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Inclusion of tetrabutylammonium cations in a chiral thiazolium/triflate network: Solid state and solution structural investigation

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ABSTRACT

A co-crystal of tetrabutylammonium and 3-[(2*S*)-2-methylbutyl]thiazolium bistriflate has been synthesized and the nature of the interactions between cations and anions has been studied in the solid state and in chloroform solutions. The cohesion of the crystal is ensured by a combination of H-bonds and electrostatic interactions. Indeed, the tetrabutylammonium cations are included in the H-bonds network linking all the thiazoliums and the triflates. In solution, the supramolecular structural organization is maintained to a great extent and a cage compound is formed, *i.e.* a lattice of thiazolium/triflate, connected *via* H-bonds, trapping and containing the tetrabutylammonium cation.

1. Introduction

Room-temperature ionic liquid (IL) salts constitute an attracting field in chemistry. These salts are defined as "molten salts" with melting points below 100 °C. The significant interest is due to their chemical and potentially useful solvent properties [1–3]. The most frequently used ILs belongs to the azolium family (e.g. imidazolium, etc.). Azolium ILs are generally considered as green solvents in organic synthesis, organometallic catalysis, separation processes, nanochemistry, electrochemistry and as new materials [4–21]. Much of the interest in azolium salts is due to their unique physico-chemical properties [22]. Indeed, the azolium cation can be considered as a tecton because it is a three H-bonds donor through the three acidic protons localized on the azolium ring and oriented in a divergent fashion [23,24]. These H-bonds induce structural directionality contrary to classical salts in which the aggregates are mainly formed through ionic bonds (Fig. 1a) [25,26]. Moreover, complementary electrostatic and π-stacking interactions can also occur [27,28]. Therefore, in the solid state, azolium salts form more or less complex molecular networks. The molecular networks formation is dictated by molecular recognition processes between complementary tectons (cations and anions) leading to assembled cores, the translation of these cores into three directions of space are leading to the formation of 3-D molecular networks. Indeed, a survey of the X-ray studies reported in the last decade on the structure of azolium salts reveals a typical trend: in the solid state, they form an extended network of cations and anions connected together by H-bonds [29–38]. The unimeric unit is always constituted of one azolium cation surrounded by at least three anions and each anion is surrounded by at least three azolium cations (Fig. 1b) [39]. The strongest H-bonds always involves the most acidic proton H_2 followed by H_4 and H_5 of the azolium ring. In the solid state, these H-bonds are weak to moderate [40]. In order to maximize the H-bond network, we have chosen to work with a thiazolium ring due to more acidic H_2 proton compare to imidazolium ring (p*K*a = 23.0 for the 1,3-dimethylimidazolium cation, p*K*a = 16.5 for the 3,4-dimethylthiazolium) [41–43].

The dilution of these solid molecular networks occurs with a partial disruption of the H-bonds network that generates supramolecular floating aggregates (i.e. nanostructured materials) [25,26]. Recently, we have reported that various ionic co-crystals can be easily formed by the mixing of azolium (e.g. 1-butyl-3-methylimidazolium triflate) with another invited organic cation (e.g. tetrabutylammonium triflate) [44,45]. In each structure, the invited cations are included in the H-bonds network that link all azolium cations and triflate anions. The H-bonds occur between the acidic

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[1] For X-ray diffraction requests.

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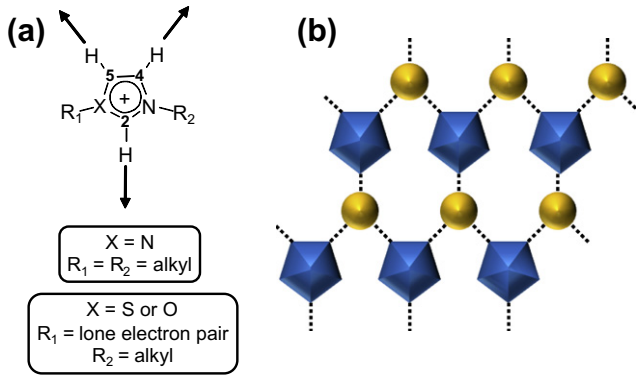

Fig. 1. Schematic representation of: (a) the three H-bond donors of azolium ring and their directionality, and (b) two-dimensional simplified solid-state model of H-bonds network (black dotted lines) between azolium cations (blue pentagons) and triflate anions (orange spheres). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

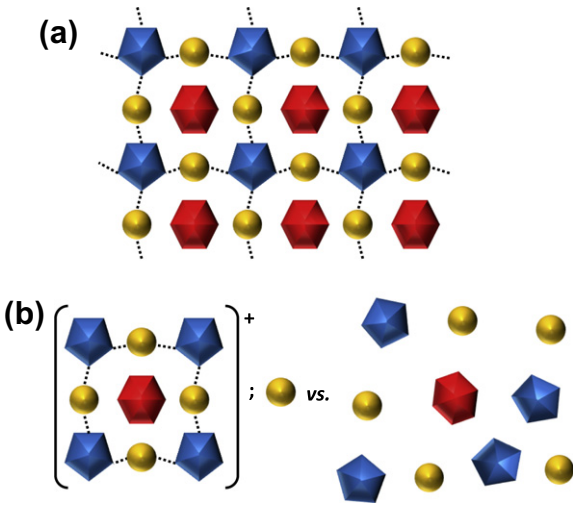

Fig. 2. Schematic representation of: (a) the two-dimensional simplified solid-state model of co-crystal of tetrabutylammonium and azolium bistriflate (H-bonds network: black dotted lines, azolium cations: blue pentagons, tetrabutylammonium cations: orange hexagons, and triflate anions: orange spheres), and (b) two plausible arrangements in solution (left: multiple ions, right: solvent separated ion pairs). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

protons of the azolium ring and the oxygen atoms of the counter-ion. In the presence of a chiral thiazolium cation, the thiazolium/triflate network formed in the solid state becomes chiral. Therefore, in the solid state, the invited cation becomes chiral due to the chirality of the local environment (i.e. peristatic chirality) [46]. In solution, two behaviours can be observed: (i) the formation of a solvent separated ion pairs (the chirality of the tetrabutylammonium cation is lost), or (ii) the azolium salts collapse around invited cations leading to chiral multiple ions (Fig. 2). We report here on the self-assembly of 3-[(2*S*)-2-methylbutyl]thiazolium triflate, **[MBT][TfO]**, and tetrabutylammonium triflate, **[TBA][TfO]**. The results prove that the **[TBA]** cation is included in the chiral azolium/triflate network both in solid state and in chloroform solutions.

2. Experimental section

2.1. Materials

All reactions were carried in oven-dried glassware under nitrogen, using standard Schlenk and vacuum line techniques. The ^{1}H and ^{13}C NMR spectra were recorded using an Advance 300 Brucker, at 300.13 and 75.49 MHz, respectively. Chemical shifts are given in ppm (δ) and measured relative to residual solvent. The 2D T-ROESY experiments were run using the software supplied by Brucker. Mixing times for T-ROESY experiments were set at 300 ms. The data matrix for the T-ROESY was made of 512 free induction decays, 1 K points each, resulting from the co-addition of 64 scans. The real resolution was 1.5–6.0 Hz/point in F2 and F1 dimension, respectively. They are transformed in the non-phase-sensitive mode after QSINE window processing. Elemental analysis were performed by the "service central d'analyses du CNRS". IR analyses were performed with a Nicolet 510 FTIR. $CDCl_3$ was obtained from Euriso-top. Trifluoromethanesulfonic anhydride was freshly prepared prior to use by distillation of a 1:1 w/w mixture of trifluoromethanesulfonic acid and phosphorus pentoxide. All other chemicals were purchased from Acros or Aldrich and used without further purification. Solvents were distilled under positive pressure of dry nitrogen before use and dried by standard methods: dichloromethane from CaH_2, toluene from Na/Hg amalgam.

2.2. Synthesis of 3-[(2S)-2-methylbutyl]thiazolium triflate **[MBT][TfO]**

A dry flask (1 L), equipped with a magnetic stir bar and a septum-inlet for nitrogen, was charged with a solution of (*S*)-2-methylbutanol (6.28 g, 71.2 mmol) and poly(vinylpyridine) (18.0 g, 63.8 mmol) in dichloromethane (300 mL). At 0 °C, we added the trifluoromethanesulfonic anhydride (8.6 g, 30.6 mmol) in a drop wise fashion. The reaction mixture was stirred for 5 min from 0 °C to room temperature and then filtered under gravity. The poly(vinylpyridinium triflate) precipitate was washed with 5 mL of dichloromethane. The organic layer was washed with saturated $NaHCO_3$ solution and when the organic layer became transparency, we dried ($MgSO_4$) and concentrated under vacuum to give the (2*S*)-2-methylbutyltriflate (yellowish oil). This oil was dissolved in anhydrous toluene under a nitrogen atmosphere and the solution was cooled to 0 °C. The thiazole (6.40 g, 75.2 mmol) was added and the resulting solution was stirred an hour. The ionic liquid layer appeared beneath the toluene phase. After extraction, the ionic liquid was washed with toluene to remove unreacted thiazole. The pale-yellow ionic liquid was dried overnight at 120 °C under vacuum. The product was stored under dry nitrogen (22.50 g, 98%). ^{1}H NMR (300 MHz, $CDCl_3$, 20 °C): δ = 0.89–0.94 (m, 6H; CH_3), 1.26 (m, 1H; CH_2), 1.40 (m, 1H; CH_2), 2.15 (m, 1H; CH), 4.53–4.73 (m, 2H; NCH_2), 8.44 (s, 1H; CH=CH), 8.62 (s, 1H; CH=CH), 10.22 (s, 1H; NCHN). ^{13}C NMR (75 MHz, $CDCl_3$, 20 °C): δ = 10.6 (CH_3), 15.9 (CH_3), 26.0 (CH_2), 36.0 (CH), 55.2 (NCH_2), 121.5 (CF_3, $^{3}J_{C-F}$ = 442 Hz); 126.3 (CH=CH), 137.5 (CH=CH), 158.2 (NCHN); IR: 3115 and 3155 cm^{-1} (C—H···F); Anal. Calc. for $C_9H_{14}F_3NO_3S_2$; M = 305.3 g mol^{-1} ; C, 35.40%; H, 4.62%. Found: C, 35.34%; H, 4.22%; $[\alpha]_D^{20}$ = +6.7 (*c* = 1.0 in $CHCl_3$).

2.3. Crystallization and X-ray diffraction

The co-crystallizations are realized in open flasks by dissolving in hot chloroform (10 mL) the 3-[(2*S*)-2-methylbutyl]thiazolium triflate (1 eq.) and tetrabutylammonium triflate (1 eq.). After a week at room temperature, single co-crystals are obtained. X-ray data were collected with a Bruker Kappa Apex2 diffractometer with Mo Kα radiation (λ = 0.71073 Å) at 100 K.

2.4. Molecular modeling

All calculations were performed on Windows® Vista platform. The initial configurations have been obtained from UFF calculations under ArgusLab 4.0.1 software (©Mark Thompson and Planaria Software LLC) [47]. In order to assess the energy content for various