Role of Protonic and Charge Transfer Doping in Solid-State Polyaniline

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Addition of triflate salts to the emeraldine base form of polyaniline in the solid state causes a lowering of its work function but not an increase of its conductivity. It is postulated that this effect is due to the formation of localized energy states in the band gap. On the other hand, strong protonic acids such as triflic acid as well as tetrafluoroboric acid lower both the work function and increase the conductivity of PANI-EB according to the known protonic form of the doping mechanism. The difference between these two kinds of doping has been demonstrated by measurement of the work function, conductivity, UV–vis, and IR spectroscopy.

Introduction

Work function (WF) is a critically important parameter in the operation of devices in which a conducting polymer is capacitively coupled to the rest of the structure. Such devices include field-effect transistors,[1] Schottky diodes,[2] and certain gas sensors.[3] Polyaniline is the material of choice for use in solid-state devices because, among other things, it is easy to synthesize electrochemically, it has high conductivity when doped, and it has been shown to be stable in ambient conditions. It is also unique among conducting polymers because it can be doped both by protonation and by oxidative doping.[4]

While there is a large volume of literature concerning the effect of doping on the conductivity of organic semiconductors,[5–7] there is relatively little describing the effect of doping on changes of work function.[8] The goal of our study has been to elucidate the differences between protonic and charge transfer doping on polyaniline. Previous work in our laboratory has shown that it is possible to control the WF of polyaniline with photogenerated triflic acid (HSO_3CF_3).[9,10] This approach can be then used to adjust the threshold voltage (V_T) of a silicon-based field-effect transistor (FET) in which a polyaniline-containing photoacid precursor serves as the gate conductor. It was noted during the course of these studies that the WF of emeraldine base (PANI-EB) was always much higher than that of PANI-EB, which was mixed with the triflic acid precursor, triphenylsulfonium triflate ($Ph_3SSO_3CF_3$). It was further found that other salts containing triflate anion doped the polyaniline through a charge transfer mechanism. This kind of doping lowered the WF of PANI but it did not affect its conductivity. On the other hand, doping with a photogenerated Bronsted acid both lowered the WF and increased the conductivity of PANI. The model of proposed microheterogeneity in PANI-EB[11–13] and localized energy states[14] could explain this apparent discrepancy. In this paper we report on the investigation of these two types of doping and how they affect the electronic properties of PANI.

Experimental Section

Reagents. Aniline (Aldrich, 99.5%), tetrafluoroboric acid (Aldrich, 48% in water), ammonium hydroxide (Fisher, 29.3% in water), methanol (Fisher), and *N,N*,-dimethylformamide (DMF) (Fisher, 99.9%) were used as received. Sodium triflate (Aldrich, 98%), tetrabutylammonium triflate (Aldrich, 99%), triphenylsulfonium triflate (Aldrich), and triphenylsulfonium tetrafluoroborate (TCI America) were dried under vacuum before use.

Polyaniline Solution Preparation. Polyaniline (PANI) was electrochemically synthesized according to the literature procedure from a solution of 0.1 M aniline in 2 M HBF_4 in water.[15] The as-grown PANI was removed from the Pt working electrode and stirred in 30% ammonium hydroxide for ca. 24 h to convert this material to the deprotonated, emeraldine base (PANI-EB) form. PANI-EB was collected by filtration and washed profusely with methanol and DI water. After drying in air for ca. 24 h, the PANI-EB powder was extracted three times with DMF with 1 mL of DMF for every milligram of solids. Extract aliquots were combined and then filtered through 0.8 μm followed by 0.2 μm syringe filters (SuporAcrodisc, GelmanSciences). The final concentration by mass of the PANI-EB in DMF was determined gravimetrically and was typically in the range 1–2 mg/mL.

Film Casting. Dopant salt solutions in DMF (~0.1 M) were freshly prepared before use. In the case of photolabile dopants, care was taken to minimize exposure to ambient light. Small volumes of dopant solutions were added to 500 μL aliquots of PANI-EB in DMF, and the mixture was agitated for ca. 1 h. Solutions of PANI-EB with dopant were cast onto substrates and dried in the dark under an ambient atmosphere for ca. 24 h. Substrates included glass slides for UV–vis spectroscopy, gold-on-glass slides for reflective FTIR spectroscopy, and FETs for WF measurements.

Dopant concentration in the solid PANI films were calculated as follows: The number of moles of PANI nitrogen was estimated from the mass of solids and the molecular weight of the aniline monomer unit. The number of moles of salt dopant was then ratioed with the moles of PANI nitrogen. The resulting mole fraction was then multiplied by 100 to report the concentration of dopant as a percentage of PANI nitrogen. For example, a reported concentration of 25% means that there was, on average, one dopant molecule for every four PANI nitrogens.

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This would correspond to a 1:1 ratio of dopant to the four monomer repeat units of PANI.

UV−Vis. UV−visible spectra were obtained with a Shimadzu UV-3101PC double-beam, scanning spectrophotometer. For solid PANI films on glass slides, a clean glass slide was placed in the reference beam. The spectra of cast films were baseline corrected to the isosbestic point at 464 nm to account for variations in the thicknesses of the films.[10] Solution spectra were obtained in 1.00 cm path length quartz cuvettes with a cuvette of DMF in the reference beam.

FTIR. Reflection attenuated total reflectance (ATR) FTIR spectra of solid PANI films on gold-coated glass slides were obtained with a BioRad FTS 6000 Spectrometer utilizing a UMA-500 microscope attachment with a Ge crystal for surface ATR measurements. Air was used as the background.

Determination of the WF with a Field-Effect Transistor. A field-effect transistor (FET) is a three terminal device in which the current passing between two terminals (called source and drain) is modulated by the third, electrically insulated electrode (the gate) that produces electric field at and near the surface of the semiconductor. In an enhancement mode device, application of a minimum potential (threshold voltage) to the gate will turn on the current flow between the source and drain when the potential is applied to the drain. The turn-on or threshold voltage (V_T) of a FET is dependent on the difference between the WF of the gate conductor and the bulk silicon. The FET structure affords a convenient opportunity to compare the WF of different materials. A simplified FET schematic is shown in Figure 3 (inset). Note that in this case the gate conductor (PANI) is capacitively coupled to the silicon substrate. No current passes through the PANI gate conductor, which is deposited on a 120 nm thick silicon oxide/silicon nitride. The measured current passes only through the silicon channel between the two n-type diffusions. The FETs used in this work were n-channel devices, meaning the substrate silicon was p-type and the induced channel was n-type. Thus the polarity of a WF change is unambiguously determined by the construction of the device. If V_T moves to lower values, the WF of the gate conductor decreases; that is, the Fermi level moves closer to the vacuum reference level and vice versa.

PANI films were cast from DMF solution onto the bare insulator of a FET via a microliter syringe. The casting solution was confined to the 400 μm by 500 μm gate area by a photolithographically defined 200 μm deep epoxy well. A single gold lead contacted both the solid PANI gate conductor and the drain of the device. With the device source lead grounded, a positive potential sweep was applied to the drain/gate lead while the drain current was measured. Drain current (I_D)−gate voltage (V_G) characteristics of the FET were recorded with an HP 4155A semiconductor parameter analyzer. The threshold voltage was estimated by regression analysis of the linear portion of the $I_D^{1/2}$ versus V_G curve.

The FET devices used in this study were part of an eight-element array. Each array was located on a separate chip. The precision of V_T data for replicate PANI castings on all eight FETs on a single chip were calculated at the 90% confidence limit to be ±0.07 V of the recorded value. The measurement uncertainty was assumed to be homoscedastic. This means that threshold voltages on a single chip can be directly compared to a high level of confidence. The average V_T for two different chips, each with eight replicate PANI castings, was compared with a t-test to be significantly different up to the 95% confidence level. This means that the threshold voltages for two different chips cannot be directly compared.
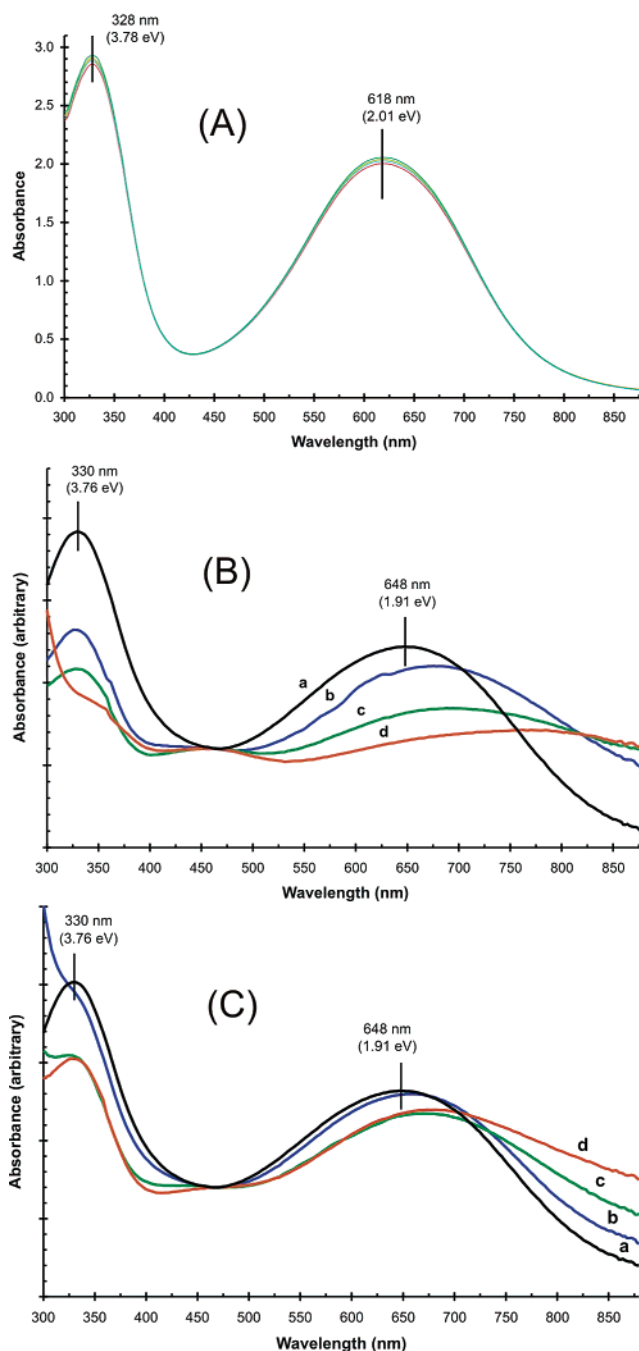

Figure 1. (A) UV−vis spectra for PANI-EB mixed with sodium triflate in DMF solution. (B) PANI-EB solid film containing sodium triflate salt in ratio with respect to the aniline unit: (a) 0.0, (b) 0.12, (c) 0.23, (d) 0.36. (C) PANI-EB in the solid film containing tetrabutylammonium triflate in the same ratios as in (B). Spectra were normalized to the absorbance at 464 nm = 1.0000.

Impedance. Impedance measurements were performed with a CH Instruments model 660 electrochemical workstation. Impedance was measured from 10^5 to 10^{-1} Hz at an amplitude of 10 mV. Materials were cast onto interdigitated microsensor electrodes (IMEs, Abtech Scientific, Richmond, VA). The digits were 100 nm of Pt on top of 0.1 nm Ti on a borosilicate glass substrate. Digits were 5 mm long and 10 μm wide and were spaced 10 μm apart. There were 25 digit pairs. Impedance values were measured but the specific conductivity of PANI was not calculated because of the uncertainty of the geometry of the cast film.
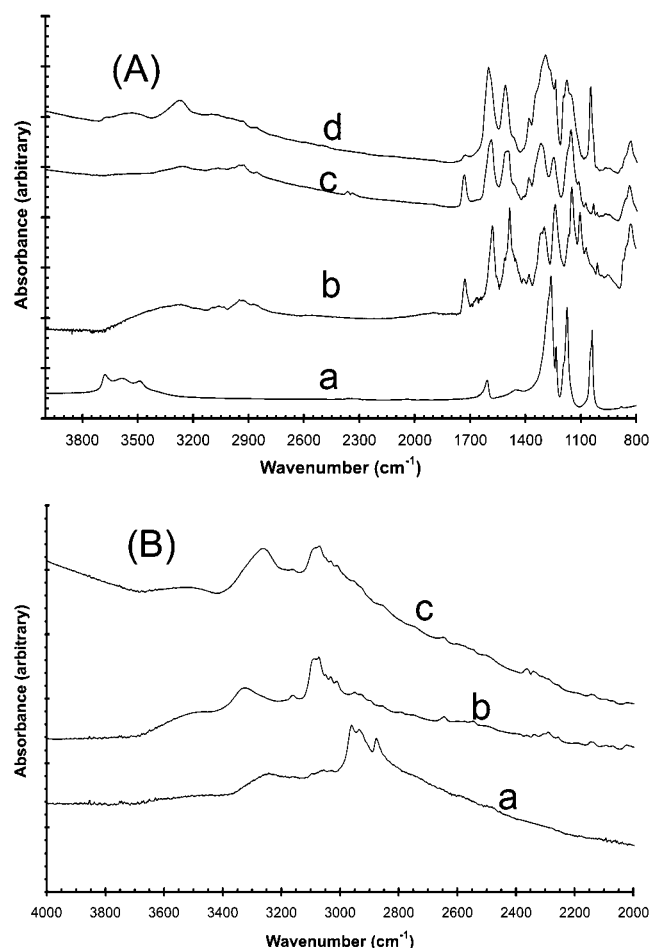
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Figure 2. (A) FTIR spectra for (a) sodium triflate in the KBr pellet and (b)−(d) PANI-EB mixed with sodium triflate in the molar ratios 0.0, 0.12, and 0.23, respectively. (B) shows spectra of PANI-EB mixed with (a) tetrabutylammonium triflate, 0.36 molar ratio, (b) Ph$_3$S triflate (as cast), and (c) Ph$_3$S triflate (irradiated for 60 s with UV light).

Results and Discussion

Spectroscopy. The electronic properties of polyaniline have been investigated with UV−vis spectroscopy as a function of oxidation state[16,17] and as a function of doping with Bronsted acids[16,18,19] and Lewis acids,[20,21] as well as donors and acceptors.[18,22] In this work, it was observed that there was substantial difference in behavior of PANI doped with triflate salts in solution and in the solid film. The spectra of the PANI-EB/ sodium triflate (NaT) mixtures in DMF solution are shown in Figure 1A. The absorption around 320 nm is due to the $\pi-\pi^*$ transition[23,24] whereas the band at 640 nm has been assigned to the charge transfer exciton formed by the transition of the benzenoid to an adjacent quinoid group.[25] There is practically no change in the spectrum of this mixture between 0 and 0.67 NaT:PANI molar ratios in solution. This is because the DMF has a high dielectric constant (38.3 at 20 °C) that results in the dissociation of the salt and solvation of the ions.

The solid films of PANI/triflate salt mixtures in the same molar ratios were cast on glass slides. The spectra of cast films were baseline corrected to the isosbestic point at 464 nm to account for variations in the thickness of the films (Figure 1B). It has been observed that *in the solid state* both absorbance peaks decrease according to Beer's Law with respect to the added sodium triflate. There is a decrease in the $\pi-\pi^*$ absorbance at 330 nm with increasing concentration of sodium triflate. This indicates a decrease in the number of $\pi-\pi^*$ transitions. In the
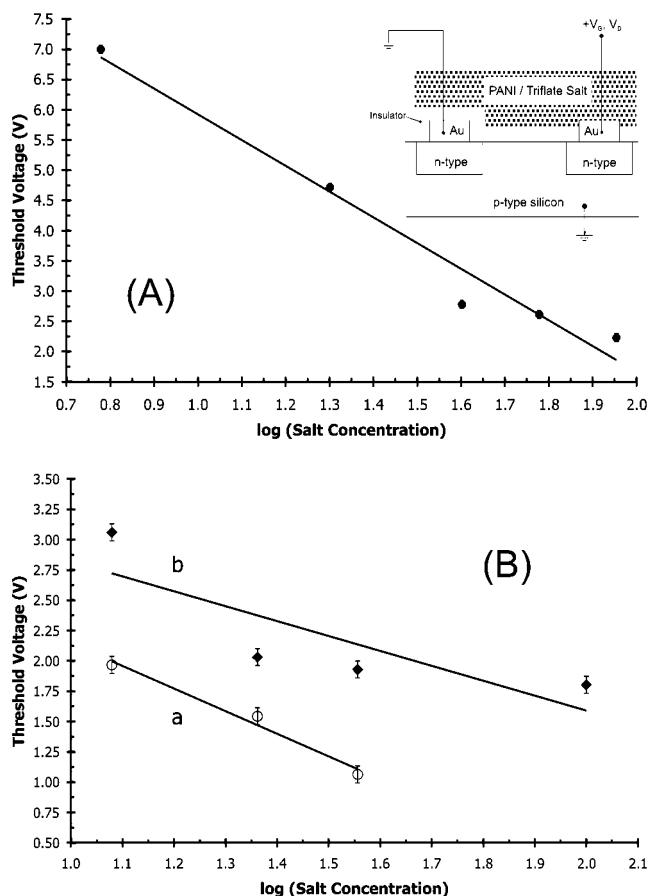

Figure 3. FET threshold voltage as a function of triflate salt concentration with respect to the PANI aniline monomer. (A) PANI-EB with sodium triflate on a single FET array chip. (B) PANI-EB with (a) sodium triflate and (b) tetrabutylammonium triflate on another chip. Connection lines are for visual aid. Error bars indicate the 90% confidence interval. Inset: FET schematic.

solid state the energy of this band corresponds to the width of the band gap (∼3.76 eV).

The accompanying red shift of the band at ca. 640 nm indicates structural changes in the polymer that are due to the changes in the inter- and intramolecular interactions between the benzenoid and quinoid units. The effect of the size of the cation is demonstrated in Figure 1C. In that case the presence of the bulkier tetrabutylammonium cation resulted in a similar but qualitatively slightly different spectrum. Finally, there is a relative increase in absorbance above 800 nm showing an increase in the number of π-polaron transitions. The developing tail continues to the near-infrared part of the spectrum and will be discussed later. The spectral shifts noted here for the sodium triflate are similar to those observed for polyaniline doped by a proton in the solid state.[10] As protons are added, polarons are formed along the polymer chains, but there is no formal change of the redox state of PANI.

Further structural insight into changes in polyaniline brought about by triflate salts can be found in the FTIR spectra. Figure 2A shows the FTIR spectra of the PANI-EB (spectrum b) and PANI-EB with increasing amounts of sodium triflate (spectra c−d). The fingerprint region (800−1800 cm^{-1}) of PANI-EB mixed with triflate salts is complicated by the overlapping bands corresponding to these salts (Figure 2A, spectrum a). The changes in this region induced by various forms of doping have been discussed in detail previously[10] and will not be repeated here. One exception is the carbonyl peak at 1730 cm^{-1} that was present in all cast films. It is due to the DMF casting solvent
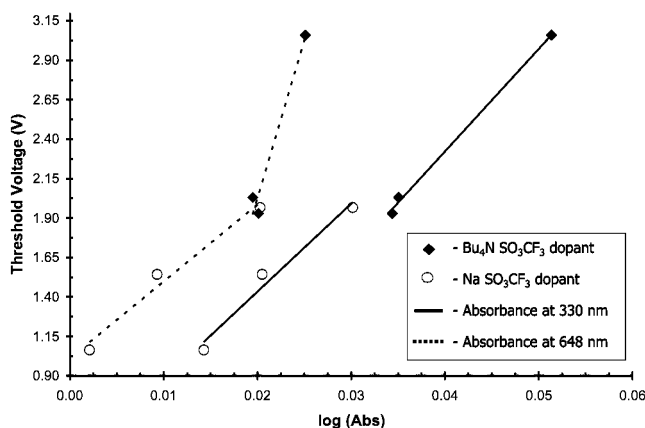
Figure 4. Cross-correlation of FET V_T measurements and UV−vis spectroscopic measurements at 330 and 648 nm. Data taken from Figures 1 and 3.

Figure 5. Normalized difference spectra of PANI-EB/sodium triflate. Data taken from Figure 1B.

incorporated in the solid films, to a greater or lesser degree. Attempts at complete removal of DMF by extended vacuum pumping at elevated temperature were unsuccessful, indicating that the solvent is strongly sorbed. This is consistent with most elemental analysis reports indicating the presence of residual solvents in PANI films.[20,21]

Of most relevance to the present study is the increase of the absorption starting at 2000 cm^{-1} and continuing through 4000 cm^{-1} to the near-infrared and visible part of the spectrum (Figure 2A, spectra c and d). It is even more prominent in films protonated by photogenerated triflic acid (Figure 2B, spectrum c). On the other hand, it is absent in PANI-EB films containing triphenylsulfonium triflate before irradiation (Figure 2B, spectrum b) or Bu$_4$N triflate (Figure 2B, spectrum a). It has been attributed to the presence of free, mobile charge carriers.[16,25] UV-vis spectra of "as cast" Ph$_3$S triflate and after irradiation can be found in ref 9. They are very similar to those shown in Figure 1B.

WF Measurements. Extrapolated threshold voltages[9] for FET with PANI-EB/triflate salt gate conductor at various molar ratios are shown in Figure 3A. It shows data for PANI-EB doped with increasing amounts of sodium triflate, all cast on a single FET array chip. Figure 3B gives data taken on a different chip. Generally, each set of points shows a shift of V_T in the negative direction with increasing salt concentration. The transistors with PANI-EB, without the triflate dopant, exhibit V_T of greater than 7 V. In contrast, PANI-EB containing even small amounts of triflate salt show a remarkably low V_T of less than 5 V and in most cases, less than 3 V. The observed shift in threshold voltage indicating a decrease of the WF is consistent with the spectral changes discussed earlier and is further evidence that triflate salts are able to dope PANI even without the presence of proton.

As mentioned in the Experimental Section, V_T values should be directly compared only on the same chip. In Figure 3B a lower V_T is observed for sodium triflate materials compared with tetrabutylammonium triflate. The difference indicates a cation effect and may be explained by the fact that Na$^+$ is more similar to H$^+$ than Bu$_4$N$^+$ and can more readily take the place of a proton in the charge transfer doping mechanism.

Figure 4 demonstrates a cross correlation between V_T and optical absorption for PANI doped with triflate salts. Absorbance values at two photon energies are plotted. The linearity of the plots indicates that the changes in the PANI WF are a real function of doping, not due to some other process. Similar trends of linearity were observed for other batches of PANI and different FET array chips, but as expected, the specific correla-
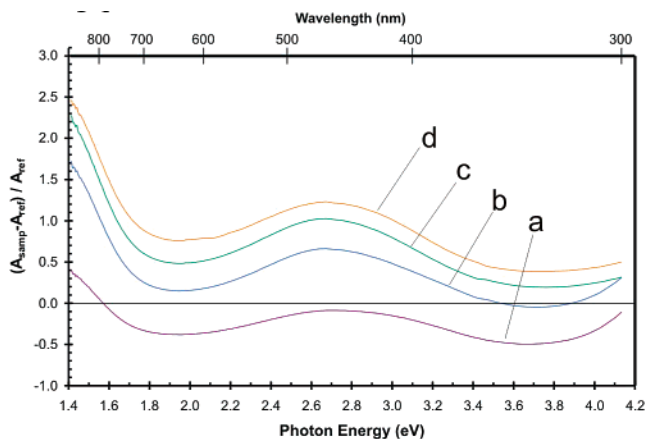
tion slopes did not directly overlap. The linearity of the plots also indicates that to a first approximation, the relative WF change can be predicted from the UV−vis spectra of a PANI/triflate salt blend.

Based on the spectroscopic and WF characterization of PANI mixed with triflate salts, a possible mechanism for the charge transfer doping is proposed. The mechanism mirrors one for proton doping of PANI.[26] Optical spectroscopy clearly indicates polaron formation in PANI samples containing triflate salts. The accepted mechanism for polaron formation in polyaniline is that the lone pair on the imine nitrogen of PANI-EB bonds with a proton to form a radical cation.[25,27] The degree of protonation determines the electronic properties of the doped PANI. The ability of the Bronsted acid to donate a proton is determined by the anion and by the dielectric constant of the medium. Similarly, the anion of a salt will influence the tendency to donate cations. Triflic acid is a strong organic acid. It therefore follows that triflate salts, particularly with small, hard cations, may behave chemically similarly to the free acid. The proposed charge transfer mechanism is shown in the following scheme:

$$=\mathbf{N:} + (\mathbf{B^+A^-}) = (=\mathbf{N:} \rightarrow \mathbf{B^+A^-}) = (=\mathbf{N:} \rightarrow \mathbf{B^+}) + \mathbf{A^-}$$

where $=\mathbf{N:}$ is the imine nitrogen of the polyaniline and B$^+$ and A$^-$ are the cation and anion of the salt, respectively. The position of the equilibrium will be determined by the relative donor/acceptor properties of the salt ion pair relative to the PANI nitrogens. It follows that it should be possible to substitute other cations in place of the proton to the similar effect. In fact, it has been shown previously that lithium salts will successfully dope PANI into a conducting state.[28−30]

Concurrent with the polaron formation, the WF of PANI is lowered, that is, the Fermi level is shifted closer to the conduction band. There are two possible mechanisms for this shift. The first is that the triflate salt is acting like a Lewis base and is injecting electrons into the PANI conduction band. Such electron donor doping takes place when PANI is exposed to a strong Lewis base, such as ammonia.[31] The other possibility is that the presence of triflate anion leads to creation of localized states within the band gap. The probability of the two mechanisms depends on the properties of the dopant ion pair. In the case of triflate salts, it seems that the formation of midgap states is more likely than the electron injection. This interpretation is supported by the UV−vis data in Figure 5. The normalized difference spectra clearly shows that the doped materials have increased absorbance at about 460 nm (2.7 eV), indicating formation of states within the band gap.

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TABLE 1

monomer ratio (%) Ph₃S BF₄: PANI	V_T (V) as−cast	V_T (V), after 60 s UV
0	>7	>7
26	>7	5.468
59	>7	2.545
93	>7	2.195

The fact that two different mechanisms (electron injection and gap state formation) can cause a WF shift in the same direction suggests the possibility for decoupling the changes in the WF from the changes in conductivity. The WF is dictated by the chemical potential of the electron, which depends on the number and location of charge carriers in the band structure. Conductivity, on the other hand, is determined by both the number of free carriers *and their mobility*. A dopant that creates carriers, but also effectively traps them, should show a change in the WF but should not increase the conductivity of the material. On the other hand, a dopant that acts through charge injection into the conduction band will simultaneously shift the conductivity and the WF.

Proton doping and salt doping of PANI-EB both dramatically shift the WF, as demonstrated by the V_T changes. Additionally, the conductivity was investigated with impedance analysis of solid samples cast on interdigitated electrode substrates. Impedance values were compared for PANI containing Na-triflate and Ph₃S-triflate. Both materials had very high impedances of ∼10⁹ Ω at low frequencies. This is expected from the proposed doping model, and is consistent with the UV−vis and NIR observations. The sample containing the photolabile Ph₃S triflate was then irradiated with UV light (5 W deuterium lamp) for 60 s to produce free protons. After irradiation, the impedance of the now proton doped film dropped to ∼10³ Ω. The dramatic increase in PANI conductivity upon proton doping in solid-state confirms the results reported previously.[10]

In experiments analogous to those performed in earlier work,[9] polyaniline was mixed with triphenylsulfonium tetrafluoroborate (Ph₃S BF₄). The material was cast from DMF solution onto FETs and the threshold voltage was measured. The material was then subjected to UV radiation for 60 s and V_T was measured again. Table 1 gives the results of the these experiments.

The high V_T measured for the as-cast materials clearly indicate that, in contrast to both photoactive and photoinactive *triflate* salts, the *tetrafluoroborate* salt does *not* dope polyaniline. Only after the material has been photolyzed to release protons can polaron formation be inferred by the dramatic lowering of threshold voltage and by spectroscopy. The above observations confirm that a salt with a less polarizing anion does not dope PANI as strongly, if at all, as the triflate salts.

Summary

Polyaniline mixed with triflate salts was characterized spectroscopically by UV−vis and FT-IR and electrochemically by measurements of the WF and conductivity. The results indicate that the triflate salts are able to dope polyaniline. The changes in FET threshold voltage mirror the lowering of the PANI WF by formation of polarons. The proposed mechanism indicates a charge transfer from the lone pair on the PANI imine nitrogen to the cation of the salt made possible by the highly polarizing nature of the triflate anion. The doping effects occur only in the solid state. There is no charge transfer doping of PANI dissolved in DMF. The shift in the PANI WF is not accompanied by a similar change of conductivity due to the

absence of mobile charge carriers, as shown by impedance measurements. This result is also corroborated by the spectral evidence in the near-IR region. This type of doping is in stark contrast to the protonic doping resulting in increased conductivity and near-IR absorption. Triphenylsulfonium tetrafluoroborate salt did not dope PANI prior to photogeneration of protons, indicating that BF₄⁻ is a less strong polarizing anion in the solid state than SO₃CF₃⁻.

In most articles describing polyaniline doping the focus is on conductivity. This is true for protons or other small doping cations, such as lithium or sodium. Such doping is accompanied also by lowering of the WF of polyaniline. Doping with oxidizing or reducing agents in which an integer value of charge is exchanged between the dopant and conducting polymer leads to changes of conductivity and the WF.[4] However, the results of this work show that doping with triflate salts lowers the WF of PANI but *does not* affect the conductivity of the polymer. In light of the proposed segmented model of PANI-EB[11] and localized electronic states[14] it is possible to speculate that doping with triflate anion leads to formation of such localized states that do not contribute to the conductivity but lower the WF of the polymer. We call this form of doping *charge transfer doping* as opposed to *oxidative* and *protonic doping*. In the case of the former a localized charge transfer complex is formed between the dopant and the polymer matrix, in which only a fractional and apparently localized charge is exchanged.[3] This distinction has important implications for use of PANI in various types of electronic structures. When PANI is used as the replacement for the metal in the gate of insulated gate field-effect transistor the value of the WF is critically important because it controls the threshold voltage. Since there is no current passing through the PANI layer in such a device, its conductivity is irrelevant. However, when PANI itself is used as a conductor of electronic current, the type of doping that leads to conductivity changes is important. Moreover, in some devices, such as thin-film transistors *both the charge transfer and protonic doping* play role in the operational characteristics of the device.

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