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Research article

Noncovalent functionalisation of polyaniline with the ionic liquid: An unneeded asset to prepare the emeraldine salt form of polyaniline using protic ionic liquids as polymerisation medium

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Abstract. Since the properties of polyaniline (PANI) are widely related to the type of its dopant, the present manuscript has an objective to define whether and to what extent the protic ionic liquids contribute to doping PANI. Hence, pyrrolidinium *p*-toluenesulfonate [Pyrr][PTS] – a protic ionic liquid – has been investigated either as a polymerisation medium or as a secondary dopant. As for the polymerisation medium, it was found that binary mixtures of [Pyrr][PTS]/water, with different weight ratios, are convenient to prepare PANI in emeraldine salt form. Furthermore, the structural analysis of the resulted PANI has revealed that the cation of [Pyrr][PTS] does not functionalise PANI backbone and [Pyrr][PTS] acts like the typical Brønsted acid in doping PANI, regardless of the amount of [Pyrr][PTS] in the polymerisation medium. To confirm this conclusion, [Pyrr][PTS] has also been studied as a secondary dopant: the conventional PANI has been prepared, deprotonated then dispersed into [Pyrr][PTS]/water with different formulations. The results have shown that [Pyrr][PTS] leads to the formation of reprotonated PANI without altering structural change. One can thus conclude that the noncovalent functionalisation of PANI with the cation of the protic ionic liquids is not an exigent requirement to prepare the emeraldine salt form of PANI in aqueous solutions of protic ionic liquids.

Keywords: *polyaniline (PANI), ionic liquids, dopant agent, ions dissociation and noncovalent interactions*

1. Introduction

Polyaniline (PANI) has attracted great attention for many applications such as electrochemical storage devices [1, 2], perovskite solar cells [3, 4] and so on [5], owing to its properties such as excellent chemical stability, simple synthesis, highly adjustable electronic and electrochemical performances, good thermal stability and so forth [1, 6–15]. Two challenges have faced the scientific community during the synthesis of PANI via oxidative chemical polymerisation. The first one is to obtain PANI in emeraldine salt form (the only conductive form of PANI), while the second

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one is to prepare PANI with homogeneous nanostructured morphology. As for the first challenge, it is agreed that an acidic medium is required to achieve the formation of PANI by chain growth with emeraldine salt form [16]. However, following the standard polymerisation procedure, the conventional acidic media is not convenient to prepare PANI with nanostructured morphology. So far, researchers have been directed toward adding ionic liquids into the conventional acidic media [1, 6]. It was reported that ionic liquids induce the formation of well-defined one-dimensional morphology of PANI in Emeraldine salt form [1, 6].

PANI in emeraldine salt form, also known as doped or protonated PANI, is the form of PANI in which some chemical species are incorporated into the backbone of PANI. Doped PANI exhibits an increment of PANI charge carriers, improvement of its electrical conductivity, and control of its surface wettability as compared to emeraldine base form (*i.e.* undoped or deprotonated PANI) [17–23]. The transformation between the emeraldine base and salt form is a reversible simple reaction. For the conversation of emeraldine base to emeraldine salt, it is enough to disperse it in conventional acidic media: an imine nitrogen forms a covalent bond with free protons resulting from the dissociation of acid (AH), and the counter ions of the medium maintain the electroneutrality of charged PANI (see Figure 1a) [24–26]. As for the ionic liquids, the mechanism of the doping process is not yet well reported, to the best of our knowledge. Some literature has mentioned that disubstituted imidazolium salts dope PANI via noncovalent interactions [8, 21, 22, 27–31] since they are characterised with the absence of labile proton [32]. For example, the hydrogen atom located on the 2-position of the imidazolium ring can interact with the imine nitrogen of PANI through a hydrogen bond (see Figure 1b). However, other literature has shown that the aprotic ionic liquids are easily removed from PANI during its purification [8, 27, 28]. Since the size as well as the type of dopant affect the properties of PANI [20], herein we present a study on the approach followed in the doping process of PANI prepared by the assistant of the protic ionic liquid.

2. Experimental part

2.1. Chemicals

Pyrrolidine (99%, Aldrich, St. Quentin Fallavier France), *p*-toluene sulfonic acid (99.8%, Sigma Aldrich, St. Quentin Fallavier, France), ammonium peroxodisulfate (98%, Sigma Aldrich, St. Quentin Fallavier, France) were used as supplied. Aniline (99.8%, Acros Organics, Geel, Belgium) was distilled and then kept under an argon atmosphere in a refrigerator before use.

2.2. Synthesis of pyrrolidinium *p*-toluene sulfonate [Pyrr][PTS]

Pyrrolidinium *p*-toluene sulfonate [Pyrr][PTS] (chemical structure shown in Figure 2) is prepared by a simple neutralisation reaction between Brönsted acid and the corresponding base [33]. Briefly, the reaction was performed in a three-necked round-bottomed flask immersed in an ice bath equipped with a reflux condenser, a thermometer and a dropping funnel. 136 g of *p*-toluene sulfonic acid were placed in the round-bottomed flask and then dissolved with the minimum amount of needed distilled water. On the other side, 55.93 g (0.79 mol) of pyrrolidine was introduced into the dropping funnel. The pyrrolidine was slowly added into the aqueous solution of *p*-toluene sulfonic acid. The temperature was observed during the addition of the pyrrolidine and kept lower than 20 °C. After finishing the addition of pyrrolidine, the resulting mixture was stirred at room temperature (*i.e.* 20 °C) overnight. The residual

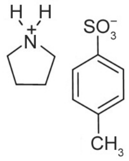

Figure 2. Chemical structure of pyrrolidinum *p*-toluene sulfonate [Pyrr][PTS].

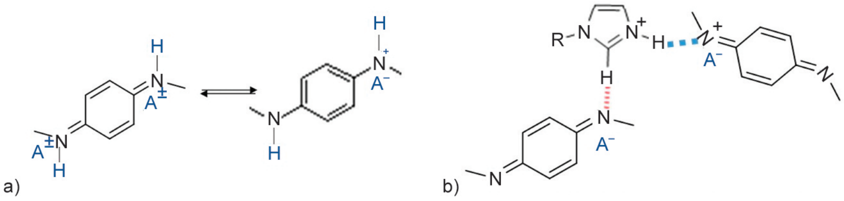

Figure 1. Doping PANI a) with conventional acidic media and b) with substituted imidazolium ionic liquids.

water was eliminated under vacuum, and the collected [Pyrr][PTS] was dried at 60 °C under vacuum.

2.3. Synthesis of the conventional PANI in emeraldine salt form (PANI-2) and emeraldine base form (PANI-2/B)

The conventional PANI in emeraldine salt form (PANI-2) was prepared using the standard synthetic procedure reported in our previous work [33]. Briefly, aniline (1 g, 0.01 mol) was dissolved in 35 mL of hydrochloric acid HCl 1 mol/L at room temperature under magnetic stirring. The resulting mixture was then cooled at 5 °C using a thermostat. The polymerisation reaction was then induced by dropwise adding an aqueous acidic solution of ammonium persulfate $(NH_4)_2S_2O_8$, containing 3.06 g of $(NH_4)_2S_2O_8$ dissolved in 15 mL of 1 mol/L HCl and cooled at 5 °C, into the aniline solution. The reaction was kept under stirring for 24 h at 5 °C. The obtained dark green precipitate was collected after filtration, washing till pH neutral with deionised water then dried for 15 h under vacuum at 60 °C. The structure of PANI was confirmed with attenuated total reflectance – fourier transform infrared spectroscopy (ATR-FTIR), as discussed in our previous work [33].

For the conversation of the emeraldine salt form (*i.e.* PANI-2) to emeraldine base form (*i.e.* PANI-2/B), the obtained PANI-2 was dispersed in ammonia solution (NH_4OH, 5%) for 24 h under vigorous magnetic stirring at room temperature. The PANI-2/B was collected following the same workup as PANI-2.

2.4. Reprotonation of PANI-2/B with the assistant of [Pyrr][PTS]

500 mg of PANI-2/B was dispersed into 5 mL of distilled water under vigorous magnetic stirring at room temperature for a half-hour. Then, an amount of [Pyrr][PTS] was added in such a way that the weight ratio of [Pyrr][PTS]/water was 7/93, 12/88, 16/84 and 48/52, respectively. The resulting mixture was kept under magnetic stirring for 24 h at room temperature, then filtrated and washed with the distilled water until pH neutral. The collected powders were dried at 60 °C for 15 h under vacuum. Table 1 introduces the designations of the different materials (PANI-2/B/PIL) resulting after dispersion in [Pyrr][PTS]/water as well as the designations of the conventional PANI in emeraldine salt form (PANI/2) and in base form (PANI-2/B).

Table 1. Abbreviated names of the conventional PANI in emeraldine salt form (PANI-2) and base form (PANI-2/B) as well as the abbreviated names of P PANI obtained after dispersion PANI-2/B in [Pyrr][PTS]/water with different weight ratio [wt%].

Obtained PANI	Conventional PANI
PANI-2	Emeraldine salt form
PANI-2/B	Emeraldine base form
PANI obtained after dispersion PANI-2/B in [Pyrr][PTS]/water with different weight ratio [wt%]	
Resulted PANI	**[Pyrr][PTS]/water wt%**
PANI-2/B/PIL-7	7/93
PANI-2/B/PIL-12	12/88
PANI-2/B/PIL-16	16/84
PANI-2/B/PIL-48	48/52

2.5. Synthesis of PANI in binary mixture of [Pyrr][PTS]/water

This synthesis was performed using the same procedure as for the conventional PANI (*i.e.* PANI-2), replacing aniline with anilinium *p*-toluene sulfonate [Ani][PTS] and hydrochloric acid with binary mixture of [Pyrr][PTS]/water as detailed in our previous work [34] The weight ratio of [Pyrr][PTS] to water was varied as 30/70, 48/52 and 70/30. To define the role of [Pyrr][PTS], pure PANI (*i.e.* PANI-1) was also prepared following the above-mentioned process without the presence of [Pyrr][PTS] in the polymerisation medium. The obtained PANI was singled as summarised in Table 2.

2.6. Characterisations

Thermogravimetric analysis (TGA) was done using Perkin Elmer (Villebon-sur-Yvette, France) model simultaneous thermal analyser STA 6000 in a nitrogen atmosphere between 25 and 900 °C at a heating rate of 10 °C/min.

Electrical conductivity measurements of the doped PANI samples were conducted at room temperature using a four-probe technique on pellets containing 200 mg of PANI and pressed at 1 t, with a thickness of 1200–1300 µm, using a Keithley 6220 current source and Keithley 2182 A nanovoltmetre.

Table 2. Abbreviated names of PANI prepared in [Pyrr][PTS]/water.

[Pyrr][PTS]/water weight ratio	Obtained PANI
0/100 ↔ no [Pyrr][PTS]	PANI-1
30/70	PANI-1-PIL30
48/52	PANI-1-PIL48
70/30	PANI-1-PIL70

Raman measurements on PANI powders were carried out using a micro-Raman spectro-meter (Renishaw®, Wottom-Under-Edge, UK) with a laser source of 633 or 514 nm at room temperature.

3. Results and discussion

PANI in emeraldine salt form has successfully been prepared in the presence of [Pyrr][PTS] in the polymerisation medium, as reported in our previous work [34]. However, how effectively [Pyrr][PTS] contribute to doping PANI remain to be uncovered. Theoretically, the process of the contribution of [Pyrr][PTS] in doping PANI is likely to be either similar to that of the aprotic ionic liquid (as mentioned in the introduction) or to the typical Brønsted acid as illustrated in Figure 3, respectively. As for the first approach (Figure 3a), a hydrogen atom attached to the nitrogen atom in the pyrrolidinium cation might exhibit hydrogen bonding with the imine function of PANI, functionalised PANI backbone and thus alter the structure and conformational change of the typical PANI. As for the second approach (Figure 3b), it is suggested since [Pyrr][PTS] is highly soluble in water. When placed in water, [Pyrr][PTS], like any salt, is dissociated according to Equation (1) and (2). The formed $[\mathrm{Pyrr}]^+$ thus releases its available proton in the medium, as shown in Equation (3):

$$[\mathrm{Pyrr}][\mathrm{PTS}]_s + \mathrm{H_2O} \rightarrow [\mathrm{Pyrr}][\mathrm{PTS}]_{aq} \tag{1}$$

$$[\mathrm{Pyrr}][\mathrm{PTS}]_{aq} \rightarrow [\mathrm{Pyrr}]^+_{aq} + [\mathrm{PTS}]^-_{aq} \tag{2}$$

$$[\mathrm{Pyrr}]^+_{aq} \rightarrow \mathrm{Pyrr} + \mathrm{H}^+ \tag{3}$$

Therefore, [Pyrr][PTS] might dope PANI like the typical brønsted acid, and the resulting pyrrolidine is removed during washing PANI. For the demonstration of which approach is correct, this work is divided into two parts: the first one discusses the effect of [Pyrr][PTS] added with different amounts into the polymerisation medium on the chemical structure of PANI, while the second part presents the possibility of reprotonation of deprotonated PANI with the assistance of [Pyrr][PTS].

3.1. Part I: [Pyrr][PTS] as polymerization medium for PANI

ATR-FTIR analysis, TGA analysis and Raman analysis of PANI-1, PANI-1-PIL30, PANI-1-PIL48 and PANI-1-PIL70 (*i.e.* PANI prepared in aqueous solutions of [Pyrr][PTS] as described in experimental section) were performed in order to reveal the influence of [Pyrr][PTS] on the structure of PANI and thus confirm the correct approach (Figure 3).

3.1.1. Infra-red spectroscopy

The obtained ATR-FTIR spectra of the resulting PANI are presented in our previous work [34]. As reported, the ATR-FTIR absorption bands located at 1559, 1472, 1294, 1106, and 787 $\mathrm{cm^{-1}}$ are the absorption characteristic bands of the typical PANI in emeraldine salt form, and the bands located at 1007 and 1032 $\mathrm{cm^{-1}}$ are assigned to $\mathrm{PTS^-}$ [34]. The characteristic bands of PANI-1-PIL do not exhibit a shift as compared to that of PANI-1, revealing that the structure of PANI is not altered by the ionic liquid. Indeed, it is reported that the infra-red spectrum of PANI prepared in disubstituted imidazolium-based ionic liquids exhibits some shift as compared to that of the typical PANI, indicating that PANI in doped with the disubstituted imidazolium cation itself [21]. One can, therefore, assume that the cation of [Pyrr][PTS] does not interact with the PANI via non-covalent interactions as no shift occurred on the spectrum of PANI-1-PIL relative to that of PANI-1. However, the characteristic bands of *p*-toluene sulfonate (located at 1007 and 1032 $\mathrm{cm^{-1}}$) are more intense for PANI-1-PIL relative to PANI-1, indicating a positive correlation between the intensity of these peaks and the concentration of [Pyrr][PTS] added into the polymerisation medium. ATR-FTIR analysis has not revealed which approach is the most correct thus, other structural analyses have been performed.

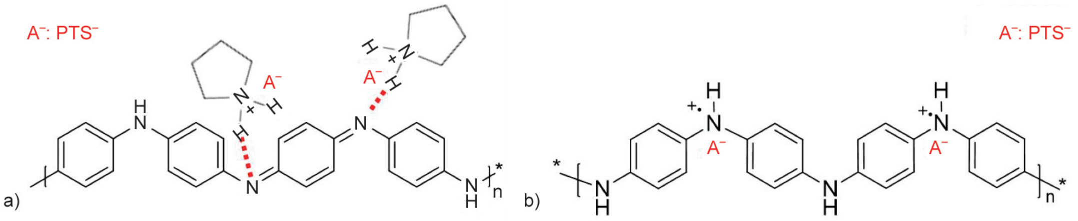

Figure 3. Possible approaches of protonation of PANI prepared in aqueous solutions of [Pyrr][PTS]: a) functionalisation of PANI with [Pyrr][PTS] itself and b) [Pyrr][PTS] as Brønsted acid in the polymerisation medium.

3.1.2. Raman spectroscopy

Raman analysis was also performed to further examine the contribution of [Pyrr][PTS] in doping PANI, and the obtained spectra are shown in Figure 4. Figure 4a shows the Raman spectra of the PANI samples using an excitation wavelength of 633 nm (red). The observed Raman bands are typical for PANI [27, 28, 35, 36], and can be assigned as follows: 1591 cm^{-1} C–C stretching of the benzenoid units, 1500 cm^{-1} C=C stretching of the quinoid ring, 1378 and 1338 cm^{-1} $C–N^{+\bullet}$ stretching in polarons, 1256 cm^{-1} C=C stretching of benzene diamine units, 1168 cm^{-1} C–H in-plane vibration of C–H, 878 cm^{-1} out of plane N–H bending, 808 cm^{-1} in-plane vibration of the benzenoid ring and out of plane vibration of C–H, 514 and 576 cm^{-1} out of plane C–N vibration, and 410 cm^{-1} out of plane N–H deformation.

Based on Figure 4a, one can notice that:

- The position of the Raman bands of the PANI-1 and all the investigated PANI-1-PIL are mostly coincident: no shift of the bands is observed; no extra bands appeared on the spectra of PANI-1-PIL as compared with the spectrum of PANI-1.
- A shoulder at 1645 cm^{-1} is clearly observed in the spectrum of PANI-1, while this is not the case in the spectra of PANI-1-PIL. Furthermore, the peak at 514 cm^{-1} displays higher intensity in the spectrum of PANI-1. These minor differences have not been explained yet in the literature, to the best of our knowledge. It might be due to the moisture since the weight loss of water is higher for PANI-1 as compared to that of PANI-1-PIL, according to themogravimetric analysis (Figure 5a). To further understand this observation, Raman analysis was also recorded at 514 nm (green) and shown in Figure 4b.

The resulting Raman spectra (Figure 4b) are different as compared to those performed at 633 nm excitation wavelength (Figure 4a) which is typically observed for PANI. Comparing the Raman spectrum of PANI-1 with that of PANI-1-PIL30 shows no impact of [Pyrr][PTS] on PANI structure as these spectra are superimposed. To conclude, Raman analysis indicates that all the investigated PANI display similar molecular structures as all the spectra are similar. Therefore, Raman analysis reveals that the PANI backbone is not functionalised with the pyrrolidinium cation.

3.1.3. Thermogravimetric analysis

To confirm the way that [Pyrr][PTS] is involved in doping PANI (Figure 3), the thermal stability of PANI-1 and PANI-1-PIL was studied and compared to that of the starting materials (*i.e.* [Pyrr][PTS] and anilinium salt [Ani][PTS]), using thermogravimetric analysis (TGA) from room temperature to 900 °C with a heating rate of 10 °C/min under nitrogen. Indeed, the temperature at which the dopant agent of the PANI is released might define the type of dopant agent. Figure 5a shows the thermograms of PANI-1 and PANI-1-PIL-70, [Ani][PTS] and [Pyrr][PTS]. As one can see, the TGA thermograms of PANI-1 and PANI-1-PIL70 present three stages of thermal decomposition as typically observed for PANI [37, 38]. The first step, weight loss, is attributed to the evaporation of water and the second step is assigned to the loss of the dopant. As for the third-step weight loss, it is attributed to the degradation and decomposition of the polymer backbone. From Figure 5a, one can see that PANI-1-PIL70 holds the dopant without any loss of about 67 °C higher as compared with PANI-1 (Figure 5b). The other PANI prepared in

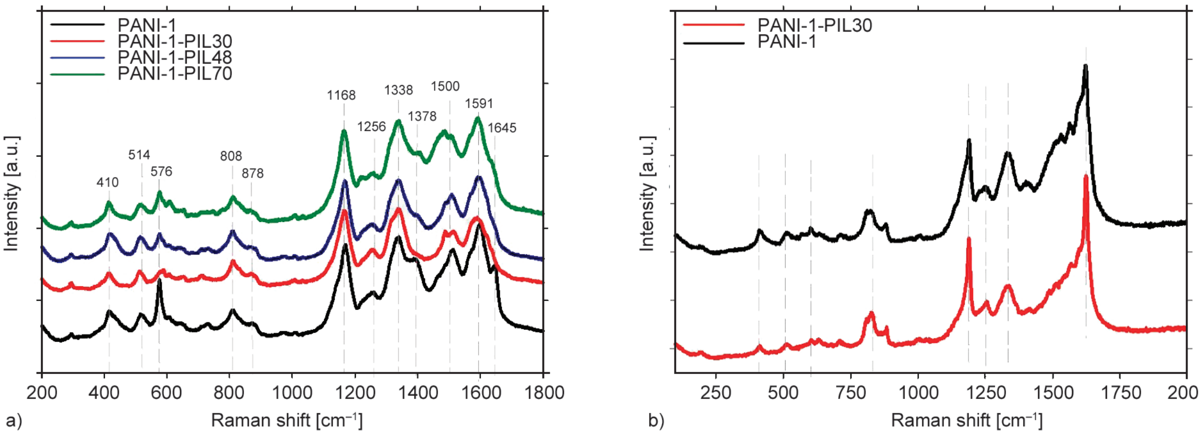

Figure 4. Raman spectra of the different investigated PANI recorded using a) 633 nm and b) 514 nm excitation wavelengths.

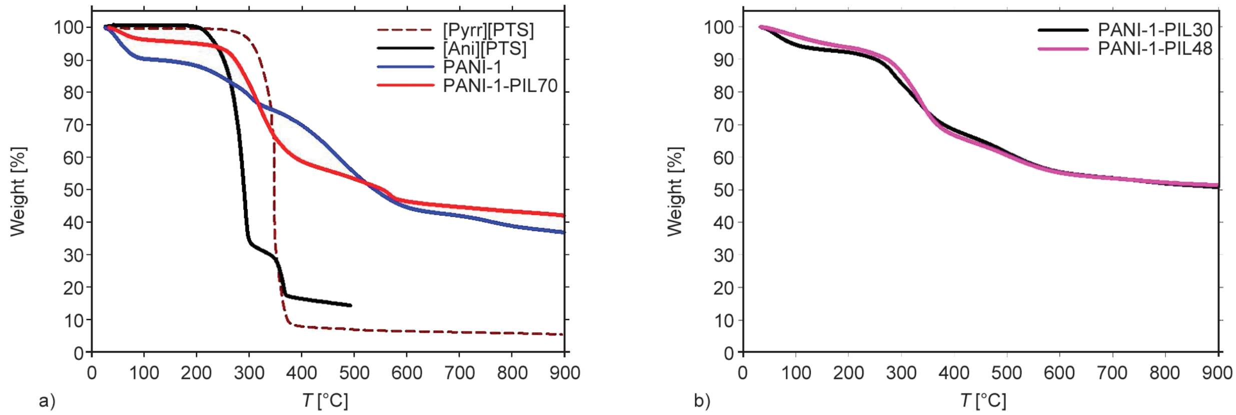

Figure 5. TGA curves of a) [Pyrr][PTS], [Ani][PTS], PANI-1, PANI-1-PIL70, and b) PANI-1-PIL30 and PANI-1-PIL48.

[Pyrr][PTS]/water (*i.e.* PANI-1-PIL30 and PANI-1-PIL48) present the same thermogram shape as that of PANI-1-PIL70 (see Figure 5b). As all PANI-1-PIL are thermally more stable than PANI-1, one can thus assume that PANI-1 and PANI-1-PIL are not dope with the same dopant type.

Comparing the thermal decomposition of the investigated PANI with that of the starting materials can reveal the type of dopant. TGA curve of [Pyrr][PTS] exhibits only one stage of thermal decomposition, which begins at 303 °C. It is noticeable that the start decomposition temperature of [Pyrr][PTS] is higher than that of PANI-1/PIL, revealing than PANI is not doped with the ionic liquid [Pyrr][PTS] itself. On the other extreme, TGA curve of [Ani][PTS] presents two stages of thermal decomposition: the first-step weight loss undergoes decomposition around 180–200 °C, while the second-step weight loss starts at temperature very loss to dopant release of PANI-1-PIL (*i.e.* 290 °C), which is also comparable with that of doping loss of PANI prepared in *p*-toluene sulfonic acid and described in the literature [37]. One can thus conclude that PANI-1-PIL is doped with PTS- and not with [Pyrr][PTS] itself.

Concerning PTS$^-$, which dopes PANI-1-PIL, it is sourced from the ionic liquid [Pyrr][PTS]. Indeed, PANI-1 is doped with the sulfate group of oxidant agent [17, 20, 39] that, on the one hand, explains the absence of the absorption characteristic bands of PTS$^-$ on the ATR-FTIR spectrum of PANI-1 (as described in Section 3.1.1) and, on the other hand, the lower thermal stability of PANI-1 compared to PANI-1-PIL. Thus, PANI-1 prepared from [Ani][PTS] is not doped with PTS$^-$, confirming that PTS$^-$ that dope PANI-1-PIL is not derived from the anilinium salt but from [Pyrr][PTS]. To sum up, PANI-1-PIL is doped with PTS$^-$ derived from [Pyrr][PTS], which acts as a typical Brønsted acid in doping PANI, revealing that the second approach (Figure 3b) is more likely to be the correct one.

3.2. Part II: [Pyrr][PTS] as secondary dopant of PANI

To confirm that [Pyrr][PTS] acts like typical brønsted acid in doping PANI, [Pyrr][PTS] has also been investigated as a secondary dopant. The methodology followed to perform this investigation is summarised in Figure 6a. The conventional PANI was prepared in emeraldine salt form and then deprotonated with the alkaline medium (step 1 in Figure 6a). The transformation of the emeraldine salt form (PANI-2) to emeraldine base form (PANI-2/B) was confirmed with the dramatic decrease of the electrical conductivity from 3 S/cm for PANI-2 to 10^{-9} S/cm for PANI-2/B. The resulting PANI-2/B was then mixed with [Pyrr][PTS] for 12 h under stirring with different weight ratios of [Pyrr][PTS]/water (step 2 in Figure 6b), and the collected product were abbreviated as PANI-2/B/PIL.

To define if PANI has been redoped with the assistance of [Pyrr][PTS], electrical conductivity has been used as a criterion since it is well known that emeraldine salt form (*i.e.* protonated/doped PANI) is electrically conductive while emeraldine base form (*i.e.* deprotonated/undoped PANI) is electrically insulating. Figure 6b presents the evolution of the electrical conductivity of the collected PANI-2/B/ PIL. It is noticeable that the electrical conductivity of PANI-2/B/PIL is higher than that of PANI-2/B, indicating that dispersing the fully deprotonated PANI-2/B (σ: 10^{-9} S/cm) in [Pyrr][PTS] leads to the generation of conductive polymer (*i.e.* doped

PANI-2/B/PIL). Furthermore, the electrical conductivity values gradually increase with the increment of the amount of [Pyrr][PTS] in the dispersing medium: the electrical conductivity increases from $2.81\cdot10^{-6}$ S/cm for PANI-2/B/PIL-7 (*i.e.* collected after being dispersed in [Pyrr][PTS]/water 7/93 wt%) to $2.30\cdot10^{-2}$ S/cm for PANI-2/B/PIL-48 (*i.e.* collected after being dispersed in [Pyrr][PTS]/water 48/52 wt%). Based on the upward trend of the ionic conductivity as a function of [Pyrr][PTS] in the dispersing medium, one can conclude that [Pyrr][PTS] contribute to doping PANI, but it is not possible, at this stage, to detail the mechanism of its contribution (Figure 3). Thus, ATR-FTIR analysis of PANI2/B, the different PANI-2/B/PIL and the neat [Pyrr][PTS] was performed and shown in Figure 6c. First of all, one can notice that the spectra of PANI-2/B/PIL are superimposed with the spectrum of PANI-2/B (*i.e.* typical ATR-FTIR spectrum of PANI), indicating that [Pyrr][PTS] does not functionalise PANI as no shift is observed on the ATR-FTIR characteristic bands of PANI. However, the band at 1039 and 1007 cm^{-1}, associated with the *p*-toluene sulfonate group, reappeared on the spectrum of PANI-2/B-PIL as compared with that of PANI-2/B. One can thus conclude that *p*-toluene sulfonate PTS^{-} (*i.e.* the anion of [Pyrr][PTS]) contributes to doping PANI while this is not the case of pyrrolidinium Pyrr^{+} (*i.e.* the cation of [Pyrr][PTS]), indicating that an aqueous solution of [Pyrr][PTS] acts like the typical Brønsted acid as illustrated in Figure 3b. To sum up, noncovalent interactions between PANI and the cation of the protic ionic liquids are not exigent requirements to reprotonate the deprotonated PANI

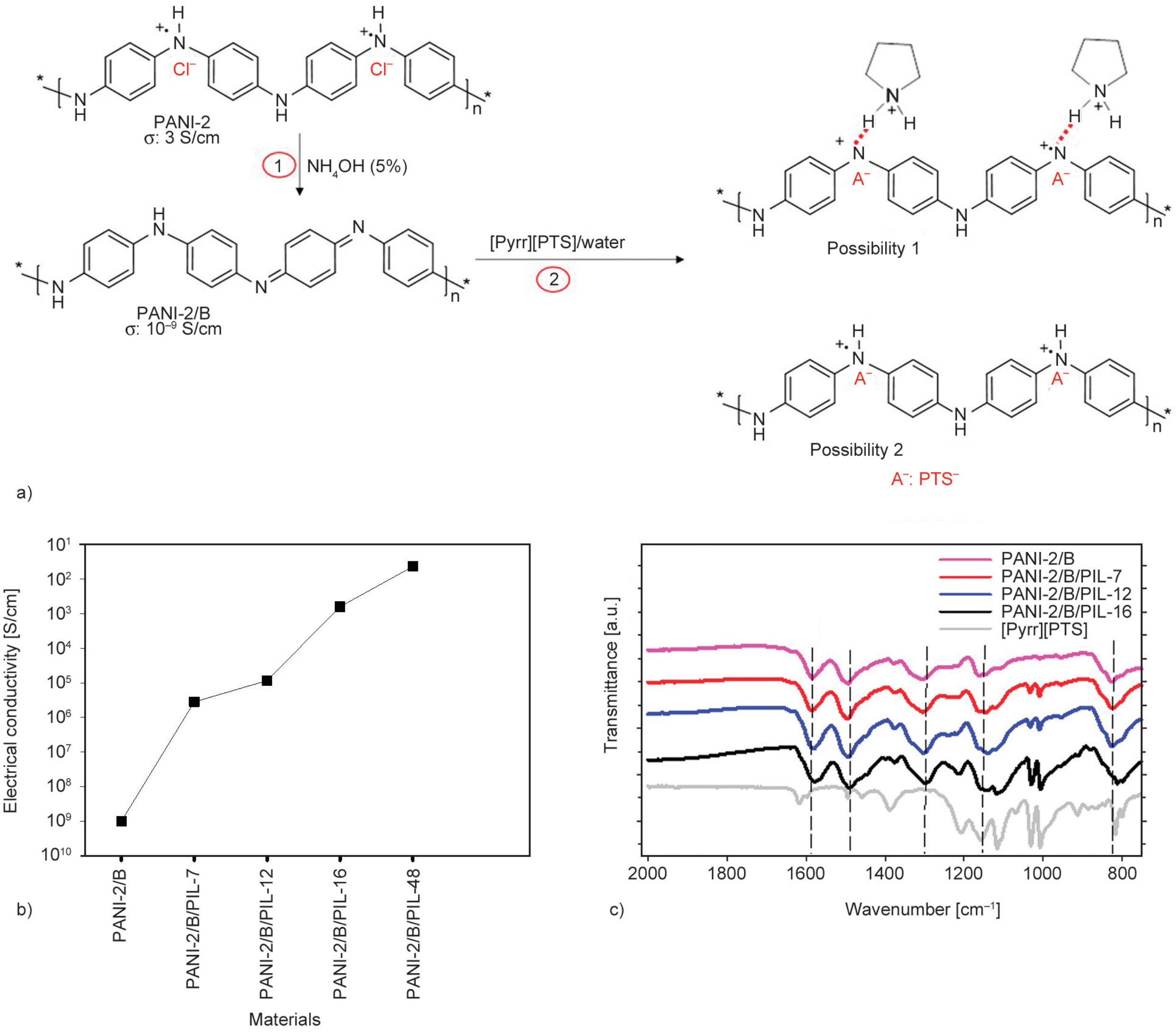

Figure 6. a) Scheme of reactions followed to reprotonate PANI with the assistant of [Pyrr][PTS], b) electrical conductivity of isolated PANI-2/B and PANI-2/B/PIL and c) FTR/ATR spectra of PANI-2/B and PANI-2/B/PIL and the neat [Pyrr][PTS].

in contrast to imidazolium-based aprotic ionic liquids [1].

4. Conclusions

Herein, a study on the process of the contribution of protic ionic liquids, namely Pyrrolidinium *p*-toluene sulfonate [Pyrr][PTS], in doping PANI has been presented. On the one hand, PANI has been successfully prepared in aqueous solutions of [Pyrr][PTS] via standard oxidative polymerisation. The structural analysis of the prepared PANI has shown the absence of the characteristic bands of pyrrolidinium cation (*i.e.* the cation of [Pyrr][PTS]), revealing the absence of hydrogen bonding between pyrrolidinium cation and PANI irrespective of the concentration of [Pyrr][PTS] in the polymerisation medium. Likewise, dispersing deprotonated conventional PANI (*i.e.* emeraldine base form) into an aqueous solution containing [Pyrr][PTS] greatly enhances the electrical conductivity without altering the chemical structure of the collected PANI, showing that reprotonated PANI has been collected without structural-induced change. To sum up, PANI in emeraldine salt form using protic ionic liquids as a polymerisation medium has been prepared even in the absence of intermolecular interactions between PANI and the cation of the protic ionic liquids. Thus, attention should be paid to the dissociation of the protic ionic liquids more than the noncovalent functionalisation of PANI with the ionic liquids.

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References

[1] Al-Zohbi F.: Research progress on polyaniline-ionic liquids for long cycle-stable supercapacitors with high capacitance. Applied Functional Materials, **2**, 51–66 (2022).
https://doi.org/10.35745/afm2022v02.01.0004

[2] Al-Zohbi F., Ghamouss F., Jacquemin J., Schmaltz B., Tabcheh M. F., Abarbri M., Cherry K., Tran-Van F.: Non-substituted imidazolium-based electrolytes as potential alternatives to the conventional acidic electrolytes of polyaniline-based electrode materials for supercapacitors. Molecules, **29**, 2569–2585 (2024).
https://doi.org/10.3390/molecules29112569

[3] Yasin S., Abu Waar Z., Moustafa M.: Investigation into the inverted planer perovskite solar cell: Advances of PANI:PSS as a hole transport material. Emergent Materials, in press (2024).
https://doi.org/10.1007/s42247-024-00732-y

[4] Dwiveda G., Munjal G., Bhaskarwar N. A., Chaudhary A.: Dye-sensitized solar cells with polyaniline: A review. Inorganic Chemistry Communications, **135**, 109087 (2022).
https://doi.org/10.1016/j.inoche.2021.109087

[5] Li D., Huang J., Kaner R. B.: Polyaniline nanofibers: A unique polymer nanostructure for versatile applications. Accounts of Chemical Research, **42**, 135–145 (2009).
https://doi.org/10.1021/ar800080n

[6] Al-Zohbi F.: A review of tailoring polyaniline ionic liquids for long cycle-stable supercapacitors with high capacitance. Journal of Chemical Reviews, **5**, 143–158 (2023).
https://doi.org/10.22034/jcr.2023.380607.1206

[7] Veerasubramani G. K., Krishnamoorthy K., Radhakrishnan S., Kim N-J., Kim S. J.: *In-situ* chemical oxidative polymerization of aniline monomer in the presence of cobalt molybdate for supercapacitor applications. Journal of Industrial and Engineering Chemistry, **36**, 163–168 (2016).
https://doi.org/10.1016/j.jiec.2016.01.031

[8] Li X., Liu Y., Guo W., Chen J., He W., Peng F.: Synthesis of spherical PANI particles *via* chemical polymerization in ionic liquid for high-performance supercapacitors. Electrochimica Acta, **135**, 550–557 (2014).
https://doi.org/10.1016/j.electacta.2014.05.051

[9] Anbalagan A. C., Sawant S. N.: Brine solution-driven synthesis of porous polyaniline for supercapacitor electrode application. Polymer, **87**, 129–137 (2016).
https://doi.org/10.1016/j.polymer.2016.01.049

[10] Bhandari S., Khastgir D.: Template-free solid state synthesis of ultra-long hairy polyaniline nanowire supercapacitor. Materials Letters, **135**, 202–205 (2014).
https://doi.org/10.1016/j.matlet.2014.07.079

[11] Gholivand M. B., Heydari H., Abdolmaleki A., Hosseini H.: Nanostructured CuO/PANI composite as supercapacitor electrode material. Materials Science in Semiconductor Processing, **30**, 157–161 (2015).
https://doi.org/10.1016/j.mssp.2014.09.047

[12] Wang X., Liu D., Deng J., Duan X., Guo J., Liu P.: Improving cyclic stability of polyaniline by thermal crosslinking as electrode material for supercapacitors. RSC Advances, **5**, 78545–78552 (2015).
https://doi.org/10.1039/c5ra17327b

[13] Khdary N. H., Abdesalam M. E., El Enany G.: Mesoporous polyaniline films for high performance supercapacitors. Journal of Electrochemical Society, **161**, G63–G68 (2014). https://doi.org/10.1149/2.0441409jes

[14] Wang G., Zhang L., Zhang J.: A review of electrode materials for electrochemical supercapacitors. Chemical Society Reviews Journal, **41**, 797–828 (2012). https://doi.org/10.1039/c1cs15060j

[15] Ramya R., Sivasubramanian R., Sangaranarayanan M. V.: Conducting polymers-based electrochemical supercapacitors-progress and prospects. Electrochimica Acta, **101**, 109–129 (2013). https://doi.org/10.1016/j.electacta.2012.09.116

[16] Sapurina I., Stejskal J.: The mechanism of the oxidative polymerization of aniline and the formation of supramolecular polyaniline structures. Polymer International, **57**, 1295–1325 (2008). https://doi.org/10.1002/pi.2476

[17] Stejskal J., Hlavatá D., Holler P., Trchová M., Prokeš J., Sapurina I.: Polyaniline prepared in the presence of various acids: A conductivity study. Polymer International, **53**, 294–300 (2004). https://doi.org/10.1002/pi.1406

[18] Sinha S., Bhadra S., Khastgir D.: Effect of dopant type on the properties of polyaniline. Journal of Applied Polymer Science, **112**, 3135–3140 (2009). https://doi.org/10.1002/app.29708

[19] Paul R. K., Pillai C. K. S.: Thermal properties of processable polyaniline with novel sulfonic acid dopants. Polymer International, **50**, 381–386 (2001). https://doi.org/10.1002/pi.639

[20] Stejskal J., Gilbert R. G.: Polyaniline. Preparation of a conducting polymer(IUPAC technical report). Pure and Applied Chemistry, **74**, 857–867 (2002). https://doi.org/10.1351/pac200274050857

[21] Li S., Yang C., Sarwar S., Nautiyal A., Zhang P., Du H., Liu N., Yin J., Deng K., Zhang X.: Facile synthesis of nanostructured polyaniline in ionic liquids for high solubility and enhanced electrochemical properties. Advance Composites and Hybrid Materials, **2**, 279–288 (2019). https://doi.org/10.1007/s42114-019-00103-w

[22] Stejskal J., Dybal J., Trchová M.: The material combining conducting polymer and ionic liquid: Hydrogen bonding interactions between polyaniline and imidazolium salt. Synthetic Metals, **197**, 168–174 (2014). https://doi.org/10.1016/j.synthmet.2014.09.002

[23] Deshpande N., Chakane S., R. Borude R.: Synthesis and characterization of polyaniline, using different dopant, for sensing application of pollutant gases. Journal of Atomic, Molecular, Condensate and Nano Physics, **3**, 27–33 (2016). https://doi.org/10.26713/jamcnp.v3i1.347

[24] Bernard M. C., Hugot-Le Goff A.: Quantitative characterization of polyaniline films using Raman spectroscopy: I: Polaron lattice and bipolaron. Electrochimica Acta, **52**, 595–603 (2006). https://doi.org/10.1016/j.electacta.2006.05.039

[25] Stafström S., Brédas J. L., Epstein A. J., Woo H. S., Tanner D. B., Huang W. S., MacDiarmid A. G.: Polaron lattice in highly conducting polyaniline: Theoretical and optical studies. Physical Review Letters, **59**, 1464–1467 (1987). https://doi.org/10.1103/PhysRevLett.59.1464

[26] Ginder J. M., Richter A. F., MacDiarmid A. G., Epstein A. J.: Insulator-to-metal transition in polyaniline. Solid State Communication, **63**, 97–101 (1987). https://doi.org/10.1016/0038-1098(87)91173-2

[27] Al-Zohbi F., Ghamouss F., Schmaltz B., Abarbri M., Zaghrioui M., Tran-Van F.: Enhanced storage performance of PANI and PANI/graphene composites synthesized in protic ionic liquids. Materials, **14**, 4275–4291 (2021). https://doi.org/10.3390/ma14154275

[28] Pahovnik D., Žagar E., Kogej K., Vohlidal J., Žigon M.: Polyaniline nanostructures prepared in acidic aqueous solutions of ionic liquids acting as soft templates. European Polymer Journal, **49**, 1381–1390 (2013). https://doi.org/10.1016/j.eurpolymj.2013.02.019

[29] Song H., Zhang J., Song P., Xiong Y.: Maize-like ionic liquid@polyaniline nanocomposites for high performance supercapacitor. e-Polymers, **19**, 313–322 (2019). https://doi.org/10.1515/epoly-2019-0032

[30] Cao Z., Xia Y.: Synthesis and tribological properties of polyaniline functionalized by ionic liquids. Journal of Materials Science, **53**, 7060–7071 (2018). https://doi.org/10.1007/s10853-018-2028-7

[31] Yang D., Fadeev A. G., Adams P. N., Mattes B. R.: GPC characterization of emeraldine base in NMP containing ionic liquids. Synthetic Metals, **157**, 988–996 (2007). https://doi.org/10.1016/j.synthmet.2007.10.002

[32] Ohno H.: Electrochemical aspects of ionic liquids. Wiley, Tokyo (2011).

[33] Al-Zohbi F., Jacquemin J., Ghamouss F., Schmaltz B., Abarbri M., Cherry K., Tabcheh M. F., Tran-Van F.: Impact of the aqueous pyrrolidinium hydrogen sulfate electrolyte formulation on transport properties and electrochemical performances for polyaniline-based supercapacitor. Journal of Power Sources, **431**, 162–169 (2019). https://doi.org/10.1016/j.jpowsour.2019.05.018

[34] Al-Zohbi F., Ghamouss F., Schmaltz B., Abarbri M., Cherry K., Tabcheh M. F., Tran-Van F.: Beyond contribution of ionic liquids in nanostructuring polyaniline morphology; its effect on the properties of the polymerization medium. Nano Materials Science, in press (2024). https://doi.org/10.1016/j.nanoms.2023.12.001

[35] Laska J., Girault R., Quillard S., Louarn G., Proń A., Lefrant S.: Raman spectroscopic studies of polyaniline protonation with bis(2-ethylhexyl) hydrogen phosphate. Synthetic Metals, **75**, 69–74 (1995). https://doi.org/10.1016/0379-6779(95)03379-X

[36] Cachet M., Quillard S., Buisson J. P., Lefrant S., Louarn G.: Vibrational study of the base form of polyaniline: Effect of the 3D character. Synthetic Metals, **101**, 793–794 (1999). https://doi.org/10.1016/S0379-6779(98)00796-6

[37] Kulkarni M. V., Viswanath A. K.: Comparative studies of chemically synthesized polyaniline and poly(o-toluidine) doped with *p*-toluene sulphonic acid. European Polymer Journal, **40**, 379–384 (2004). https://doi.org/10.1016/j.eurpolymj.2003.10.007

[38] Saranya S., Selvan R. K., Priyadharsini N.: Synthesis and characterization of polyaniline/mnwo4 nanocomposites as electrodes for pseudocapacitors. Applied Surface Science, **258**, 4881–4887 (2012). https://doi.org/10.1016/j.apsusc.2012.01.104

[39] Al Zohbi F., Ghamouss F., Schmaltz B., Abarbri M., Cherry K., Tabcheh M. F., Tran Van F.: Nanostructuring polyaniline using non-substituted imidazolium-based ionic liquid as polymerization medium enabling faster supercapacitor Operation. Applied Functional Materials, **3**, 1–11 (2022). https://doi.org/10.35745/afm2022v02.03.0001