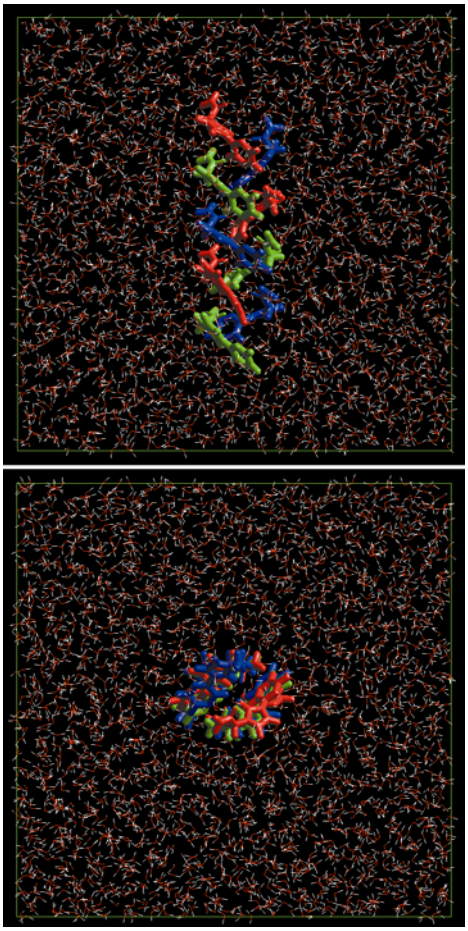
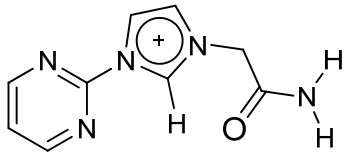


Fig. S1 The molecular mechanics optimized structure for a nanomer in a 45 Å × 45 Å × 45 Å box filled with 3010 water molecules. Top panel: the view perpendicular to the axis. Bottom panel: the view along the helical axis.



2

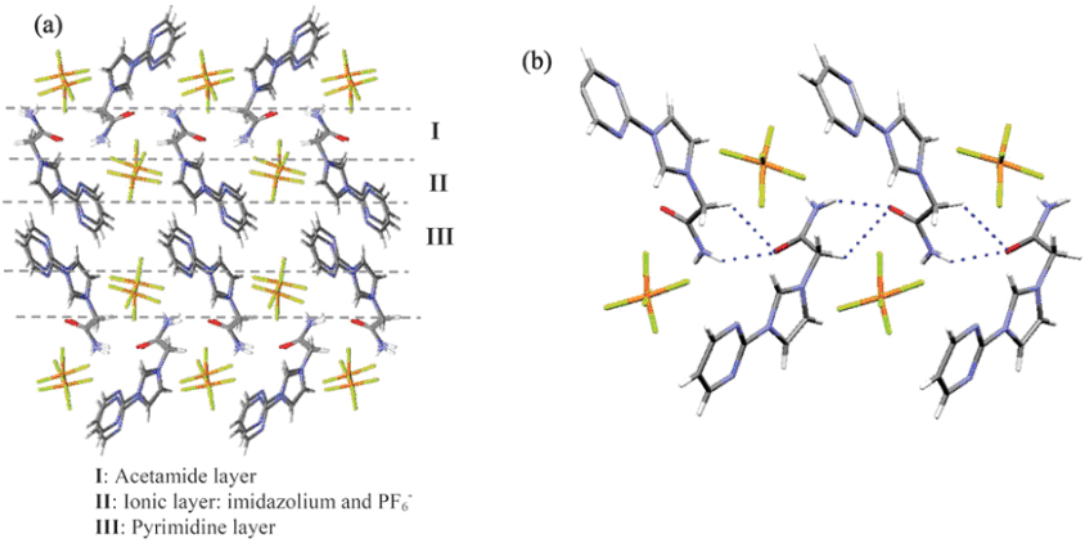


Fig. S2 The molecular structure of 1-acetamido-3-(2-pyrimidyl)-imidazolium cation (**2**) and the crystal packing of its PF_6^- salt. (a) Stacking of the tri-layer structure. (b) One-dimensional anti-oriented catemer was formed by N–H···O and C–H···O hydrogen bonds.

Crystal data for 1:

Chemical formula	$C_9H_{10}F_6N_5OP$
Formula Mass	349.19
Crystal system	Orthorhombic
a/Å	5.5476(8)
b/Å	11.7755(16)
c/Å	20.368(2)
α/°	90
β/°	90
γ/°	90
Unit cell volume/Å^3	1330.5(3)
Temperature/K	293(2)
Space group	$P2_12_12_1$
No. of formula units per unit cell, *Z*	4
Radiation type	MoKα
Absorption coefficient, *μ*/mm^{-1}	0.288
No. of reflections measured	2785
No. of independent reflections	2346
R_{int}	0.0172
Final R_1 values ($I > 2\sigma(I)$)	0.0368
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.0944
Final R_1 values (all data)	0.0427
Final $wR(F^2)$ values (all data)	0.0993
Goodness of fit on F^2	1.036
Flack parameter	-0.02(14)
CCDC number	180990

References

[S1] G. M. Sheldrick, *Acta Crystallogr.* 2008, **A64**, 112.

[S2] Y. Zhao and D. G. Truhlar, *Acc. Chem. Res.* 2008, **41**, 157.

[S3] Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

[S4] W. L. Jorgensen, J. Chandrasekhas, J. D. Madura, R. W. Impey and M. L. Klein, *J. Chem. Phys.* 1983, **79**, 926.

[S5] HyperChem Professional 8.0.3, Hypercube, Inc., 1115 NW 4th Street, Gainesville, FL 32601.