

# The material combining conducting polymer and ionic liquid: Hydrogen bonding interactions between polyaniline and imidazolium salt



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## ABSTRACT

New type of interaction between polyaniline and ionic liquid leading to conducting polyaniline form is reported. Blue non-conducting polyaniline base was exposed to ionic liquid, 1-ethyl-3-methylimidazolium trifluoromethanesulfonate, and changed its colour to green. This was associated with the increase in conductivity by ten orders of magnitude from  $6 \times 10^{-11} \text{ S cm}^{-1}$  to  $0.43 \text{ S cm}^{-1}$ . The FTIR spectroscopic analysis suggests that (1) hydrogen bonding of hydrogen in imidazolium heterocycle with imine nitrogen in polyaniline combined with (2) hydrogen bonding of amine groups in polyaniline to oxygen atoms in trifluoromethanesulfonate anion are responsible for the observed effects. The quantum-chemical calculations of the corresponding hydrogen bonding interactions support this concept. The thermogravimetric analysis demonstrates improved thermal stability of the material compared with a standard polyaniline hydrochloride.

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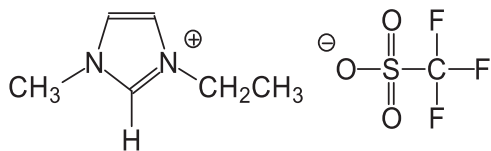
## 1. Introduction

Conducting polymers represent a class of functional materials that are important mainly for their electrical properties [1]. Among them, polyaniline (PANI) and polypyrrole are the most studied polymer semiconductors having the conductivity typically of the order of  $0.1\text{--}10 \text{ S cm}^{-1}$  in their salt form. In addition to the conductivity, their responsive properties, *i.e.* the ability to change their physical and chemical properties in response to various external stimuli, are important. They are based on the chemical switching between various redox states or salt–base transitions, and are exploited especially in sensors and energy-conversion devices. Depending on reaction conditions, conducting polymers are produced in various morphologies, such as globules, nanofibres, nanotubes, thin films or colloidal dispersions [2]. Chemical properties of conducting polymers become important in catalysis and noble-metal recovery, electrochemical properties in corrosion protection of metals or in supercapacitors. Conducting polymers are coloured and their optical properties are also of importance. The protonation of conducting polymer with various inorganic or organic acids allows for the control of their conductivity, water contact angles, density, and other physical parameters [3].

Ionic liquids [4], the organic salts having a melting point below room temperature, have recently been extensively studied due to their low volatility, good thermal stability at elevated temperature, ionic conductivity, controlled hydrophilicity, *etc.* Among applications, the field of electrochemistry operating in the absence of water is the most promising [5,6], because of wide electrochemical window [7,8],  $>5 \text{ V}$ , that ensures excellent stability over broad range of potentials [9]. Aprotic ionic liquids based on imidazolium cation (Fig. 1) and counter-ions afforded by strong organic or inorganic acids belong to extensively studied group. Ionic liquids exhibit an ionic conductivity, typically  $10^{-5}\text{--}10^{-1} \text{ S cm}^{-1}$ , which is comparable with the aqueous solutions of strong acids [10]. In addition, ionic liquids can act as non-aqueous proton conductors by promoting the Grotthuss mechanism (proton hopping) over the vehicular one [10] (proton transfer). This becomes important in applications, such as in fuel cells operating above the boiling point of water [11]. Various interfacial interactions between ionic liquids and electronic conductors have also been proposed [6] but have not been investigated in detail.

There are applications, which may benefit by the combined use of conducting polymers and ionic liquids. These include the fields where the mixed electronic and ionic conductivity is needed. It will be important if such systems would operate in the presence or in the absence of water. New materials comprising both moieties are expected to be active in interfacial processes in which ionic charge-carriers transform to electronic ones, *i.e.* when they act

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**Fig. 1.** Typical ionic liquids are asymmetrically disubstituted imidazolium salts containing various counter-ions, 1-ethyl-3-methylimidazolium trifluoromethanesulfonate, being an example used in the present study.

as ion–electron transducers. Polyaniline alone is expected to have mixed electron and proton conductivity. For example, the decrease in impedance and enhanced electron transfer from electrolyte to carbon-nanotubes electrode was reported after modification with PANI [12]. Batteries, fuel cells, supercapacitors, or analytical electrodes are the pertinent examples. A mixed electron–proton conductivity has been illustrated in PANI alone in the aqueous solutions of acids [13]. Non-aqueous media, such as ionic liquids, however, are much more attractive in the electrochemical applications, as they allow for extension of the electrochemical window to higher potentials. The exceptional stability of the electrochemical performance in materials combining conducting polymers and ionic liquids has been reported for the electrochemical actuators [5]. The pernigraniline salt, an oxidized form of PANI, which is considered to be instable in aqueous media, was stable in ionic liquid [14]. This opens new prospects in the application of PANI in electrochemistry and batteries.

The fact that the ionic liquids of imidazolium type interact with PANI base have been illustrated in gel-permeation chromatography, when aggregation of PANI macromolecules in *N*-methylpyrrolidone containing ionic liquid was reduced compared with an addition of lithium chloride [15]. This means that ionic liquid becomes hydrogen-bonded to PANI and overrides the intramolecular hydrogen bonding between imine and amino groups in PANI chains [16,17]. Interaction between PANI and imidazolium ionic liquid have been suggested in the electrochemical preparation of this polymer [18]. Polyaniline self-assembly has also been affected during the polymerization of aniline when the ionic liquid was present in the aqueous reaction mixture [19–23]. Polyaniline was proposed to form a charge-transfer complex with imidazolium cation [24]. The specific interaction of the quinonoid moiety of the PANI base with the imidazolium ring of the ionic liquid has been suggested in the literature [25]. The experiments testing the interaction between PANI and ionic liquids, however, have always included the presence of organic acids, such as formic or camphorsulfonic acids [24], or inorganic acid [19–23], which complicate the interpretation of observed processes due to classical protonation phenomena.

In the present communication, we report the increase in the conductivity of PANI base by ten orders of magnitude after immersion in an ionic liquid, 1-ethyl-3-methylimidazolium trifluoromethanesulfonate (EMIm-TFM). Resulting material, comprising both the conducting polymer and ionic liquid, is thus composed of intrinsically electronic and ionic conductors.

## 2. Experimental

### 2.1. Polyaniline and its interaction with ionic liquid

Polyaniline hydrochloride powder was prepared by the polymerization of 0.2 M aniline hydrochloride (Fluka, Switzerland) with 0.25 M ammonium peroxydisulfate (Lach:NER, Czech Republic) in aqueous medium [26]. Thin PANI hydrochloride films were deposited *in situ* at the same time on glass or silicon substrates immersed in the reaction mixture. Polyaniline salts, both the

powders and films, were converted to PANI bases in 1 M ammonium hydroxide, rinsed with acetone, and dried.

The powders of PANI base or the films were subsequently immersed in the ionic liquid, 1-ethyl-3-methylimidazolium trifluoromethanesulfonate (EMIm-TFM; 99%; IoLiTec Ionic Liquid Technologies GmbH, Germany) for at least 5 days. The colour of PANI-base films changed from blue to green. A care was taken to avoid moisture and the samples were kept in a desiccator over silica gel. The products were again rinsed with acetone and kept over silica gel at room temperature.

### 2.2. Characterization

UV-visible spectra of the films grown on glass supports were recorded with a Lambda 20 spectrometer (Perkin Elmer, UK). Fourier-transform infrared (FTIR) spectra of the films deposited on silicon windows were registered with a Thermo Nicolet NEXUS 870 FTIR Spectrometer with a DTGS TEC detector. An absorption subtraction technique was applied to remove the spectral features of the silicon substrate. Thermogravimetric analysis (TGA) of powders was carried out in a 50 mL min<sup>-1</sup> air flow at a heating rate of 10 °C min<sup>-1</sup> with a Perkin Elmer TGA 7 Thermogravimetric Analyzer.

The conductivity of PANI powders compressed at 540 MPa to pellets of 13 mm diameter and 1 mm thick with a manual hydraulic press was measured by a four-point van der Pauw method using SMU Keithley 237 as current source, and a Multimeter Keithley 2010. For low-conducting samples, <10<sup>-3</sup> S cm<sup>-1</sup>, a two-point method used a Keithley 6517 electrometer after deposition of gold electrodes on both sides of pellets.

Quantum chemical calculations have been carried out to get deeper insight into the interactions of PANI base with ionic liquid. The model calculations were performed at the density functional level of theory (DFT) using the Gaussian 09 programme package [27]. The B3LYP functional and the 6-311++G(d,p) basis set were used and the geometry optimizations were unconstrained. The B3LYP functional and the basis set of this size were successfully applied in the studies of hydrogen bonding [28], including ionic liquid based complexes [29–32]. Frequency analysis (no imaginary frequency) was used to characterize the stationary points as true minima in all cases except for the largest complex due to computational limitations. In that case, the local minimum was supported by the fact that orientations of the interacting molecules were analogous to those found in smaller optimized complexes. Stabilization energies of all the complexes have been calculated using the supermolecular approach and corrected for the basis set superposition error (BSSE) using the counterpoise method suggested by Boys and Bernardi [33].

## 3. Results and discussion

Polyaniline is produced by the oxidation of aniline in acidic aqueous media as a conducting emeraldine salt, here hydrochloride [26]. This green PANI form displays three characteristic absorption bands in the UV-vis spectra [34,35] at approximately 350, 430, and 810 nm (Fig. 2), which are accepted in the literature to reflect  $\pi-\pi^*$  transition in substituted benzenoid rings, and polaron- $\pi^*$  and  $\pi$ -polaron transitions, respectively [36,37]. Emeraldine salt converts to a blue non-conducting PANI base in alkaline media, e.g., after immersion in ammonia solution. The absorption band of  $\pi-\pi^*$  transition shifts to 340 nm, and the second band located at 610 nm is usually associated with  $n-\pi^*$  transition (Fig. 2). The change in colour is reflected also in electrical properties. The electron density distribution over the PANI chain changes after deprotonation and the conductivity of PANI decreases by eleven orders of magnitude

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