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Molecular architecture using novel types of non-covalent π-interactions involving aromatic neutrals, aromatic cations and π-anions†

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A solid-state complex utilizing non-covalent interactions between two aromatic cations is synthesized and characterized. The X-ray study of the structure shows that the anion templated π^+–π^+ interactions are the major driving force in the crystal packing, while π^+–π, π–π, π–anion and π^+–anion interactions assist the overall stabilization of self-assembly. In addition, we also identify the cation-mediated non-covalent interaction between two π anions (π^-–π^- interaction). The interaction energies of the important driving forces (π^+–π^+, π^+–π, π–anion, π^+–anion, and π^-–π^- interactions) observed in the crystal structure are calculated using dispersion-corrected density functional theory (DFT-D).

Intensive studies of π-interactions[1] including H–π,[2] π–π,[3] cation–π,[4] and anion–π[5] interactions have been conducted in the past two decades and these π-interactions are utilized for molecular recognition, molecular assembly, and crystal packing of organic materials, nanomaterials and biomolecules.[6] Theoretical interpretations based on high level *ab initio* calculations have been instrumental in understanding the nature of π-interactions. Recently, it has been reported that π^+–π interactions are much stronger than π–π and H–π interactions, but different from typical non-aromatic cation–π interactions because of the strong dispersion interactions between the stacked aromatic ring systems.[7] Since positively charged π systems require anionic species for stabilization, conceptually cation–anion neutral interaction could be exploited in designing solid-state assembly of anion-templated molecular architectures. Toward this direction, as a complement species of anions, the positively charged π systems can be exploited, thereby the resulting π interactions would play an important role in π-stacking. The π^+–π interactions are often found in nature, and have been successfully utilized in the design of a solid-state complex.[8] Recently, anion-templated π^+–π^+ interactions have been theoretically investigated, where the H bonding between counter anion and π^+-moiety stabilizes the complex.[9] The binding energies of such complexes are much higher than those of π–π and π^+–π complexes, with the electrostatic contribution larger than the dispersion term.

Given that the π^+–π and π^+–π^+ interactions are genuinely different from the π–π and cation–π interactions in terms of magnitude and directionality, a molecular entity composed of π^+ and π moieties would result in the crystal packing being defined by π^+–π and π^+–π^+ interactions. Toward this direction, we design a molecular entity which could lead to crystal assembly featuring both π^+–π^+ and π^+–π interactions, which are experimentally realized by producing the X-ray crystallographic structure where the π^+–π^+ interactions are imprinted as its distinct characteristics by playing a major role in crystal packing. We also note that the cation-mediated non-covalent interaction between two π anions (π^-–π^- interaction) are also present amidst the π^+–π^+, π^+–π, π–π, π–anion and π^+–π^- interactions.

To have many π^+-moieties, we have prepared a molecular system (Fig. 1) which is the triply protonated form of 4′-(4-pyridyl)-2,2′:6′,2′′-terpyridine (PTP)‡ where three π^+-moieties (pyridinium moieties) are mutually bridged by the central π-moiety (pyridine). Therefore, given that anion-templated π^+-moieties bind each other more strongly than those of π^+–π and of π–π complexes, the major driving force for the crystal packing in $PTPH_3{\cdot}3X^-$ ($X = NO_3$; Fig. 1a) would be π^+–π^+, while other π-interactions would assist the overall stabilization of the crystal packing, but not necessarily in energetically favourable orientations. The X-ray crystallographic study§ reveals the presence of a triply protonated PTP molecule, three nitrate anions and a solvent water molecule constituting the asymmetric unit. The pyridyl nitrogen atoms of Rings 1A, 1B and 3

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† Electronic supplementary information (ESI) available: Crystallographic information file (CIF) of the title complex; Tables S1–S3 contains geometrical parameters related to noncovalent interactions and Table S4 contains structure refinement parameters; Fig. S1–S3 illustrate the $NO_3{\cdots}NO_3$ interactions, stacking arrangement and different non-π interactions respectively. CCDC 867497. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2ce26577j

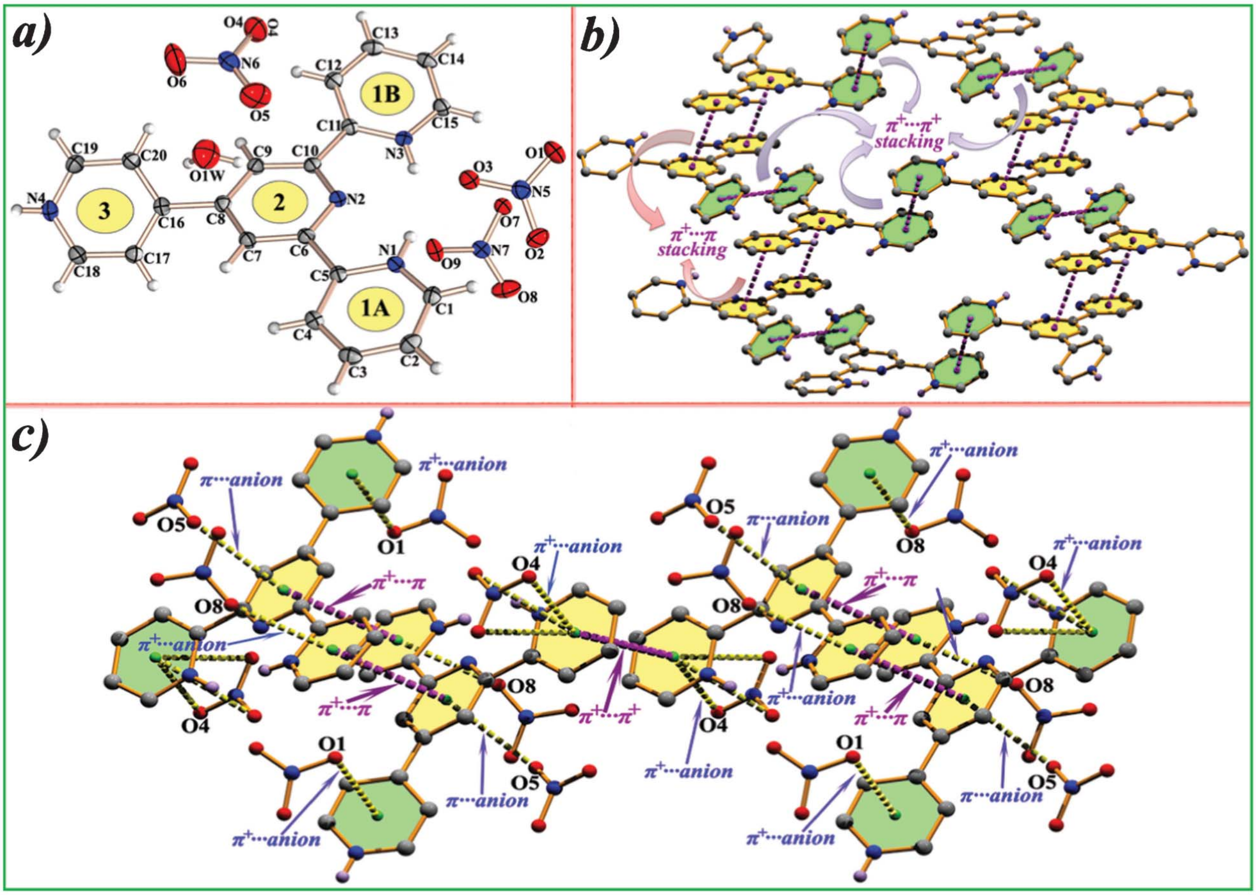

Fig. 1 (a) An ORTEP (anisotropic displacement ellipsoid) diagram with atom numbering scheme of the title complex. Thermal ellipsoids are drawn at the 30% probability level. Rings 1A, 1B and 3 are aromatic cations (π^+), while Ring 2 is neutral (π); (b) stacking arrangement of $PTPH_3$ molecules through π^+–π^+ and π^+–π interactions; (c) stacking arrangement of $PTPH_3$ molecules through π^+–π^+, π^+–π, π^+–anion and π–anion interactions.

of the $PTPH_3$ molecule are protonated at the stipulated reaction condition.

The solid-state structure of the title complex includes a combination of N–H···O, O–H···O, C–H···O hydrogen bonds, π^+–π, π^+–π^+, π^+···anion, π···anion and π^-–π^- interactions (Tables S1–S3, ESI†). The molecular packing in the complex is such that the π^+–π and π^+–π^+ stacking interactions between the pyridinium and pyridine rings of the partner molecules are optimized. The pyridinium ring 1A of the molecules at (x, y, z) is in contact with the pyridine ring 2 of the partner molecule at $(1 - x, 1 - y, 1 - z)$ with a ring centroid separation of 3.692(1) Å. Another pyridinium ring 3 at (x, y, z) is in contact with ring 1A of the neighboring molecule at $(2 - x, 1 - y, 1 - z)$ with a ring centroid separation of 4.316(1) Å (Table S2, ESI†). These two types of π^+–π and π^+–π^+ stacking interactions lead to the formation of stacked ribbon-like structure (Fig. 1b). Moreover, another pyridinium ring 1B of the molecules at (x, y, z) and $(1 - x, -y, -z)$ are strictly parallel, with an interplanar spacing of 3.293(1) Å and an inter-centroid separation of 3.528(1) Å, corresponding to a ring offset of 1.265 Å. This π^+–π^+ stacking interaction combines the ribbons into a π-stack layered assembly (Fig. 1b). Interestingly, three oxygen atoms (O4, O5 and O6) of the nitrate anion are in contact in either side of the π^+–π^+ stacked pyridinium 1B rings in the molecule at (x, y, z) and $(1 + x, y, z)$, where the separation distances between the oxygen atoms and ring centroids are 3.697(2), 3.488(2) and 3.756(2) Å respectively (Table S3, ESI†). The shortest separation distances are below the sum of the van der Waals radii, reflecting significant anion···π^+ interaction by which the entire assembly exhibits a unique combination of anion···π^+/π^+–π^+/π^+···anion network (Fig. 1c). In another substructure, O5 and O8 atoms are in contact with the central pyridine ring 2 and pyridinium ring 1A respectively, which results in a unique combination of non-covalent interactions, to be designated as anion···π/π–π^+/π^+···anion network (Fig. 1c). The nitrate anions also occupy the interlayer regions by NO_3···NO_3 interactions (Fig. S1, ESI†). The water oxygen atom O1w acts as double donor to the nitrate oxygen atoms O4 and O6 to generate a $R_4^4(12)$ type water–nitrate dimeric unit (Table S1, Fig. S2, ESI†). A packing view showing these π^+–π^+, π^+–π, π^+···anion, π^-–π^- interactions and hydrogen bonded synthon has been depicted in Fig. S2, ESI.†

To understand the main driving forces in the crystal packing, we have calculated interaction energies of π^+–π^+, π^+–π, π–anion, π^+–anion and π^-–π^- interactions observed in the crystal structures using DFT-D(B97-D/TZV2P)[10,11] (Fig. 2). As shown in Fig. 2a, the

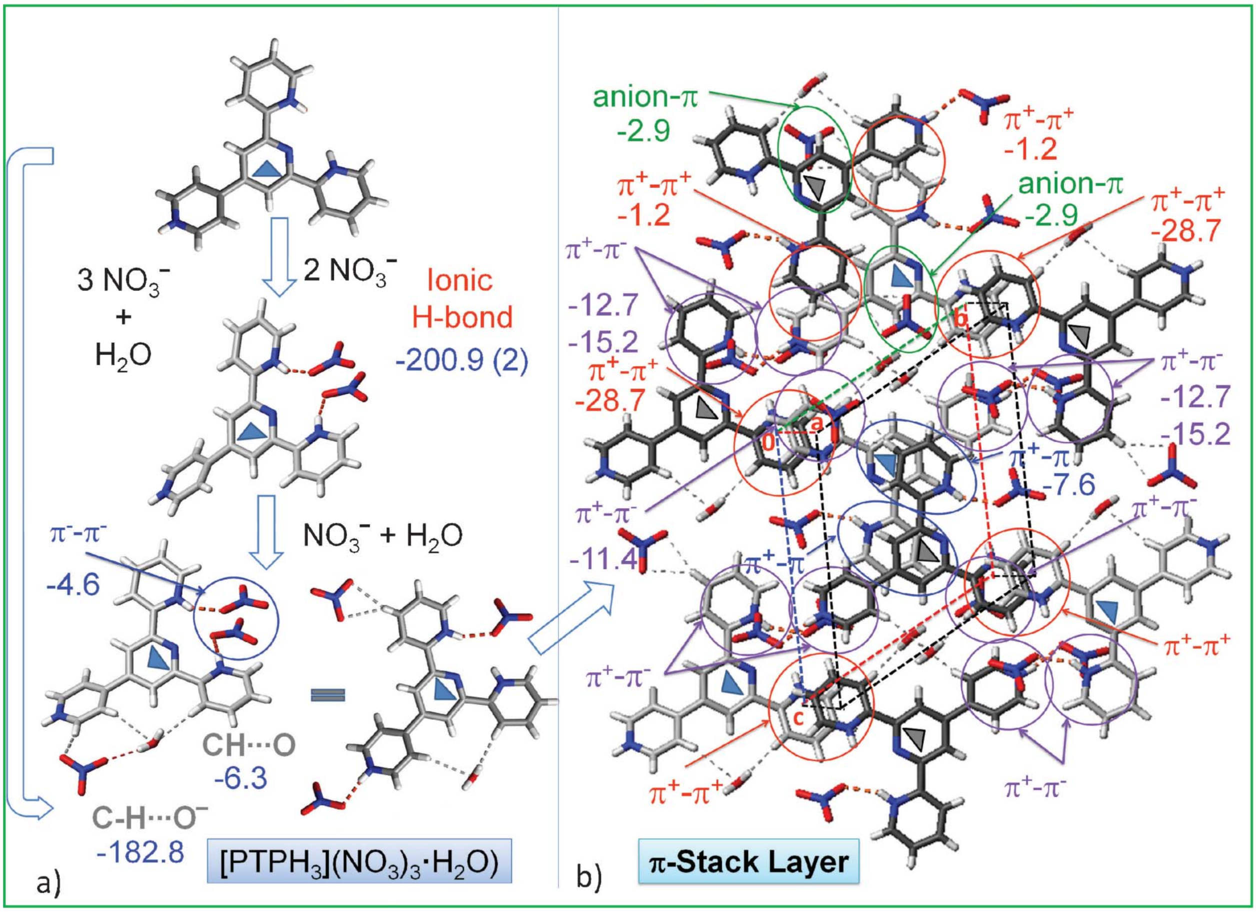

Fig. 2 Dispersion-corrected density functional theory (DFT-D) interaction energies (PBE-D/aVDZ BSSE corrected energies in kcal mol^{-1}). The clusters of [PTPH$_3$](NO$_3$)$_3$·H$_2$O (a) are arranged with diverse π–stacking interactions (b) in accordance with the crystal structure whereby crystal geometries are being replaced with the moiety optimized geometries.

formation of H-bonded clusters between PTPH$_3$, NO$_3$ and H$_2$O would essentially precede crystal packing that involves π-interactions. It should be noted here that NO$_3^-$ is not only an anion but also a π$^-$-system.

In the crystal structure, all the π-interactions are observed in one π-stack layer (Fig. 2b). It is observed that four π$^+$–π$^+$ interactions are located on the four edges of the crystal unit cell (Fig. 2b). Additionally, four π$^+$–anion interactions are also observed inside the unit cell. The binding energies are calculated by computing the energies between the independent interacting moieties whereby the independently optimized moieties would have the geometry of crystal structure. For example, in the π-stack layer, pyridinium–NO$_3^-$ with pyridinium–NO$_3^-$ shows the π$^+$–π$^+$ interaction, while that with pyridine shows the π$^+$–π interaction and so on. The binding energy of each of the four π$^+$–π$^+$ interactions observed on the edge of the unit cell is −28.7 kcal mol^{-1}. Each of the two π$^+$–π interactions located on the center of the unit cell also has large binding energy of −7.6 kcal mol^{-1}. In addition, due to the compact packing of [PTPH$_3$](NO$_3$)$_3$·H$_2$O, all three NO$_3^-$ moieties are positioned in such a way to form π$^+$–anion (*i.e.*, π$^+$–π$^-$) interactions with the π$^+$-rings of other [PTPH$_3$](NO$_3$)$_3$·H$_2$O clusters with the binding energies of −15.2, −12.7 and −11.4 kcal mol^{-1}. Anion–π (or π–π$^-$) interaction and another highly displaced π$^+$–π$^+$ interaction have the respective binding energies of −2.9 and −1.2 kcal mol^{-1}. Meanwhile, the stable [PTPH$_3$](NO$_3$)$_3$·H$_2$O cluster includes cation-templated π$^-$–π$^-$ complexes (−4.6 kcal mol^{-1}) in addition to ionic H-bond and CH···O$^-$–O interactions (Fig. 2 and S3, ESI†). Since the distance between the two nitrogen atoms of NO$_3$···NO$_3$ is 3.24 Å, the interaction between the two NO$_3^-$ moieties of π$^-$ character could be regarded as cation-templated π$^-$–π$^-$ interactions. It is noted here that by keeping the positions of the strongly bound H-bonded clusters of [PTPH$_3$](NO$_3$)$_3$·H$_2$O, the π-interactions are arranged in such a way that some of them are optimally positioned and some are not, so that π$^+$, π$^-$, and π moieties are packed in order to have the overall maximization of stablization due to π-interactions. In this regard, interactions with weaker binding energies are not necessarily representative of the optimal geometry of that kind of interaction.[7,9]

Molecular modelling studies show the π$^+$–π$^+$ interaction as the major driving force of the crystal packing, while other π-interactions assist the overall stabilization of the crystal packing, but not necessarily in energetically favourable orientations. A reassessment of conventional π-systems in the context of this new interaction may shed new light on the already existing knowledge in diverse fields. We believe the π^+–π^+ interaction holds much promise for material design and devices. In addition, we have also addressed a new type of cation-mediated non-covalent interaction between the two π anions of NO_3^- moieties.

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References

‡ The PTP ligand was prepared following the literature method.[12] The PTP ligand (0.5 mmol, 0.313 g) was dissolved in a HNO_3 solution of pH = 1.13 at room temperature (~25.0 °C) by continuous stirring and then filtered to remove any undissolved materials. The filtrate was kept for crystallization at room temperature (~25.0 °C). Block shaped, colorless single crystals were formed after several days from the mother liquor by slow evaporation at room temperature. The crystals were separated by filtration, washed with ice-cold water and then air-dried. Anal. Calcd for $C_{20}H_{19}N_7O_{10}$: C, 46.42%; H, 3.70%; N, 18.94%; found: C, 46.40%; H, 3.71%; N, 18.92%.

§ A crystal with suitable dimensions was mounted on a 'Bruker SMART APEX II' diffractometer equipped with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 150(2) K. The structure was solved by direct methods and refined by full-matrix least squares on F^2 with the SHELX-97 package.[13] All the hydrogen atoms attached to the carbon atoms were placed at their geometrically idealized positions, whereas the remaining hydrogen positions have been determined from the difference Fourier map. A summary of crystal data and relevant refinement parameters are given in Table S4, ESI.† CCDC 867497 contains the supplementary crystallographic data for this paper.

1 (*a*) E. A. Meyer, R. K. Castellano and F. Diederich, *Angew. Chem., Int. Ed.*, 2003, **42**, 1210–1250; (*b*) F. J. M. Hoeben, P. Jonkheijm, E. W. Meijer and A. P. H. Schenning, *J. Chem. Res.*, 2005, **105**, 1491–1546; (*c*) K. S. Kim, P. Tarakeshwar and J. Y. Lee, *Chem. Rev.*, 2000, **100**, 4145–4186; (*d*) C. A. Hunter, K. R. Lawson and C. J. Urch, *J. Chem. Soc., Perkin Trans. 1*, 2001, **2**, 651–669; (*e*) P. Hobza, H. L. Selzle and E. W. Schlag, *Chem. Rev.*, 1994, **94**, 1767–1784; (*f*) K. E. Riley, M. Pitonak, P. Jurecka and P. Hobza, *Chem. Rev.*, 2010, **110**, 5023–5063; (*g*) V. Georgakilas, M. Otyepka, A. B. Bourlinos, V. Chandra, N. Kim, K. C. Kemp, P. Hobza, R. Zboril and K. S. Kim, *Chem. Rev.*, 2012, **112**, 6156–6214.

2 (*a*) S. K. Burley and G. A. Petsko, *Science*, 1985, **229**, 23–28; (*b*) P. Hobza, H. L. Selzle and E. W. Schlag, *J. Chem. Phys.*, 1990, **93**, 5893–5897; (*c*) P. Tarakeshwar, H. S. Choi and K. S. Kim, *J. Am. Chem. Soc.*, 2001, **123**, 3323–3331; (*d*) P. Tarakeshwar, S .J. Lee, J. Y. Lee and K. S. Kim, *J. Chem. Phys.*, 1998, **108**, 7217–7223; (*e*) Z. Xu, N. J. Singh, J. Lim, J. Pan, H. N. Kim, S. Park, K. S. Kim and J. Yoon, *J. Am. Chem. Soc.*, 2009, **131**, 15528–15533; (*f*) Y. K. Kim, H. N. Lee, N. J. Singh, H. J. Choi, J. Y. Xue, K. S. Kim, J. Yoon and M. H. Hyun, *J. Org. Chem.*, 2008, **73**, 301–304.

3 (*a*) C. A. Hunter and J. K. M. Sanders, *J. Am. Chem. Soc.*, 1990, **112**, 5525–5534; (*b*) P. Hobza, H. L. Selzle and E. W. Schlag, *J. Phys. Chem.*, 1996, **100**, 18790–18794; (*c*) A. L. Ringer, M. S. Figgs, M. O. Sinnokrot and C. D. Sherrill, *J. Phys. Chem. A*, 2006, **110**, 10822–10828; (*d*) M. Piacenza and S. Grimme, *J. Am. Chem. Soc.*, 2005, **127**, 14841–14848; (*e*) E. C. Lee, D. Kim, P. Jurecka, P. Tarakeshwar, P. Hobza and K. S. Kim, *J. Phys. Chem. A*, 2007, **111**, 3446–3457; (*f*) S. L. Cockroft, C. A. Hunter, K. R. Lawson, J. Perkins and C. J. Urch, *J. Am. Chem. Soc.*, 2005, **127**, 8594–8595; (*g*) C. A. Hunter, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1584–1586; (*h*) S. K. Min, W. Y. Kim, Y. Cho and K. S. Kim, *Nat. Nanotechnol.*, 2011, **6**, 162–165; (*i*) K. S. Kim, S. Karthikeyan and N. J. Singh, *J. Chem. Theory Comput.*, 2011, **7**, 3471–3477.

4 (*a*) D. A. Dougherty and D. Stauffer, *Science*, 1990, **250**, 1558–1560; (*b*) K. S. Kim, J. Y. Lee, S. J. Lee, T. K. Ha and D. H. Kim, *J. Am. Chem. Soc.*, 1994, **116**, 7399–7400; (*c*) D. A. Dougherty, *Science*, 1996, **271**, 163–168; (*d*) D. Kim, S. Hu, P. Tarakeshwar, K. S. Kim and J. M. Lisy, *J. Phys. Chem. A*, 2003, **107**, 1228–1238; (*e*) K. S. Oh, C.-W. Lee, H. S. Choi, S. J. Lee and K. S. Kim, *Org. Lett.*, 2000, **2**, 2679–2681; (*f*) J. C. Ma and D. A. Dougherty, *Chem. Rev.*, 1997, **97**, 1303–1324.

5 (*a*) D. Quiñonero, C. Garau, A. Frontera, P. Ballester, A. Costa and P. M. Deyà, *J. Phys. Chem. A*, 2005, **109**, 4632–4637; (*b*) D. Kim, P. Tarakeshwar and K. S. Kim, *J. Phys. Chem. A*, 2004, **108**, 1250–1258; (*c*) D. Quiñonero, C. Garau, C. Rotger, A. Frontera, P. Ballester, A. Costa and P. M. Deyà, *Angew. Chem., Int. Ed.*, 2002, **41**, 3389–3392.

6 (*a*) J. Y. Lee, B. H. Hong, W. Y. Kim, S. K. Min, Y. Kim, M. V. Jouravlev, R. Bose, K. S. Kim, I. C. Hwang, L. J. Kaufman, C. W. Wong, P. Kim and K. S. Kim, *Nature*, 2009, **460**, 498–501; (*b*) B. H. Hong, S. C. Bae, C.-W. Lee, S. Jeong and K. S. Kim, *Science*, 2001, **294**, 348–351; (*c*) B. H. Hong, J. Y. Lee, C.-W. Lee, J. C. Kim, S. C. Bae and K. S. Kim, *J. Am. Chem. Soc.*, 2001, **123**, 10748–10749; (*d*) S. K. Seth, D. Sarkar and T. Kar, *CrystEngComm*, 2011, **13**, 4528–4535; (*e*) S. K. Seth, D. Sarkar, A. D. Jana and T. Kar, *Cryst. Growth Des.*, 2011, **11**, 4837–4849; (*f*) S. K. Min, Y. Cho, D. R. Mason, J. Lee and K. S. Kim, *J. Phys. Chem. C*, 2011, **115**, 16247–16257.

7 N. J. Singh, S. K. Min, D. Y. Kim and K. S. Kim, *J. Chem. Theory Comput.*, 2009, **5**, 515–529.

8 (*a*) N. J. Singh, D. Shin, H. M. Lee, H. T. Kim, H.-J. Chang, J. M. Cho, K. S. Kim and S. Ro, *J. Struct. Biol.*, 2011, **174**, 173–179; (*b*) A. Das, A. D. Jana, S. K. Seth, B. Dey, S. R. Choudhury, T. Kar, S. Mukhopadhyay, N. J. Singh, I. C. Hwang and K. S. Kim, *J. Phys. Chem. B*, 2010, **114**, 4166–4170.

9 I. Geronimo, E. C. Lee, N. J. Singh and K. S. Kim, *J. Chem. Theory Comput.*, 2010, **6**, 1931–1934.

10 (*a*) J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865–3868; (*b*) S. Grimme, *J. Comput. Chem.*, 2004, **25**, 1463–1473; (*c*) T. Schwabe and S. Grimme, *Phys. Chem. Chem. Phys.*, 2007, **9**, 3397–3406; (*d*) K. E. Riley, M. Pitoňák, J. Černý and P. Hobza, *J. Chem. Theory Comput.*, 2010, **6**, 66–80.

11 TURBOMOLE V6.0 2009, A Development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989–2007, TURBOMOLE GmbH, since 2007, available from http://www.turbomole.com.

12 (*a*) J. Wang and G. S. Hanan, *Synlett*, 2005, **8**, 1251–1254; (*b*) J. E. Beves, E. L. Dunphy, E. C. Constable, C. E. Housecroft, C. J. Kepert, M. Neuburger, D. J. Price and S. Schaffner, *Dalton Trans.*, 2008, 386–396.

13 G. M. Sheldrick, *SHELXL97, Program for the Refinement of Crystal Structures*, University of Göttingen, Göttingen, Germany, 1997.