Dibenzylimidazolium Halides: From Complex Molecular Network in Solid State to Simple Dimer in Solution and in Gas Phase

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1,3-Dibenzylimidazolium bromide has been synthesized and the nature of the interactions between cations and anions has been studied in the solid state, in solution and in the gas phase. The cohesion of the crystal is ensured by a combination of hydrogen bonds, and aromatic stacking interactions. In solution and in the gas phase, the supramolecular structural organization due to T-stacking is maintained to a great extent.

Introduction

Over the last years, organic chemists in academia and industry have been excited about the prospect of a new green chemical revolution based on ionic liquids (ILs) that could dramatically reduce the use of hazardous and polluting organic solvents.[1,2] ILs are defined as special "molten salts" with melting points below 100 °C. Although these compounds have been known since the end of the 19th century, it was only at the beginning of the 1990s that this class of fluids entered the chemistry scene, in particular 1,3-dialkylimidazolium halides that constitute one of the most popular and best studied classes of ILs.[2] ILs are generally used as solvents in organic synthesis and organometallic catalysis, enzymatic catalysis, separation processes, nanochemistry, electrochemistry and as new materials.[3]

Much of the interest in imidazolium salts is due to their unique physicochemical properties.[4] In fact, they differ significantly from "classical" dipolar organic solvents. Recent studies have demonstrated that pure 1,3-disubstituted imidazolium ILs are better described as hydrogen-bonded polymeric supramolecules.[5] This illustrates the importance of studying the structures and interactions developped in imidazolium-based ILs for both fundamental and practical applications. Supramolecular organization is a general trend for imidazolium-based ILs in the solid phase and is proposed to be maintained to a great extent in the liquid or gas phase.[5] Imidazolium-based ILs possess preorganized structures mainly through hydrogen bonds that induce structural directionality contrary to classical salts in which the aggregates are mainly formed through ionic bonds (charge-ordering structure).[5] Further supramolecular interactions developed in imidazolium-based ILs are π-stacking interactions, aliphatic interactions and dipolarizability/polarizability.[6] The dilution of these fluids occurs with a partial disruption of the hydrogen bonding network and generates supramolecular floating aggregates of the type $\{[(I)_x(X)_{x-n}]^{n+},[(I)_{x-n}(X)_x]^{n-}\}$ (I = imidazolium cation, X = anion).[5] Moreover, the mixture with other compounds (a solvent for example) can be considered to yield nanostructured materials. The existence of a critical aggregation concentration (CAC) for imidazolium-based ILs has been investigated in water and in organic solvent using several experimental techniques, such as measurement of surface tension or conductivity, small angle neutron scattering, mass spectroscopy, calorimetry, potentiometry and NMR spectroscopy.[7,8]

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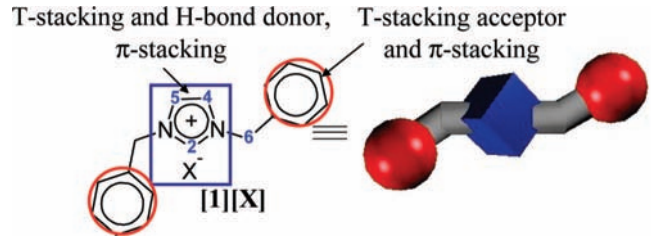

Figure 1. Structure of dibenzylimidazolium halides ($X^- = Cl^-$, Br^-, I^-).

Knowledge of the intimate nature, type and strength of non-bonding interactions in these supramolecular assemblies is therefore fundamental to understand the very unique properties of ILs. Recently, the use of UV spectrophotometry demonstrated that the aggregation process in water, occurs in the following order: (i) the formation of a floating hydrogen bonded network between hydrated imidazolium cations; (ii) interaction between anions and imidazoliums cations; and (iii) π-stacking interaction of imidazolium rings to form a IL quasi-structure.[6] On the basis of this study, the π-stacking interactions seem to be a lesser importance than hydrogen bonds in the aggregation process.[8]

ILs with halide anions are water-soluble and capable of self-assembly in polar solutions. We report here the use of *N*,*N*-dibenzyl substituents on the imidazolium ring to generate highly complex structures with potential new and interesting properties. These dibenzylimidazolium halide ILs present an increased cohesion in the solid state (X-ray diffraction analysis) and self-assemble by aromatic T-stacking of the imidazolium salts in polar and nonpolar solutions (^{1}H NMR and HRMS) (Figure 1).

Results and Discussion

Design and Synthesis. Molecular networks in the solid state, i.e., infinite molecular assemblies possessing translational symmetry, have attracted considerable interest over the last years. The design of such molecular architectures may be based on concepts developed in the area of molecular tectonics.[9] For the design of molecular networks, the guiding concepts are (i) molecular recognition processes between complementary tectons leading to assembling cores; (ii) translation of the assembling cores into one, two or three directions of space leading thus the formation of 1-, 2- or 3-D molecular networks respectively.[10] In other words, the assembling cores which correspond to

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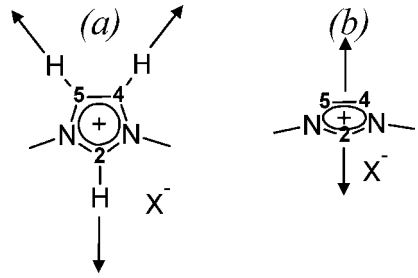

Figure 2. (a) Three T-stacking and H-bond donors of an imidazolium ring and their directionality. (*b*) π-Stacking.

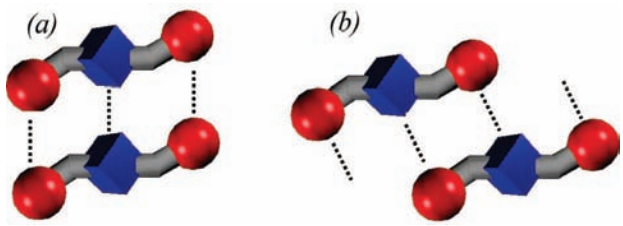

Figure 3. Schematic representation of the 2-D network form via stacking interactions between dibenzylimidazolium bromide salts.

recognition patterns become structural nodes of the network upon translation. This second requirement imposes that all tectons engaged in the formation of the network must possess interaction sites oriented in a divergent fashion. It is worth noting that the assembled system is the most stable situation under given conditions (temperature, pressure, concentration, solvent, etc.). The recognition event may be set up through a variety of reversible attractive intermolecular interactions such as van der Waals, electrostatic, π-stacking or H-bonding. The imidazolium cation can be considered as a tecton because it is a three H-bond donor, bearing three acid protons localized on the imidazolium ring, oriented in a divergent fashion. In 3D, π-stacking can also occur (Figure 2).[5]

An overview of the X-ray studies reported in the last years on the structure of 1,3-dialkylimidazolium salts[11] reveals a typical trend: in the solid state they form an extended network of cations and anions connected together by hydrogen bonds. The unimeric unit is always constituted of one imidazolium cation surrounded by at least three anions, and each anion is surrounded by at least three imidazolium cations.[12] The strongest hydrogen bond always involves the most acidic H_2 ($pK_a = 23.0$ for the 1,3-dimethylimidazolium cation)[13] followed by H_4 and H_5 of the imidazolium ring. These hydrogen bonds are weak to moderate (H···X bond lengths > 2.2 Å; C−H···X bond angles between 100−180°).[14] The number of anions that surround the cation (and vice-versa) vary according to the anion size and the nature of the N-imidazolium substituents.

Herein, we designed imidazolium salts to maximize the stacking interaction by the introduction of benzyl groups on the imidazolium moiety. With this methodology, we impose additional π-stacking interactions between the electron-rich and electron-poor rings. Principally, two geometries can be obtained by the stacking of similar or different aromatics rings. Figure 3a shows the classical aromatic face-to-face stacking interaction and Figure 3b illustrates aromatic stacking (T or π), described as the partially positively charged hydrogen atom of one aromatic system that points perpendicular to the center of the aromatic plane of the other aromatic system.[15]

The synthesis of the salts are extremely simple and are prepared according to previously reported procedures.[16] The substitution on (bromomethyl)benzene by 1-benzylimidazole is realized in a dry flask under positive nitrogen pressure in toluene. The reaction proceeds in 95% yield. The halide salts are air stable.

TABLE 1: Distances (Å) and Angles (deg) of Y−H···X Hydrogen Bonds in Dibenzylimidazolium Bromide

	Y···H	H···X	Y···X	Y−H···X	symmetry operators for X
$C_2-H_2\cdots O_{1'}$	0.95(0)	2.78(5)	3.61(3)	146(2)	x, $^3/_2 - y$, $^1/_2 + z$
$C_4-H_4\cdots O_{1''}$	0.95(0)	2.29(9)	3.17(2)	152(5)	$2 - x$, $1 - y$, $-z$
$O_{1'}-H_{1A}\cdots Br^a$	0.90(5)	2.48(2)	3.35(4)	161(9)	x, $^3/_2 - y$, $^1/_2 + z$
$O_{1'}-H_{1B}\cdots Br^a$	1.03(0)	2.39(7)	3.40(8)	166(9)	x, y, z

[a] Symmetry operators: $O_{1'}$, x, $^3/_2 - y$, $^1/_2 + z$; H_{1A}, x, $^3/_2 - y$, $^1/_2 + z$; H_{1B}, x, $^3/_2 - y$, $^1/_2 + z$.

Solid State Analysis. Crystallization of the bromide imidazolium synthesized here was carried out efficiently from hot water. Aqueous solution of the imidazolium salt (33 wt %) was heated until homogenization and then left at room temperature. Relatively big crystals (3.2 × 3.0 × 1.0 mm) suitable for X-ray analysis were obtained. The single crystals crystallized in a monoclinic system with a $P2_1/c$ space group. It is worth mentioning that for this imidazolium salt water molecules are present in the lattice implying that the cohesion of the crystal is ensured not only by the two ions (see Figures S1 and S2 in Supporting Information).

The crystal structure reveals an atypical organization compared to previously observed for other ILs, i.e., an extended 3-D network of cations and anions connected together by hydrogen bonds.[11] In the present system, the hydrogen bond network is formed via water molecules between the cations and the anions. Each imidazolium is surrounded closely to two water molecules each one connected with two anions (see Figure S3 in Supporting Information). Very weak to moderate hydrogen bonds (H···X > 2.2 Å; Y−H···X between 140 and 170°) take place in the crystal (Table 1).

Typically, the distances observed are within van der Waals distance thus more than Coulombic interactions are clearly present. It is important to notice that the hydrogen bond between the proton-donor group C−H_2 and a proton-acceptor oxygen atom of a water molecule is very weak (C−H···X > 2.78 Å; C−H···X = 146°). In this crystalline structure, the hydrogen bonds seem unusual: (i) the protons of the imidazolium ring are not connecting directly with the anions but via weak interaction with water molecules ($H_2\cdots O_{1'}$ and $H_4\cdots O_{1''}$), and (ii) the H_4 proton forms a weak hydrogen bond with a water molecule ($H_4\cdots O_{1''}$). In the previously reported crystalline structures, even for noncoordinating and nonsymmetrical anions, such as triflate, weak to moderate interactions were observed between the cations and the anions, especially for the most acidic proton.[17]

We can partially describe our 2D structure by the formation of chains of water molecules and bromide ions by hydrogen bonds (Figure 4). The distance between two adjacent phenyl rings is 3.68(5) Å and the orbital overlap is quasi-inexistent. However, the distance between an imidazolium (π-deficient) and a phenyl ring (π-rich) is approximately 3.4 Å, indicative of a strong π-stacking interaction between the two rings. As in classical stacking, the two rings are not totally parallel, to obtain better orbital overlapping without steric hindrance.

Another important stacking interaction was observed in the crystalline structure: T-stacking occurs between the H_5 proton (a partially positively charged hydrogen atom) and the phenyl ring. In fact, the H_5 proton points perpendicularly to the center of the phenyl plane (the distance is approximately 2.75 Å) (Figure 4).

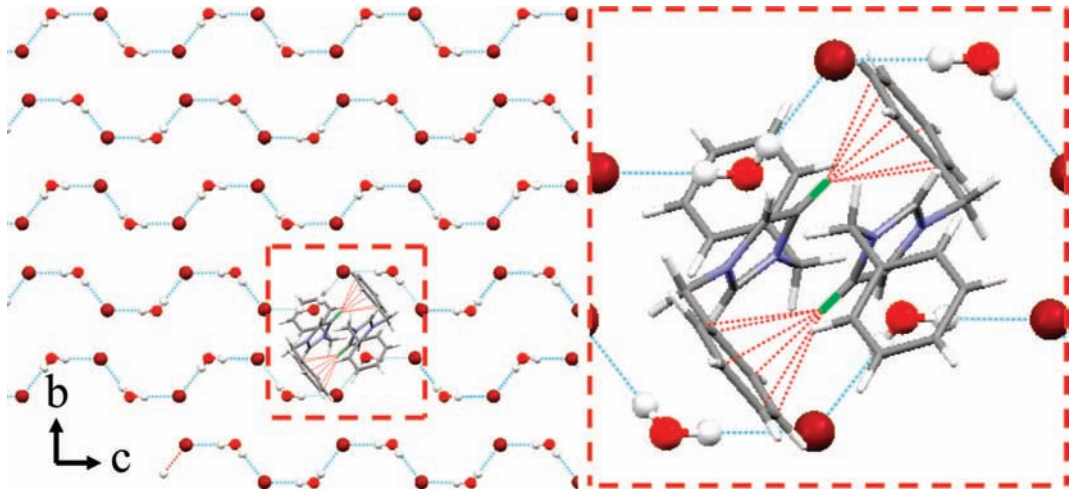

Figure 4. Network and dimer in **[1][Br]** (H_5 in green, H-bonds in blue and T-stacking in red). (Another view is shown in S4, Supporting Information.)

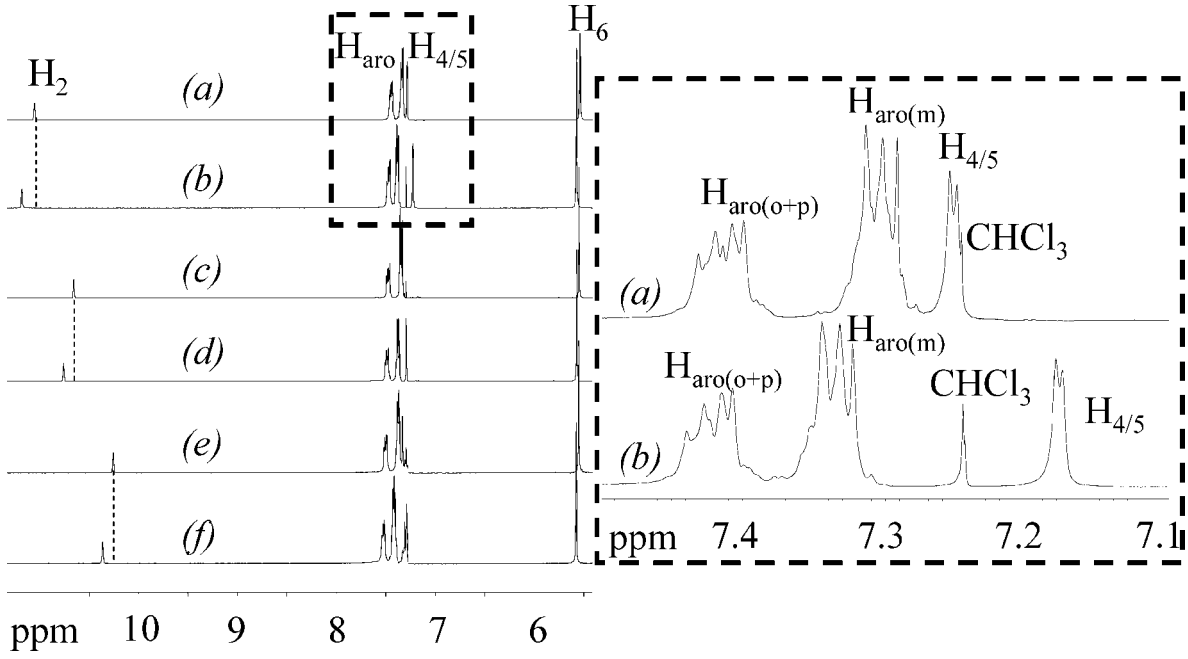

Figure 5. ^{1}H NMR spectra in $CDCl_3$ at 25 °C of (a) 60 mM **[1][Cl]**; (b) 30 mM **[1][Cl]**; (c) 60 mM **[1][Br]**; (d) 30 mM **[1][Br]**; (e) 60 mM **[1][I]**; (f) 30 mM **[1][I]**.

Indeed, the 3D arrangement of the molecules in the crystal structure is formed by two 2D networks, the first network being composed by the bromide anions via water molecules and the second one occurring by T-stacking between the imidazolium and the phenyl rings. The principal interaction (the T-stacking) governs the formation of a dimer, included in the bromide/water network (Figure 4). Hydrogen bonds and aromatic stacking interactions play the key role in the assembly of this ordered structure.

Solution Analysis. The self-assembly of the imidazolium salts in a dimeric structure, observed in the solid state, was also observed in solution. In fact, we observed changes in ^{1}H NMR chemical shifts that were dependent on the concentration of the imidazolium salt (Figure 5).

Different observations were done for the ^{1}H NMR study of bromide, chloride and the iodide salts (Figure 5) in D_2O or $CDCl_3$. (i) First, ^{1}H NMR chemical shifts in $CDCl_3$ vary for H_2, depending on the anion (the H_2 proton exchange at approximately 90% with deuterium in D_2O solution, see Figure 5 and Table 2). H_2 shifts to high field values for chloride, bromide and iodide anion. We can reasonably deduce that the force of hydrogen bonds between the cation and the anion decrease following the order: $[Cl^-] > [Br^-] > [I^-]$ (i.e., the acidity, Table 2). (ii) Second, the ^{1}H NMR chemical shifts are concentration-dependent. It is the case for the most acidic protons (H_2), for the aromatics ($H_{4/5}$), for the methylene protons (H_6) and for the phenyl ring (the values are reported in Table 2).

TABLE 2: Dimerization Constant (K_{dim}, M^{-1}) and ^{1}H NMR Chemical Shifs (ppm) in D_2O (H_6) and $CDCl_3$ (H_2) Solution for Dibenzylimidazolium Halide[a]

	D_2O			$CDCl_3$		
anion	δ_{free}	δ_{dimer}	K_{dim} (M^{-1})	δ_{free}	δ_{dimer}	K_{dim} (M^{-1})
$[Cl^-]$	5.51	5.33	640	12.70	10.91	500
$[Br^-]$	5.63	5.30	790	12.45	10.36	700
$[I^-]$				12.00	10.14	2100

[a] Calculated using eq 1 with ^{1}H NMR parameters; δ_{free} measured at 0.1 mM; δ_{dimer} measured at 120 mM.

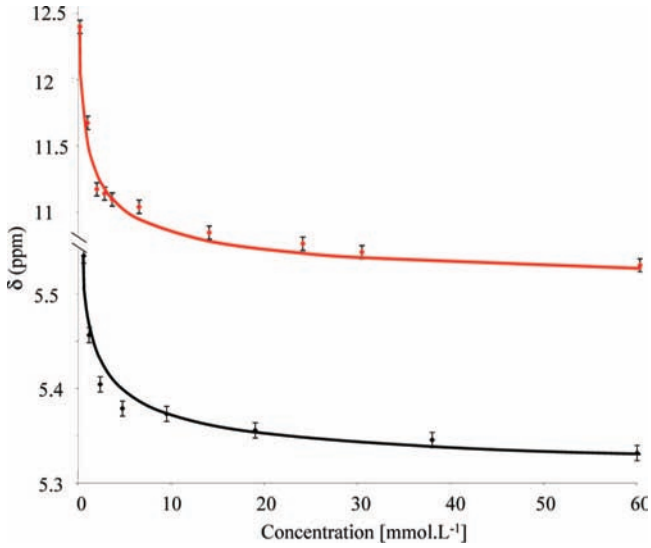

Figure 6. Binding isotherms for the H_2 of imidazolium in $CDCl_3$ (red) and for H_6 of the benzyl substituant in D_2O (black) of **[1][Br]**. The solid lines show the best fitted curve for a 1:1 dimerization process.

(i) Variation of the Halide. The ^1H NMR spectra of the imidazolium salts at submillimolar concentrations in D_2O or $CDCl_3$ (0.1 mM at 298 K) is consistent with a noninteracting species.[18] In a 60 mM solution, the signals for H_2 protons shifted from δ 12.70 to 10.91 ppm for the chloride salt, from δ 12.45 to 10.36 ppm for the bromide salt and from δ 12.00 to 10.14 ppm for the iodide salt in $CDCl_3$. The signals for H_6 protons shifted from δ 5.51 to 5.33 ppm for the chloride salt and from 5.63 to 5.30 ppm for the bromide salt in D_2O. These concentration-dependent shifts are indicative of an intermolecular interaction that is more pronounced in more concentrated solutions. Because addition of NaCl, NaBr or NaI to a diluted solution of chloride, bromide and iodide imidazolium salts (0.5 mM) did not induce any ^1H NMR chemical shift variation, ion pair formation of the imidazolium cation with the anion can be eliminated. Hence, self-association of the imidazolium cation may be the origin of the observed chemical shift variation. However, the anion probably also interacts with these dimers once formed by reducing their overall charge.

(ii) Variation of the Imidazolium's Concentration. The self-assembly of the imidazolium cations in a dimeric structure is supported by the fact that all ^1H NMR signals shift: the aromatic protons of the phenyl ring, the H_2 and the H_6 are upfielded, whereas only the H_4 and H_5 protons are downfielded when the concentration increases (Figure 5). This can be related to the geometry of the complex, caused by a T-stacking interaction and appears to be general for the studied salts. These observations are an indication that the dimeric structure observed in the solid state is conserved in D_2O and $CDCl_3$ solutions (H_4, H-bonds with solvent or with anion; H_5, T-stacking; and other aromatic protons π-stacking between imidazolium and phenyl rings). To determine the binding constant for the self-assembly of the imidazolium cations in solution, we performed ^1H NMR studies at different imidazolium concentrations, ranging from 1 to 60 mM.[19] A plot of the observed chemical shift versus concentration gives an isothermic binding curve (Figure 6 and S5−S9 in Supporting Information). As the complexation is fast on the NMR time scale, the observed chemical shift δ_{obs} is the weighted average of the shifts for the complexed (δ_{dimer}) and the uncomplexed molecule (δ_{free}). According to the method of Bangerter and Chan,[20] for a dimerization equilibrium, the observed chemical shift δ_{obs} depends on the total concentration C and the association constant K_{dim}, as expressed by the following equation:

$$\delta_{obs} = \delta_{free} + \frac{1 + 4K_{dim}C - \sqrt{1 + 8K_{dim}C}}{4K_{dim}C}(\delta_{dimer} - \delta_{free}) \quad (1)$$

The dimerization constant of the imidazolium cations is provided in Table 2; chemical shift variation of H_2 was used for the calculation of the dimerization constant in $CDCl_3$ solution and H_6 in D_2O solution. Because the dimerization constants have similar values in D_2O and $CDCl_3$ for the chloride and the bromide salts, the dimer seems to exist equally in water or chloroform solution. Chemical shift variation of the imidazolium $H_{4/5}$ protons has also been observed in both $CDCl_3$ and D_2O. Moreover, an interesting observation was made: the iodide salt is water insoluble, whereas the other salts are slightly soluble. Two reasons could be responsible for this fact: (i) the organic nature of the salt, and (ii) weaker or no hydrogen bonds between the imidazolium cation and the iodide anion, as proposed above. In other words, the weak interactions between the imidazolium cations and the halide anions promote the dimeric association of two imidazoium cations. This assertion is proved by the high association constant calculated for the iodide IL in $CDCl_3$ solution (2100 M^{-1} at 25 °C).

In addition to the ^1H NMR titration presented above, a high resolution mass spectrometry (HRMS) study has been carried out to demonstrate the presence of the dimer. Recently, information on the ability of ILs to give supramolecules has been obtained for the gas phase by tandem mass spectrometric experiments and molecular modeling.[21] The HRMS was used with an electrospray ionization (ESI), in positive mode, to "fish" loosely bonded supramolecules of ILs in solution and transfer them to a mass spectrometer to investigate their assemblies. The positive ions are formed in solution and then transferred by ESI directly to the gas phase. ESI is characterized by the gentleness by which the gaseous ions are formed, being able to transfer to the gas phase very labile, loosely bonded supramolecules such as, for instance, hydrogen-bonded amino-acid and assemblies.[22] ESI-HRMS has becomed the major technique to study salt cluster ion formation and properties.[23] The ESI mass spectrum of **[1][Br]**, in water, at 30 mM, and in the positive ion mode give a signal at *m/z* 249 correspond to unimer but also a signal at *m/z* 577, 578, 579, 580, 581, 582, 584, 586 (Figure 7). This last is due to the isotopic distribution of a dimer adduct with a bromide.

It was previously reported that $\{[(I)_x(X)_{x-n}]^{n+}$ and $[(I)_{x-n}(X)_x]^{n-}\}$ loosely bound IL aggregates can be detected and isolated via mass selection.[21] However, in our case, no higher aggregates were observed at this concentration by mass spectrometry. This result can be rationalized as the loosely hydrogen-bonded supramolecular networks for ILs and is not conserved during the ESI evaporation, and only the strongest dibenzylimidazolium dimer complex is maintained in the gas phase. Moreover, the dimer was not detected by MS analysis at a concentration below 0.1 mM. This observation is consistent with submillimolar concentrations of **[1][Br]**, being considered as a noninteracting species for the calculation of the association constant (see below).

Gas Phase Analysis. To confirm the MS results and to gain further insights into the binding interactions in the gas phase, we performed a computational study of the 1,3-dibenzylimidazolium salts using semiempirical PM3 energy minimization calculation (Gaussian 03W 6.0, restricted shell). In the energy

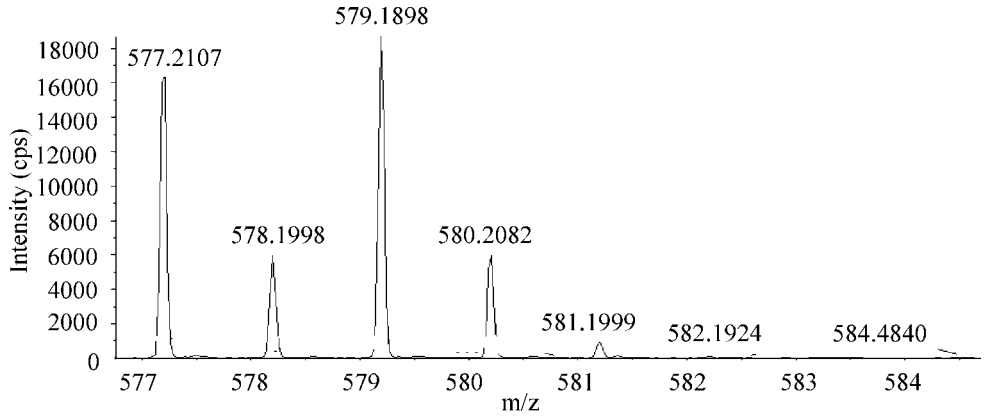

Figure 7. Partial HRMS spectra of a **[1][Br]** solution in water at 30 mM. Only the four significant digits of the HRMS-ESI spectra are shown.

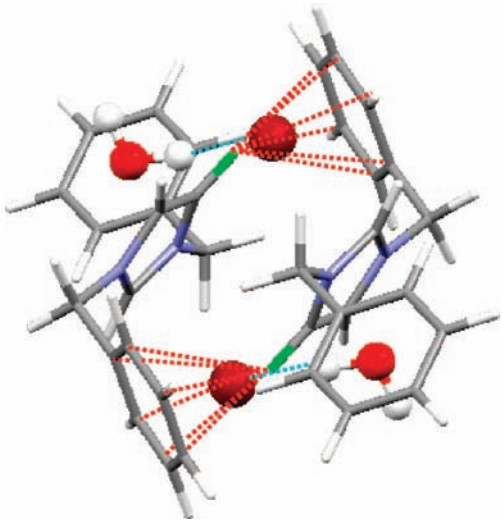

Figure 8. Dimer structure obtained after PM3 calculation (restricted shell) in **[1][Br]** (H_5 in green, H-bonds in blue and T-stacking in red).

TABLE 3: Enthalpy Variations (kcal.mol^{-1}) for the Dimerization of Dibenzylimidazolium Halide[a]

anion	ΔH (with 2 H_2O)	ΔH (without H_2O)
[Cl^-]	−48	−35
[Br^-]	−29	−32
[I^-]	−29	−22

[a] Calculated using Gaussian 03W 6.0 with PM3 geometry optimization, restricted shell.

minimized dimeric structure the dimer is held together by T-stacking interactions (distance 2.72 Å, in crystalline structure 2.75 Å; see Figure 8 and Table 3). At least two anions are bound to the opposite sides of this dimer by H-bonds with water molecules in aqueous solution (distance 1.85(2) Å, in crystalline structure 2.29(9) Å).

For many reactions entropy effect is small and it is the enthalpy change (ΔH) that mainly determines whether the reaction can take place spontaneously.[24] The enthalpy change is essentially due to the difference in the bond energies (including resonance and strain energies) between the monomeric and the dimeric species. Because the calculated enthalpy variation is very negative, the dimerization process may take place spontaneously (Table 3).

Moreover, the dimerization process is more enthalpy-driven when calculations are performed in the presence of water molecules. The anions' solvation seems to be an important parameter to consider in the dimerization process. In fact, the stacking is weaker when the H_4 form a hydrogen bond directly with a halide anion (see Figure S10 in Supporting Information).

Conclusions

In conclusion, we have presented here the possibility to maximize the stacking of aromatic rings in imidazolium halide salts. This stacking was demonstrated in the solid state by X-ray analysis and in solution by ^{1}H NMR. Contrary to classical crystal structures of imidazolium salts, the H-bond network is unexpected. The understanding of such supramolecular properties may lay the basis for a more rational design of switchable self-aggregating systems in the future. This can by useful to obtain switchable self-aggregating systems by inducing a competition between the dimer self-assembly and classical complexation of host molecules.

Experimental Section

General Procedure for the Synthesis of 1,3-Dibenzylimidazolium Halides [1][X]. A dry flask (250 mL), equipped with a magnetic stir bar and a septum-inlet for nitrogen, was charged with a solution of (halogenomethyl)benzene (8.42 mmol) in toluene (50 mL). In a Schlenk, a solution of 1-benzylimidazole in toluene (10.1 mmol) was added to the other flask in a dropwise fashion by cannulation at 0 °C. The reaction mixture was stirred for 20 min to 0 °C at room temperature and then filtered under gravity. The solid is washed with diethyl ether to remove unreacted 1-benzylimidazole. The white solid is dried overnight at 120 °C in a vacuum. The product is stored under dry nitrogen.

1,3-Dibenzylimidazolium Bromide [1][Br]. (2.6g, 95%). ^{1}H NMR (300 MHz, $CDCl_3$, 20 °C, TMS): δ = 5.5 ppm (s, 4H, 6), 7.2−7.3 ppm (m, 2H, 4, 5), 7.3−7.4 ppm (m, 10H; H_{aro}), 10.5 ppm (s, 1H; 2). ^{13}C NMR (75 MHz, $CDCl_3$, 20 °C): δ = 53.2 ppm (6), 121.8 ppm (4/5), 128.9 ppm (C_m),129.3 ppm (C_o), 129.3 ppm (C_p), 132.7 ppm (2), 136.6 ppm (C_{aro}−CH_2). Anal. Calc for $C_{17}H_{17}BrN_2 \cdot 2H_2O$: C, 55.90; H, 5.79; N, 7.67. Found: C, 54.84; H, 5.77; N, 7.87. MP: 85 °C.

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Supporting Information Available: CCDC reference numbers 665763. Experimental procedure, all partial profiles for the synthesis, characterization, ^{1}H NMR titration, supplementary crystallographic data and molecular views. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Handy, S. T. *Chem. Eur. J.* **2003**, *9*, 2938–2944.

(2) (a) Holbrey, J. D.; Seddon, K. R. *Clean Products Processes* **1999**, *1*, 223–236. (b) Hagiwara, R.; Ito, Y. *J. Fluorine Chem.* **2000**, *105*, 221–227. (c) Scammells, P. J.; Scott, J. L.; Singer, R. D. *Aust. J. Chem.* **2005**, *58*, 155–169.

(3) (a) Zhao, H.; Malhotra, S. V. *Aldrich. Acta* **2002**, *35*, 75–83. (b) Chauvin, Y.; Olivier-Bourbigou, H. *CHEMTECH* **1995**, *25*, 26–30. (c) Seddon, K. R. *J. Chem. Technol. Biotechnol.* **1997**, *68*, 351–356. (d) Sheldon, K. R. *Chem. Commun.* **2001**, 2399–2407. (e) Baudequin, C.; Baudoux, J.; Levillain, J.; Cahard, D.; Gaumont, A. C.; Plaquevent, J. C. *Tetrahedron: Asymm.* **2003**, *14*, 3081–3093. (f) Mehnert, C. P. *Chem. Eur. J.* **2005**, *11*, 50–56. (g) Blaser, H.-U.; Studer, M. *Green Chem.* **2003**, *5*, 112–117. (h) Song, C. E. *Chem. Commun.* **2004**, 1033–1043. (i) Park, S.; Kazlauskas, R. J. *Curr. Opin. Biotechnol.* **2003**, *14*, 432–437. (j) Kragl, U.; Eckstein, M.; Kaftzik, N. *Curr. Opin. Biotechnol.* **2002**, *13*, 565–571. (k) Poole, C. F. *J. Chromatogr. A* **2004**, *1037*, 49–82. (l) Stalcup, A. M.; Cabovska, B. *J. Liq. Chromatogr. Relat. Technol.* **2004**, *27*, 1443–1459. (m) Antonietti, M.; Kuang, D. B.; Smarsly, B.; Yong, Z. *Angew. Chem., Int. Ed.* **2004**, *43*, 4988–4992. (n) Geetha, S.; Trivedi, D. C. *Bull. Electrochem.* **2003**, *19*, 37–48.

(4) Chiappe, C.; Pieraccini, D. *J. Phys. Org. Chem.* **2005**, *18*, 275–297.

(5) (a) Dupont, J. *J. Braz. Chem. Soc.* **2004**, *15*, 341–350. (b) Avent, A. G.; Chaloner, P. A.; Day, M. P.; Seddon, K. R.; Welton, T. *J. Chem. Soc., Dalton Trans.* **1994**, 3405–3413.

(6) Zhang, H.; Liang, H.; Wang, J.; Li, K. *Z. Phys. Chem.* **2007**, *221*, 1061–1074.

(7) (a) Bowers, J.; Butts, C. P.; Martin, P. J.; Vergara-Gutierrez, M. C.; Heenan, R. K. *Langmuir* **2004**, *20*, 2191–2198. (b) Dorbritz, S.; Ruth, W.; Kragl, U. *Adv. Synth. Catal.* **2005**, *347*, 1273–1279. (c) Malham, I. B.; Letellier, P.; Turmine, M. *J. Phys. Chem. B* **2007**, *110*, 14212–14222. (d) Katayanagi, H.; Nishikawa, K.; Shimozaki, H.; Miki, K.; Westh, P.; Koga, Y. *J. Phys. Chem. B* **2004**, *108*, 19451–19457. (e) Consorti, C. S.; Suarez, P. A. Z.; de Souza, R. F. S.; Burrow, R. A.; Farrar, D. H.; Lough, A. J.; Loh, W.; da Silva, L. H. M.; Dupont, J. *J. Phys. Chem. B* **2005**, *109*, 4341–4349.

(8) (a) Schneider, H. J.; Yatsimirsky, A. *Principles and Methods in Supramolecular Chemistry*; Wiley-VCH: Weinheim, 2000. (b) Steed, J. W.; Atwood, J. L.; *Supramolecular Chemistry*; Wiley: Chichester, U.K., 2000. (c) Philip, D.; Stoddart, J. F. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1154–1196. (d) Lehn, J.-M. *Supramolecular Chemistry: Concepts and Perspectives*; VCH: Weinheim, 1995.

(9) Mann, S. *Nature* **1993**, *365*, 499–505.

(10) Fowler, F. W.; Lauher, J. W. *J. Am. Chem. Soc.* **1993**, *115*, 5991–6000.

(11) (a) Gordon, C. M.; Holbrey, J. D.; Kennedy, A. R.; Seddon, K. R. *J. Mater. Chem.* **1998**, *8*, 2627–2636. (b) Dupont, J.; Suarez, P. A. Z.; de Souza, R. F.; Burrow, R. A.; Kintzinger, J. P. *Chem. Eur. J.* **2000**, *6*, 2377–2381. (c) van den Broeke, J.; Stam, M.; Lutz, M.; Kooijman, H.; Spek, A. L.; Deelman, B.-J.; van Koten, G. *Eur. J. Inorg. Chem.* **2003**, 2798–2811. (d) Holbrey, J. D.; Reichert, W. M.; Nieuwenhuyen, J. S.; Seddon, K. R.; Rogers, R. D. *Chem. Commun.* **2003**, 1636–1837. (e) Saha, S.; Hayashi, S.; Hamaguchi, H. *Chem. Lett.* **2003**, *32*, 740–741. (f) Downard, A.; Earle, M. J.; Hardacre, C.; McMath, S. E. J.; Nieuwenhuyzen, M.; Teat, S. *J. Chem. Mater.* **2004**, *16*, 43–46. (g) Holbrey, J. D.; Reichert, W. M.; Rogers, R. D. *Dalton Trans.* **2004**, *15*, 2267–2271. (h) Golovanov, D. G.; Lyssenko, K. A.; Antipin, M. Y.; Vygoskii, Y. S.; Lozinskaya, E. I.; Shaplov, A. S. *Cryst. Eng. Comm* **2005**, *6*, 53–56. (i) Fujimoto, T.; Kawahata, M.; Nakakoshi, Y.; Yamaguchi, K.; Machinami, T.; Nischikawa, K.; Tashiro, M. *Anal. Sci.* **2007**, *23*, 107–108. (j) Nakakoshi, Y.; Shiro, M.; Fujimoto, T.; Machinami, T.; Seki, H.; Tashiro, M.; Nischikawa, K. *Chem. Lett.* **2006**, *35*, 1400–1401. (k) Getsis, A.; Mudring, A.-V. *Acta Crystallogr.* **2005**, *E61*, 2945–2946.

(12) Dupont, J.; Suarez, P. A. Z. *Phys. Chem. Phys. Chem.* **2006**, *8*, 2441–2452.

(13) (a) Amyes, T. L.; Diver, S. T.; Richard, J. P.; Rivas, F. M.; Toth, K. *J. Am. Chem. Soc.* **2004**, *126*, 4366–4374. (b) Alder, R. W.; Allen, P. R.; Williams, S. J. *J. Chem. Soc., Chem. Commun.* **1995**, 1267–1268.

(14) Jeffrey, G. A. *An Introduction to Hydrogen Bonding*; Oxford University Press: Oxford, U.K., 1997.

(15) (a) For π-stacking in supramolecular aggregates see: Lahiri, S.; Thompson, J. L.; Moore, J. S. *J. Am. Chem. Soc.* **2000**, *122*, 11315–11319. (b) Sirish, M.; Schneider, H. J. *J. Am. Chem. Soc.* **2000**, *122*, 5881–5882. (c) Guckian, K. M.; Schweitzer, B. A.; Ren, R. X.-F.; Sheils, C. J.; Tahmassebi, D. C.; Kool, E. T. *J. Am. Chem. Soc.* **2000**, *122*, 2213–2222.

(16) Wasserscheid, P.; Welton, T. *Ionic Liquids in Synthesis*; Wiley-VCH: Weinheim, 2003; Chapter *2*.

(17) Leclercq, L.; Suisse, I.; Nowogrocki, G.; Agbossou Niedercorn, F. *Green Chem.* **2007**, *9*, 1097–1103.

(18) (a) Schmuck, C. *Chem. Eur. J.* **2000**, *6*, 709–718. (b) Dixon, R. D.; Geib, S. J.; Hamilton, A. D. *J. Am. Chem. Soc.* **1992**, *114*, 365–366.

(19) (a) Wilcox, C. S. In *Frontiers in Supramolecular Chemistry and Photochemistry*; Schneider, H. J., Dürr, H. Eds.; VCH: Weinheim, 1990. (b) Connors, K. A. *Binding Constants*; Wiley: New York, 1987.

(20) (a) Bangerter, B. W.; Chan, S. I. *J. Am. Chem. Soc.* **1969**, *91*, 3910–3919. (b) Davis, J. C., Jr.; Deb, K. K. *Adv. Magn. Reson.* **1970**, *4*, 201–270.

(21) (a) Gozzo, F. C.; Santos, L. S.; Augusti, R.; Consorti, C. S.; Dupont, J.; Eberlin, M. N. *Chem. Eur. J.* **2004**, *10*, 6187–6193. (b) Bini, R.; Bortolini, O.; Chiappe, C.; Pieraccini, D.; Siciliano, T. *J. Phys. Chem. B* **2007**, *111*, 598–604.

(22) (a) Koch, K. J.; Gozzo, F. C.; Nanita, S. C.; Takats, Z.; Eberlin, M. N.; Cooks, R. G. *Angew. Chem., Int. Ed.* **2002**, *41*, 1721–1724. (b) Takats, Z.; Nanita, S. C.; Cooks, R. G. *Angew. Chem., Int. Ed.* **2003**, *42*, 3521–3523. (c) Cooks, R. G.; Zhang, D. X.; Koch, K. J.; Gozzo, F. C.; Eberlin, M. N. *Anal. Chem.* **2001**, *73*, 3646–3655.

(23) (a) Wang, G.; Cole, R. D. *Anal. Chem.* **1998**, *70*, 873–881. (b) Hao, C.; March, R. E. *J. Mass Spectrom.* **2001**, *36*, 509–521.

(24) Smith, M. B.; March, J. *Mechanisms and Methods of Determining Them in March's Advanced Organic Chemistry*, 6th ed.; John Wiley & Sons: New York, 2007.

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