

Intriguing $\pi^+-\pi$ Interaction in Crystal Packing

Amrita Das,[†] Atish Dipankar Jana,[‡] Saikat Kumar Seth,[§] Biswajit Dey,[†]
Somnath Ray Choudhury,[†] Tanusree Kar,[§] Subrata Mukhopadhyay,^{*,†} N. Jiten Singh,^{||}
In-Chul Hwang,^{||} and Kwang S. Kim^{*,||}

Department of Chemistry, Jadavpur University, Kolkata 700 032, India, Department of Physics, Sripat Singh College, Jiaganj, Murshidabad, West Bengal 742 123, Department of Materials Science, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700 032, India, and Center for Superfunctional Materials, Department of Chemistry, Pohang University of Science and Technology, San 31, Hyojadong, Namgu, Pohang 790-784, Korea

Received: October 23, 2009; Revised Manuscript Received: February 23, 2010

The $\pi^+-\pi$ interactions are utilized to design the solid-state assembly of host–guest complexes where guests are anions. The doubly protonated MPTPH₂ (MPTP = 4'-(4-methoxyphenyl)-2,2':6',2''-terpyridine) complexed with H₂O and Cl[−] or Br[−] are synthesized, crystallized, and characterized by X-ray analysis. By using the density functional theory calculations which can properly describe the dispersion energy, the assembling phenomena are analyzed in terms of $\pi^+-\pi$ and $\pi-\pi$ interactions as well as H-bonding interactions. The planar structure of MPTPH₂(Cl)₂·2H₂O or MPTPH₂(Br)₂·2H₂O facilitates the crystal packing, since the $\pi^+-\pi$ interactions play an important role in the solid-state assembly.

Introduction

Diverse types of π interactions¹ including H- π ,² $\pi-\pi$,³ cation- π ,⁴ and anion- π ⁵ interactions have been widely utilized for molecular recognition, molecular assembly, and crystal packing of organic materials, nanomaterials, and biomolecules.⁶ Recently, it was found that the $\pi^+-\pi$ interactions are much stronger than the $\pi-\pi$ interactions and H- π interactions but different from typical nonaromatic 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, they can be utilized for useful anion receptors. Anion binding and sensing is an active area of research aimed at building self-acting molecular devices.⁸ Design and synthesis of receptors to bind anionic guests is highly demanding due to its potential applications in biological processes and environmental remediation.⁹ In such a design, the host–guest complementarity has been widely exploited. It would be particularly useful to design solid-state assembly of host–guest complexes for anion-templated molecular devices. Then, the geometrical structure of a receptor molecule influences the solid-state assembly of host–guest complexes and the mode of anion binding. In this case, as complementary species of anions, the positively charged π systems can be exploited; therefore, the $\pi^+-\pi$ interactions would play an important role in π -stacking. Indeed, here we report such systems, MPTPH₂, i.e., doubly protonated MPTP complexed with H₂O and Cl[−] (**1**) or Br[−] (**2**). These systems have been synthesized, crystallized, and characterized with X-ray analysis. The origin of the interaction energies for such assembling is discussed with density functional theory (DFT)

employing the novel exchange-correlation functional¹⁰ so that the dispersion energy can be properly obtained.

Experimental Section

Materials and Measurements. All reactions were carried out under aerobic conditions and in an aqueous medium. All chemicals used were of reagent grade and used as received. Freshly boiled, doubly distilled water was used throughout the synthetic procedures. Elemental analyses (C, H, N) were performed on a Perkin-Elmer 240C elemental analyzer.

Synthesis of [MPTPH₂(Cl)₂·2H₂O (1**) and [MPTPH₂(Br)₂·2H₂O (**2**)]** (MPTP = 4'-(4-Methoxyphenyl)-2,2':6',2''-terpyridine). The MPTP ligand was prepared following the literature method.¹¹ Aqueous suspensions of MPTP ligand (1.0 mM, 0.339 g) were dissolved at room temperature (~25.0 °C) by adding HCl or HBr with continuous stirring until the pH reached nearly 1.0 and then filtered to remove any undissolved materials. The yellow filtrate in either situation was kept for crystallization at room temperature (~25.0 °C). Block shaped yellow single crystals of **1** and block shaped reddish yellow single crystals of **2** were separated 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 C₂₂H₂₃N₃O₃Cl₂ (**1**): C, 58.93; H, 5.17; N, 9.37%. Found: C, 58.78; H, 5.05; N, 9.29%. Anal. Calcd for C₂₂H₂₃N₃O₃Br₂ (**2**): C, 49.18; H, 4.31; N, 7.82%. Found: C, 49.02; H, 4.25; N, 7.74%.

X-ray Crystal Structure Determination of **1 and **2**.** Crystals with suitable dimensions for **1** and **2** were mounted on a “Bruker SMART APEX II” diffractometer equipped with graphite monochromated Mo K α radiation (λ = 0.71073 Å) at 150(2) K. A total of 10098 and 9841 reflections were measured for **1** and **2**, respectively. A total of 3435 [$I > 2\sigma(I)$] and 2809 [$I > 2\sigma(I)$] data for **1** and **2**, respectively, were used for solution and refinement by full-matrix least-squares on F^2 with the SHELX-97 package.¹² The non-hydrogen atoms were refined anisotropically. The methyl hydrogens, hydrogens attached to

* To whom correspondence should be addressed. E-mail: smukhopadhyay@chemistry.jdvu.ac.in (S.M.); kim@postech.ac.kr (K.S.K.).

[†] Jadavpur University.

[‡] Sripat Singh College.

[§] Indian Association for the Cultivation of Science.

^{||} Pohang University of Science and Technology.

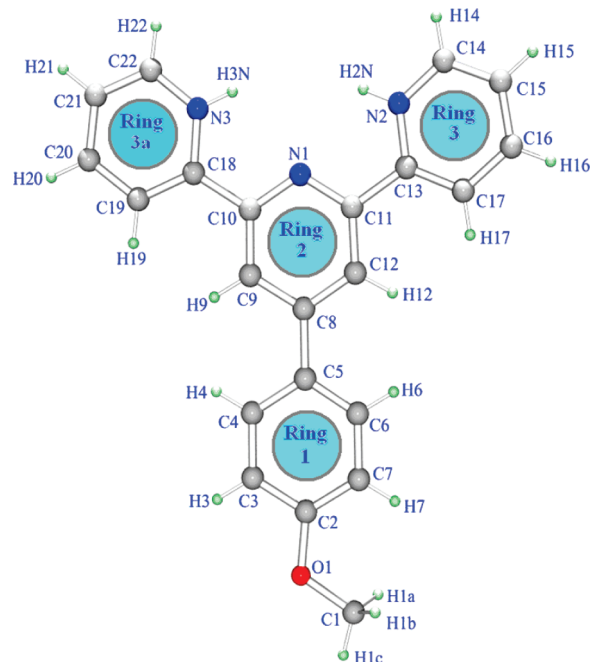


Figure 1. MPTPH₂ species shown with a common atom numbering scheme as found in complexes **1** and **2**. Rings 3 and 3a are positively charged due to the protonation. (Crystallographic data for **1** and **2** are given in the Supporting Information.)

ring nitrogen atoms, and water hydrogen positions have been determined from difference Fourier map and refined isotropically. All other hydrogen atoms were placed at their geometrically idealized positions. In **1**, one of the oxygen atoms (O2W) of the two solvent water molecules (O1W and O2W) is disordered over three distinct sites and the hydrogen atoms attached to this water molecule could not be located from the difference Fourier map. No attempt was made to put the hydrogen atoms at their calculated positions for these disordered components because this water molecule has little relevance to the main theme of the present work. The final *R* values are 0.0537 and 0.0496 for **1** and **2**, respectively. Crystallographic data and structure refinement and important H-bonding parameters for **1** and **2** are given in the Supporting Information (Tables I and II). CCDC Nos. 743500 (for **1**) and 743501 (for **2**) contain the supplementary crystallographic data for this paper.

Results and Discussion

Characterization and X-ray Analysis of [MPTPH₂](Cl)₂·2H₂O (1**) and [MPTPH₂](Br)₂·2H₂O (**2**)** (MPTP = 4'-(4-Methoxyphenyl)-2,2':6,2''-terpyridine). MPTP is a particularly suitable receptor for binding chloride and bromide anions. It forms a 1:2 host:guest complex in the solid state by binding the halide ions at two of the three sites available. At pH ~1, the parent molecules get protonated, enhancing their binding ability.

The X-ray structural analysis of the single crystal reveals that the asymmetric units of both **1** and **2** consist of one doubly protonated MPTP molecule, two water molecules, and two halide ions (chloride for **1** and bromide for **2**). The ball-and-stick diagram of the doubly protonated MPTP molecule with a common atom-labeling scheme is depicted in Figure 1. The MPTPH₂ species is nonplanar, consisting of one phenyl ring and three pyridine rings. The N atoms (N1, N2, and N3) on the three adjacent pyridine rings generate an isosceles triangle with N1 on the tip of the central pyridine ring, where N1 forms the

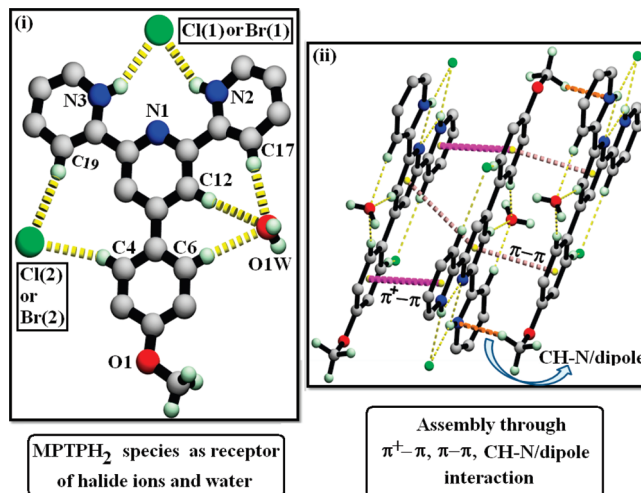


Figure 2. (i) Role of MPTPH₂ species as a receptor for halide ions as well as water molecules by forming the MPTPH₂:(2X, H₂O) complex (X = Cl/Br). (ii) Supramolecular trimeric species of MPTPH₂:(2X, H₂O) units formed through $\pi^+-\pi$ (pink), $\pi-\pi$ (magenta), and CH \cdots N/dipole (orange) interactions.

apex and N2 and N3 form the base of this triangle. An interesting feature is that N2 and N3 atoms get protonated under the stipulated reaction conditions. This protonation effectively renders the MPTPH₂ species the capability to function as host molecules for anionic halide guests. In the solid state, these doubly protonated MPTPH₂ species form a 1:2 host:guest complex. Two halide ions nicely fit into two basins of the MPTPH₂ species through the (N-H)⁺ \cdots X⁻ ionic H-bond¹³ and CH ^{δ +} \cdots X⁻ interactions¹⁴ (X = Cl, Br) (Figure 2i).

As can be seen from Figure 2i, one of the halide ions X(1) [X(1): Cl1 for **1**, Br1 for **2**] is accommodated in one of the basins of the MPTPH₂ species along its symmetry axis (passing through O1 and N1) with N2-H2 \cdots X(1) and N3-H3 \cdots X(1) hydrogen bonds, while the other halide ion X(2) [X(2): Cl2 for **1**, Br2 for **2**] is also accommodated with C4-H4 \cdots X(2) and C19-H19 \cdots X(2) hydrogen bonds at one of the side basins of the MPTPH₂ species. A water molecule (O1W) also binds in the other side basin through C6-H6 \cdots O1W, C12-H12 \cdots O1W, and C17-H17 \cdots O1W hydrogen bonds.

Binding of halide ions and water molecules by the MPTPH₂ species is responsible for the solid-state packing of the MPTPH₂:(2X, H₂O) host:guest complexes. Due to the presence of anionic halide guests, the MPTPH₂ species interact strongly among themselves through π -interactions of $\pi^+-\pi$ and $\pi-\pi$ types, which leads to the π -stacking formation (Figure 2ii). As an intradimer interaction, one can note the $\pi^+-\pi$ and $\pi-\pi$ interactions of ring 1 \cdots ring 2, ring 1 \cdots ring 3a, and ring 2 \cdots ring 3 (Figure 2ii, Table 1). This π -stacking leads to the formation of a layer of π -systems along the crystallographic *a*-axis.

Then, due to the self-complementary nature, adjacent ribbons are joined at their edges through the formation of R₄²(8) supramolecular water-halide synthon, resulting in a 2-D supramolecular assembly in the *ab* plane (Figure 3). This self-complementarity arises from the affinity of halide ions toward water molecules. This synthon is energetically stable and has been observed¹⁵ previously, but its importance in supramolecular organization in many of the crystalline compounds has not been recognized so far. The R₄²(8) water-halide synthon found in **1** and **2** is a stable water-halide motif found in many other hydrated crystalline materials (a preliminary Cambridge structural database (CSD version 5.27, November 2005 release)

TABLE 1: Geometrical Parameters (Distance in Å) for the π -Stacking Moieties Involved in the $\pi^+-\pi$ Interactions for Complexes 1 and 2

rings $i-j$	symmetry	Rc ^a	R1v ^b	R2v ^c
Complex 1				
rings 1–3a	$-x, 1-y, -z$	3.687(3)	3.293	3.257
rings 3a–1	$-x, 1-y, -z$	3.687(3)	3.257	3.293
rings 1–2	$-x, 1-y, -z$	3.613(2)	3.310	3.251
rings 2–1	$-x, 1-y, -z$	3.613(2)	3.251	3.310
rings 2–2	$-x, 1-y, -z$	3.994(2)	3.326	3.326
Complex 2				
rings 1–3a	$2-x, 1-y, 1-z$	3.719(3)	3.317	3.339
rings 3a–1	$2-x, 1-y, 1-z$	3.719(3)	3.339	3.317
rings 1–2	$3-x, 1-y, 1-z$	3.615(3)	3.367	3.304
rings 2–1	$3-x, 1-y, 1-z$	3.615(3)	3.304	3.367
rings 2–2	$2-x, 1-y, 1-z$	4.101(2)	3.377	3.378

^a Centroid distance between rings i and j . ^b Vertical distance from ring centroid i to ring j . ^c Vertical distance from ring centroid j to ring i .

search reveals 207 hydrated crystal structures where this motif plays an important role in supramolecular organization). This motif may be assumed as an analogue of the water tetramer¹⁶ where two water molecules are replaced by two halide ions.

Structural Analysis and Interaction Forces for Crystal Packing. Density functional theory (DFT) calculations using the B97-D/TZV2P basis set (DFT-D)¹⁰ are performed to investigate the structure and energetics upon the initial complexation of MPTPH₂ with two Cl[−] ions together with one H₂O and the subsequent π -stacking process of MPTPH₂:(2Cl–H₂O) (Figure 4). The calculations were carried out using TURBO-MOLE V5.10.¹⁷ The gas-phase-optimized geometry of MPTPH₂ is nonplanar, whereby both the pyridinium rings are $\sim 18^\circ$ twisted from the middle pyridine ring plane, and the methoxybenzene ring is twisted by $\sim 23^\circ$. The methoxybenzene ring remains twisted by $\sim 23^\circ$ even with the coordination of two Cl[−] anions to the basins of MPTPH₂, but the pyridinium rings are in a plane with the pyridine ring. An additional coordination of H₂O into the third basin of MPTPH₂ induces a complete planarity on the whole ring system. This results in the elongated

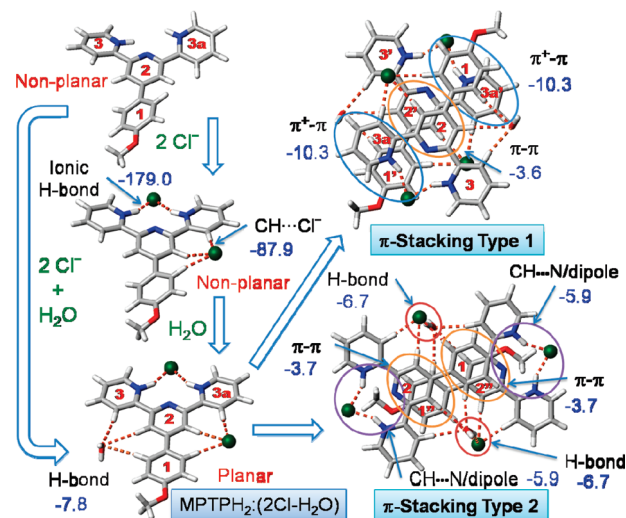


Figure 4. DFT-optimized geometries of MPTPH₂, MPTPH₂:2Cl, MPTPH₂:(2Cl–H₂O), and the MPTPH₂:(2Cl–H₂O) dimer involving two types of π -stacking interactions in accordance with the crystal coordinate of complex 1. Interaction energies (in kcal/mol) for each of the interaction types are displayed in blue color. Rings of MPTPH₂ are labeled as 1, 2, 3a, and 3. The interacting rings of the second and third MPTPH₂ of the π -stacking type 1 and 2 are, respectively, labeled as prime (') and double prime (').

delocalization of the π -electron density; therefore, the two positive charges on the pyridinium moieties are no longer completely localized on the two protonated rings. Natural bond orbital (NBO) charge analysis (Figure 5) shows that in MPTPH₂ the total charge of the system is concentrated in two pyridinium rings (having ~ 0.9 au in each ring). The sum of atomic charges of pyridine, benzene ring of methoxybenzene, and methoxy are, respectively, -0.06 , 0.35 , and -0.04 au. In MPTPH₂:(2Cl–H₂O), the following is observed: (a) there is charge transfer from both of the Cl[−] to the MPTPH₂; (b) the sum of atomic charges of each pyridinium ring is reduced to 0.7 au; (c) the sum of atomic charges of the pyridine ring is zero; (d) the sums of atomic charges of the benzene ring of methoxybenzene and methoxy are, respectively, 0.24 and -0.14 au.

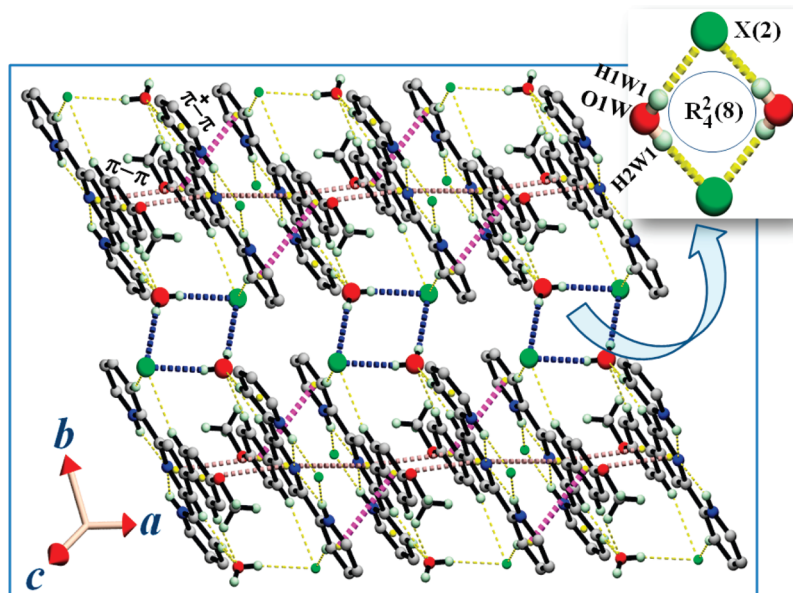


Figure 3. Stable water–halide cluster ($2\text{H}_2\text{O}\cdot 2\text{X}$ [X, Cl/Br]) that exists in 1 and 2. In both cases, the $\text{R}_4^2(8)$ water–halide synthon acts as supramolecular glue between the ribbons of MPTPH₂ species formed by $\pi^+-\pi$, $\pi-\pi$, and $\text{CH}\cdots\text{N/dipole}$ interactions which lead to a 2-D sheet in the ab plane ($\text{CH}\cdots\text{N/dipole}$ interactions are omitted for clarity).

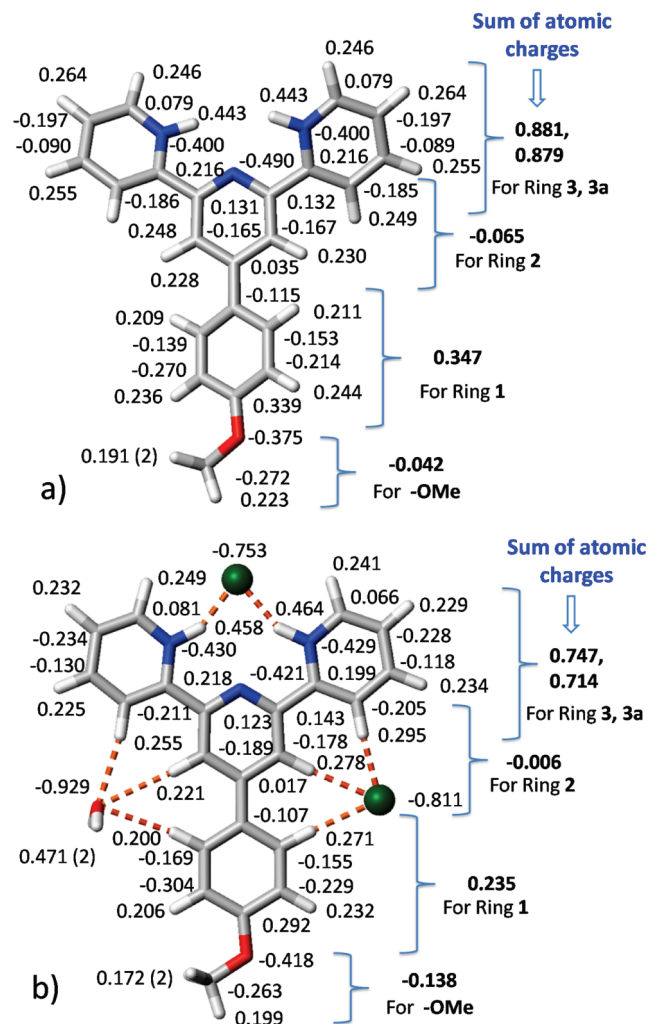


Figure 5. NBO charges of MPTPH₂ and MPTPH₂:(2Cl-H₂O).

Hence, these changes are observed due to charge transfer from Cl⁻ to MPTPH₂ and π -electron delocalization due to the ring planarity of MPTPH₂ in MPTPH₂:(2Cl-H₂O). For our further discussion, the protonated rings will be designated simply as π^+ systems, while the nonprotonated rings, as π systems.

Two monomers of MPTPH₂:(2Cl-H₂O) can be stacked to form two different types of π -stacking, type 1 and type 2 (Figure 4). The type-1 π -stacking shows two $\pi^+-\pi$ interactions and one $\pi-\pi$ interaction, while the type-2 π -stacking shows two of both $\pi-\pi$ and CH \cdots N/dipole interactions. The dimerization in type-2 π -stacking also involves the formation of two H-bonds between H₂O bound in one basin of MPTPH₂:(2Cl-H₂O) and Cl⁻ bound to another basin of the second MPTPH₂:(2Cl-H₂O). These interaction energies are calculated by computing the energies between the independent interacting moieties. For example, in the type-1 π -stacking, pyridinium with methoxybenzene shows the $\pi^+-\pi$ interaction, while that of pyridine-pyridine interaction shows the $\pi-\pi$ interaction.

Hence, in the type-1 π -stacking, the interaction energy of the $\pi^+-\pi$ interaction is -10.3 kcal/mol, while that of the $\pi-\pi$ interaction is -3.6 kcal/mol.¹⁸ Similarly, in the type-2 π -stacking, the $\pi-\pi$ interaction shows an interaction energy of -3.7 kcal/mol. The methyl group of CH₃O- forms the CH \cdots N (of pyridine) and CH \cdots dipole (of N⁺-H \cdots Cl⁻) interaction with an energy of -5.9 kcal/mol, while the H-bond interaction energy between Cl⁻ of MPTPH₂:(2Cl-H₂O) and the water molecule on the top/bottom is -6.7 kcal/mol. The trimeric form of

MPTPH₂:(2Cl-H₂O) consisting of the two types of π -stacking interactions is bound, from both upper and lower sides, by two H-bonds of H₂O in the middle of MPTPH₂:(2Cl-H₂O) with two bound Cl⁻ on the upper and lower sites of MPTPH₂:(2Cl-H₂O). The water-halide hydrogen bonds act as supramolecular glue between π -stacked MPTPH₂:(2Cl-H₂O) layers.

Conclusion

Nonbonding intermolecular interactions involving aromatic rings are crucial in diverse areas of chemistry and biology. Here, we have shown that the $\pi^+-\pi$ interactions play an important role in complexation and packing of molecules in the solid state, both from crystallographic and theoretical studies. There would be a strong possibility of utilizing this force in designing functional materials. Indeed, we have shown that the doubly protonated MPTP receptor forms an anion-complexed assembly of the host-guest supramolecules. The binding of the halide ions by the receptor is achieved by overcoming the competition with that by the solvent water molecules. Upon complexing of MPTPH₂ with two Cl⁻ and one H₂O, MPTPH₂:(2Cl-H₂O) becomes planar. The packing in the solid state is governed dominantly by the $\pi^+-\pi$ interaction. We have also noted that in this process a water tetramer-like water-halide assembly is formed and acts as supramolecular glue between π -stacked MPTPH₂:(2Cl-H₂O) layers.

Acknowledgment. A.D. gratefully acknowledges University Grants Commission (New Delhi) for a research fellowship under the scheme "UGC Research Fellowship in Science for Meritorious Students 2007-2008". S.M. is grateful to UGC-CAS programme in the Department of Chemistry, Jadavpur University, for financial support of this work. S.K.S. is grateful to the DST-funded National Single Crystal X-ray Diffraction facility at the Department of Inorganic Chemistry, IACS, Kolkata 700 032, India, for crystal data collection. K.S.K. acknowledges the support of KOSEF (WCU: R32-2008-000-10180-0, EPB Center: 2009-0063312), BK21(KRF), GRL (KICOS), and KISTI (KSC-2008-K08-0002). A.D.J. acknowledges the financial assistance from UGC India through its research award No. F. 30-1/2009 (SA-II).

Supporting Information Available: Crystallographic data and refinement and important H-bonding parameters for compounds **1** and **2**; B97-D/TZV2P-optimized atomic coordinates and total energy values of MPTPH₂, MPTPH₂:2Cl, and MPTPH₂:(2Cl-H₂O); coordinates used for B97-D/TZV2P single point energy calculations of π -stacking, type 1 and type 2. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References and Notes

- (1) (a) Kim, K. S.; Tarakeshwar, P.; Lee, J. Y. *Chem. Rev.* **2000**, *100*, 4145-4185. (b) Hunter, C. A.; Lawson, K. R.; Urch, C. J. *J. Chem. Soc., Perkin Trans.* **2001**, *2*, 651-669.
- (2) (a) Burley, S. K.; Petsko, G. A. *Science* **1985**, *229*, 23-28. (b) Tarakeshwar, P.; Choi, H. S.; Kim, K. S. *J. Am. Chem. Soc.* **2001**, *123*, 3323-3331. (c) Gazit, E. *FASEB J.* **2002**, *16*, 77-83. (d) Lee, E. C.; Hong, B. H.; Lee, J. Y.; Kim, J. C.; Kim, D.; Kim, Y.; Tarakeshwar, P.; Kim, K. S. *J. Am. Chem. Soc.* **2005**, *127*, 4530-4537. (e) Cockroft, S. L.; Hunter, C. A. *Chem. Commun.* **2009**, 3961-3963. (f) Xu, Z.; Singh, N. J.; Lim, J.; Pan, J.; Kim, H. N.; Park, S.; Kim, K. S.; Yoon, J. *J. Am. Chem. Soc.* **2009**, *131*, 15528-15533. (g) Kim, Y. K.; Lee, H. N.; Singh, N. J.; Choi, H. J.; Xue, J. Y.; Kim, K. S.; Yoon, J.; Hyun, M. H. *J. Org. Chem.* **2008**, *73*, 301-304.
- (3) (a) Hobza, P.; Sponer, J. *J. Am. Chem. Soc.* **2002**, *124*, 11802-11808. (b) Sponer, J.; Jurecka, P.; Hobza, P. *J. Am. Chem. Soc.* **2004**, *126*, 10142-10151. (c) Sinnokrot, M. O.; Valeev, E. F.; Sherrill, C. D. *J. Am. Chem. Soc.* **2002**, *124*, 10887-10893. (d) Tsuzuki, S.; Honda, K.; Uchimaru,

- T.; Mikami, M.; Tanabe, K. *J. Am. Chem. Soc.* **2002**, *124*, 104–112. (e) Piacenza, M.; Grimme, S. *J. Am. Chem. Soc.* **2005**, *127*, 14841–14848. (f) Lee, E. C.; Kim, D.; Jurecka, P.; Tarakeshwar, P.; Hobza, P.; Kim, K. S. *J. Phys. Chem. A* **2007**, *111*, 3446–3457. (g) Cockroft, S. L.; Hunter, C. A.; Lawson, K. R.; Perkins, J.; Urch, C. J. *J. Am. Chem. Soc.* **2005**, *127*, 8594–8595. (h) Hunter, C. A.; Sanders, J. K. M. *J. Am. Chem. Soc.* **1990**, *112*, 5525–5534.
- (4) (a) Dougherty, D. A.; Stauffer, D. *Science* **1990**, *250*, 1558–1560. (b) Kim, K. S.; Lee, J. Y.; Lee, S. J.; Ha, T.-K.; Kim, D. H. *J. Am. Chem. Soc.* **1994**, *116*, 7399–7400. (c) Zacharias, N.; Dougherty, D. A. *Trends Pharmacol. Soc.* **2002**, *23*, 281–287. (d) Kim, D.; Hu, S.; Tarakeshwar, P.; Kim, K. S.; Lisy, J. M. *J. Phys. Chem. A* **2003**, *107*, 1228–1238. (e) Yi, H.-B.; Diefenbach, M.; Choi, Y. C.; Lee, E. C.; Lee, H. M.; Hong, B. H.; Kim, K. S. *Chem.—Eur. J.* **2006**, *12*, 4885–4892.
- (5) (a) Quinonero, D.; Garau, C.; Frontera, A.; Ballester, P.; Costa, A.; Deya, P. M. *J. Phys. Chem. A* **2005**, *109*, 4632–4637. (b) Kim, D.; Tarakeshwar, P.; Kim, K. S. *J. Phys. Chem. A* **2004**, *108*, 1250–1258. (c) Quinonero, D.; Garau, C.; Rotger, C.; Frontera, A.; Ballester, P.; Costa, A.; Deya, P. M. *Angew. Chem., Int. Ed.* **2002**, *41*, 3389–3392. (d) Kim, D.; Lee, E. C.; Kim, K. S.; Tarakeshwar, P. *J. Phys. Chem. A* **2007**, *111*, 7980–7986.
- (6) (a) Lee, J. Y.; Hong, B. H.; Kim, W. Y.; Min, S. K.; Kim, Y.; Jouravlev, M. V.; Bose, R.; Kim, K. S.; Hwang, I.-C.; Kaufman, L. J.; Wong, C. W.; Kim, P.; Kim, K. S. *Nature* **2009**, *460*, 498–501. (b) Desiraju, G. R. *Angew. Chem., Int. Ed.* **2007**, *46*, 8342–8356. (c) Meyer, E. A.; Castellano, R. K.; Diederich, F. *Angew. Chem., Int. Ed.* **2003**, *42*, 1210–1250. (d) Hong, B. H.; Lee, J. Y.; Lee, C.-W.; Kim, J. C.; Bae, S. C.; Kim, K. S. *J. Am. Chem. Soc.* **2001**, *123*, 10748–10749. (e) Hoebe, F. J. M.; Jonkheijm, P.; Meijer, E. W.; Schenning, A. P. H. J. *Chem. Rev.* **2005**, *105*, 1491–1546. (f) Singh, N. J.; Lee, H. M.; Suh, S. B.; Kim, K. S. *Pure Appl. Chem.* **2007**, *79*, 1057–1075.
- (7) Singh, N. J.; Min, S. K.; Kim, D. Y.; Kim, K. S. *J. Chem. Theor. Comput.* **2009**, *5*, 515–529.
- (8) (a) Khuong, T.-A. V.; Nuñez, J. E.; Godinez, C. E.; Garcia-Garibay, M. A. *Acc. Chem. Res.* **2006**, *39*, 413–422. (b) Best, M. D.; Tobey, S. L.; Anslyn, E. V. *Coord. Chem. Rev.* **2003**, *240*, 3–15.
- (9) (a) Singh, N. J.; Jun, E. J.; Chellappan, K.; Thangadurai, D.; Chandran, R. P.; Hwang, I.-C.; Yoon, J.; Kim, K. S. *Org. Lett.* **2007**, *9*, 485–488. (b) Gale, P. A.; Garcia-Garrido, S. E.; Garric, J. *Coord. Chem. Rev.* **2008**, *37*, 151–190. (c) Antonisse, M. M. G.; Reinhoudt, D. N. *Chem. Commun.* **1998**, 443–448. (d) Miyaji, H.; Sato, W.; Sessler, J. L. *Angew. Chem., Int. Ed.* **2000**, *39*, 1777–1780. (e) Mizuno, T.; Wei, W.-H.; Eller, L. R.; Sessler, J. L. *J. Am. Chem. Soc.* **2002**, *124*, 1134–1135. (f) Yoon, J.; Kim, S. K.; Singh, N. J.; Kim, K. S. *Chem. Soc. Rev.* **2006**, *35*, 355–360.
- (10) (a) Furche, F.; Ahlrichs, R. *J. Chem. Phys.* **2002**, *117*, 7433–7447. (b) Grimme, S. *J. Comput. Chem.* **2004**, *25*, 1463–1473. (c) Schwabe, T.; Grimme, S. *Phys. Chem. Chem. Phys.* **2007**, *9*, 3397–3406.
- (11) (a) Anthonysamy, A.; Balasubramanian, S.; Chinnakali, K.; Fun, H.-K. *Acta Crystallogr.* **2007**, *E63*, o1148–o1150. (b) Anthonysamy, A.; Balasubramanian, S.; Shanmugaiyah, V.; Mathivanan, N. *Dalton Trans.* **2008**, 2136–2143.
- (12) Sheldrick, G. M. *SHELXL97: Program for the Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997.
- (13) Llinares, J. M.; Powell, D.; Bowman-James, K. *Coord. Chem. Rev.* **2003**, *240*, 57–75.
- (14) Ihm, H.; Yun, S.; Kim, H. G.; Kim, J. K.; Kim, K. S. *Org. Lett.* **2002**, *4*, 2897–2900.
- (15) Junk, P. C.; Kepert, C. J.; Semenova, L. I.; Skelton, B. W.; White, A. H. *Z. Anorg. Allg. Chem.* **2006**, *632*, 1293–1302.
- (16) Lee, H. M.; Suh, S. B.; Lee, J. Y.; Tarakeshwar, P.; Kim, K. S. *J. Chem. Phys.* **2000**, *112*, 9759–9772.
- (17) (a) Ahlrichs, R.; Bär, M.; Häser, M.; Kälmler, C. *Chem. Phys. Lett.* **1989**, *162*, 165–169. (b) Eichkorn, K.; Treutler, O.; Oehm, H.; Häser, M.; Ahlrichs, R. *Chem. Phys. Lett.* **1995**, *242*, 652–660.
- (18) Mishra, B. K.; Sathyamurthy, N. *J. Phys. Chem. A* **2005**, *109*, 6–8.

JP910129U