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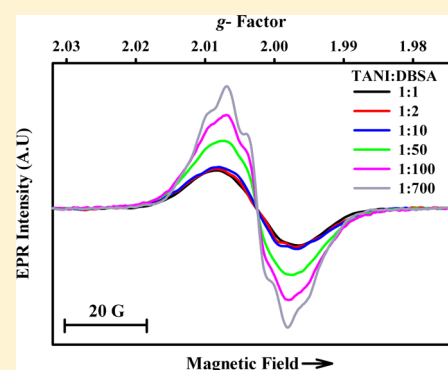
# Intramolecular Transport of Charge Carriers in Trimeric Aniline upon a Three-Step Acid Doping Process

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**ABSTRACT:** The “acid doping” of a methyl-capped aniline trimer, *N*-[4-(dimethylamino)phenyl]-*N*-(4-{[4-(dimethylamino)phenyl]imino}-2,5-cyclohexadien-1-ylidene)-amine (TANI), was performed stoichiometrically to study the nature of charge carriers induced by the acid protonation process. The redox centers in TANI were found to undergo a reversible three-step protonation with 1 equiv, 2 equiv and a large molar excess of dodecylbenzenesulfonic acid (DBSA) in chloroform, as evidenced by three different chromophores (doping levels I, II and III) observed using UV–vis–NIR. Acidity of the dopants and solvent polarity were controlling factors. As revealed by electron paramagnetic resonance spectroscopy (EPR), the doping levels I, II, and III achieved by doping 0.1 mM TANI/chloroform solutions with different amounts of DBSA exhibited relative spin densities of 1:1.2:2.2. Since the expected maximum spin population of TANI through acid doping is two spins per molecule, the reduced paramagnetism given by the doubly protonated TANI (doping level II) indicated partially coupled unpaired spins. The third protonation step (doping level III) produced almost double the unpaired spin concentration compared to the lower doping levels and a multiline EPR spectrum likely comprising two overlapping signals of similar overall line width. The hyperfine couplings contributing to the splittings in this signal were estimated by simulation incorporating 6-H and 1-N nuclei most likely from one highly localized unpaired spin on a terminal dimethylamino group, with an underlying apparent singlet arising from a delocalized unpaired spin; the diradical proposed as the species exhibiting the multiplet EPR signal is isolated by the bridging ammonium cation created by the third doping step. The phenomena suggested the stepwise evolution of partly formed diamagnetic bipolarons from polaron interactions at doping level II and the transformation to the more isolated unsymmetrical system we label “two polarons on a chain” in a triplet state at doping level III. The results provide the characterization of novel doping behaviors for a trimeric aniline molecule in organic solution.



## INTRODUCTION

Polyaniline (PANI), as one of the most studied conducting polymers, has attracted considerable attention during the past 20 years due to its adjustable conductivity, good stability and mechanical flexibility. It has been widely used in sensors, solar cells, rechargeable batteries, light emitting diodes and electrochromic materials.<sup>1–6</sup> Unlike most conducting polymers depending on oxidative and reductive doping, PANI changes into its conducting form, known as the emeraldine salt form (ES), through the so-called nonredox or acid doping of its insulating emeraldine base form (EB).<sup>7</sup> Two types of charge carriers created in that process have been described: the delocalized paramagnetic singly charged polaron with spin = 1/2, and the localized doubly charged diamagnetic bipolaron. The bipolaron structure is widely accepted as being formed by the energetically favorable coalescence of two polarons into a nonparamagnetic dication.<sup>8</sup> In such a bipolaron structure, the two unpaired spins are coupled and form a unique deformation segment. It was postulated that in relatively longer chains, the

“two polarons on a chain” structure is predominant because of reduced coupling between two sites, while the bipolaron structure ( $S = 0$ ) tends to form in oligomers with shorter length of the conjugated system, evidenced by the loss of EPR signals.<sup>9,10</sup>

Oligomeric PANI analogues have been synthesized with a variety of well-defined conjugational lengths for the past decade, mostly because of their good solubility in common solvents, ease of crystallization, and chemical manipulation.<sup>11–15</sup> While oligomers of the thiophene family have frequently been used to study the electronic properties evolved upon oxidation in conjugated structures both experimentally and theoretically, the systematic study of stoichiometric acid–base doping–dedoping of aniline oligomers has rarely been conducted.<sup>16–18</sup> For example, Janssen et al. synthesized and

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studied the doping and redox behavior of a series of meta–para aniline oligomers. However, the relationship between chemical structure evolved through quantitative protonation and the resulting EPR signals and properties was not addressed in detail.<sup>19,20</sup>

In this contribution, TANI, a trimeric aniline with 4 redox centers including 2 imino nitrogens atoms and 2 amino nitrogens, similar to PANI, was synthesized and studied upon stepwise acid doping. It exhibited three distinct doped states (levels I, II, and III) with increasing amount of organic acid added in chloroform solution, behavior more complex than the single doped state ES of PANI achieved with 2 equiv of acid. The follow-up titration with tetrabutylammonium hydroxide (TBAH), a Brønsted base, proved the reversibility of the three-step doping process. Although the concept of “secondary doping” beyond the ES species was proposed by MacDiarmid and Epstein, the phenomenon was attributed to the change in PANI-ES conformation from “compact coil” to “expanded coil” induced by *m*-cresol instead of a newly formed chemical structure caused by additional acid doping.<sup>21</sup> Here, we confirm and characterize the three-step acid doping of TANI's redox centers through a polaron, two partially coupled polarons, and a triplet “two polarons on a string” transformation process, providing a new view of the transport properties of the different charge carriers.

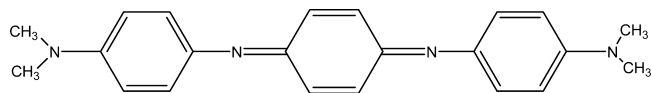
Moreover, the three-level doping that produces a wide range of optical absorbance phenomena compared to PANI makes the TANI molecule a more versatile and unique candidate for sensors and electrochromic materials worthy of further study.

## EXPERIMENTAL SECTION

**Materials.** Dodecylbenzene sulfonic acid (DBSA) (70% in heptanol), methanesulfonic acid (MSA) (99.5%), HCl (1 M in methanol) and TBAH (1 M in methanol) were purchased from Sigma Aldrich. Toluene and chloroform were anhydrous grade from Sigma Aldrich. Dimethylformamide (DMF) was molecular biology grade from Aldrich. Dimethyl sulfoxide- $d_6$  (DMSO- $d_6$ ) was purchased from Sigma Aldrich. Chemicals used during the synthesis of *N*-[4-(dimethylamino)phenyl]-*N*-(4-{[4-(dimethylamino)phenyl]imino}-2,5-cyclohexadien-1-ylidene)-amine (TANI), including *p*-phenylenediamine (99%), ammonium persulfate (98%), and *N,N*-dimethylaniline (99.5%), were also purchased from Sigma Aldrich.

**Synthesis of Aniline Trimer.** TANI in its undoped or EB form (Scheme 1) was prepared by a one-step method reported

Scheme 1. TANI



in our previous contribution.<sup>22</sup> A 0.86 g (8 mmol) sample of *p*-phenylenediamine was dissolved in the mixed solvent of 100 mL 1 M HCl aqueous solution and 40 mL ethanol. The solution was constantly stirred as it was chilled to  $-5^{\circ}\text{C}$  using an ice-salt bath. 1.8 g (8 mmol) of ammonium persulfate was dissolved in 30 mL of distilled water and added to the *p*-phenylenediamine solution. After about 5 min, a color change from light yellow to dark brown was observed. At this time 2.0 mL (16 mmol) of *N,N*-dimethylaniline was quickly added. A blue suspension immediately formed, and the reaction mixture was maintained between  $-5$  and  $0^{\circ}\text{C}$  for 2 h. The solid

product was collected by Büchner vacuum filtration using Nylon 6-6 filter paper with  $0.2\ \mu\text{m}$  pore size and washed with 40 mL of 1 M HCl aqueous solution followed by 80 mL of distilled water. The product was then treated with 40 mL of 1 M aqueous solution of ammonium hydroxide for 2 h. The solid was collected and the precipitate cake was washed with distilled water until the filtrate gave a neutral pH. The remaining solid was then dried overnight in a vacuum oven at  $60^{\circ}\text{C}$ . The yield was 30%. Further purification was performed using flash chromatography with silica gel (40–200 mesh). The eluant was hexane:chloroform = 60%:40% (v/v) with an additional 2% of triethylamine. Thin layer chromatography (TLC) was used to verify the purity of the product.  $^1\text{H}$  NMR in DMSO- $d_6$  was then used to analyze the compound.

$^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ ):  $\delta$  (ppm) 7.00 (s, 4H, Ar–H ortho to =N), 6.94 (d, 4H, Ar–H ortho to –N), 6.78 (d, 4H, Ar–H ortho to N-(CH $_3$ ) $_2$ ), 2.96 (s, 12H, N-(CH $_3$ ) $_2$ ).

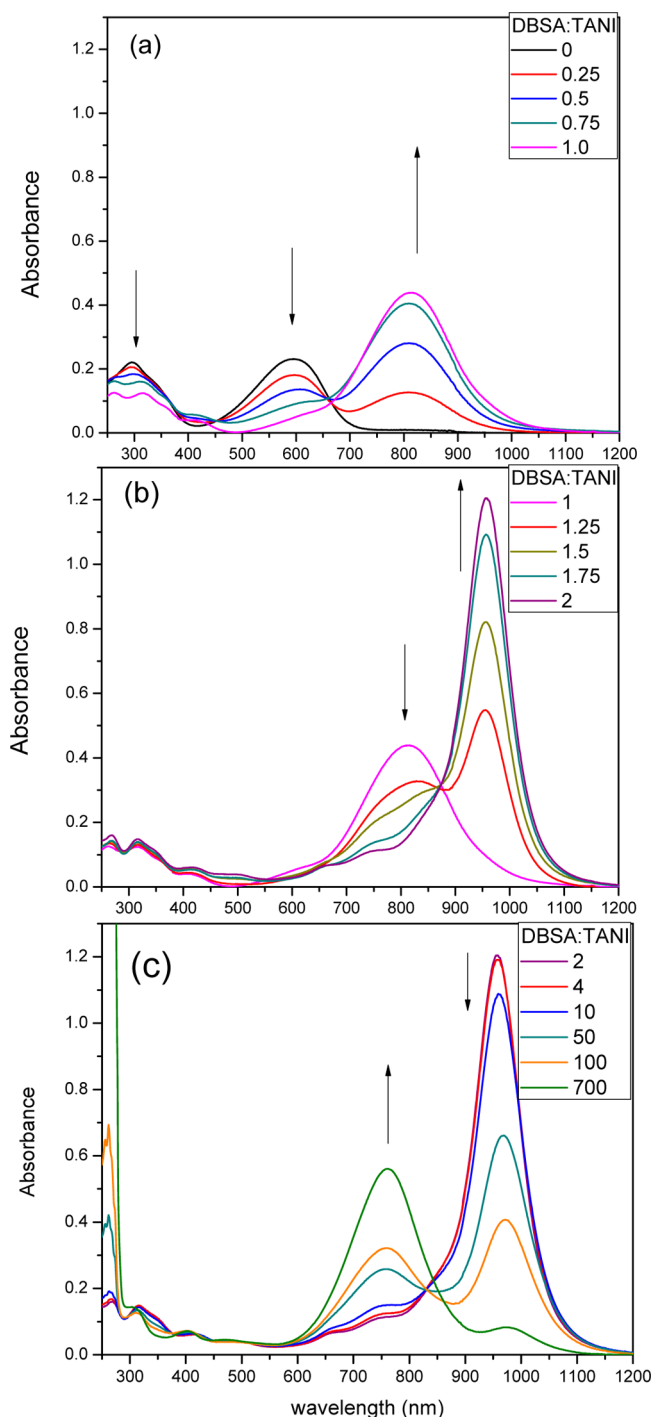
**“Acid Doping”.** TANI solutions (0.1 mM in 10 mL solvents) were titrated at ambient temperature with the appropriate amounts of DBSA, MSA, and HCl in toluene, chloroform, and DMF, respectively, to achieve molar ratios given in the text and figures. At high DBSA concentration, and for dedoping with TBAH, DBSA and TBAH (when used to dedope after addition of DBSA) were mixed into 5 mL of 0.2 mM TANI solution in sequence, and the resulting solution was diluted to 10 mL. Thus, TANI in all solutions was always 0.1 mM. Very small amounts of methanol were added in the titrations with HCl/MeOH and TBAH/MeOH, so no solvent effect from methanol is expected in our experiments.

**Spectroscopic Measurements.** Measurements of ultra-violet–visible–near-infrared (UV–vis–NIR) and electron paramagnetic resonance (EPR) spectra were carried out at room temperature immediately after the solutions were prepared.

UV–vis–NIR absorption spectra (250–1200 nm) were recorded using a Shimadzu UV-3101PC spectrophotometer with samples held in 1 mm optical path length quartz cells. EPR spectra were recorded on a Bruker E500 ElexSys EPR spectrometer operating at X-band using an ER4122SHQE resonator cavity. Data acquisition and manipulation were performed using XepView and WinEPR software (Bruker). Samples of the TANI/DBSA mixtures were held in 4 mm o.d. (3 mm i.d.) precision bore quartz EPR tubes. Experimental parameters used to acquire the EPR spectra were as follows: modulation amplitude, 1 G (or 0.1 G for the experimental spectrum that was simulated); microwave power, 1 mW; modulation frequency, 100 kHz; microwave frequency, 9.86 GHz; sweep time, 327 s; conversion time, 335 ms; time constant, 1310 ms; number of scans, 4. All spectra were recorded at ambient temperature under identical instrumental conditions. Spin concentration was calculated by double integration of EPR signals assigning a value of unity to the spectrum of TANI at doping level I. Since the EPR samples varied in ionic composition and could be lossy to different extents, we present the spin concentrations only in relative terms and note that intensities corresponded to less than one spin per molecule for all doping levels. Simulation of EPR spectra was performed using Simfonia software (Bruker).

## RESULTS AND DISCUSSION

The stepwise protonation of TANI was achieved by titrating the 0.1 mM TANI/chloroform solution with DBSA as shown in Figure 1. In Figure 1a, the absorption spectrum of TANI in its undoped or EB form exhibits a maximum at 597 nm



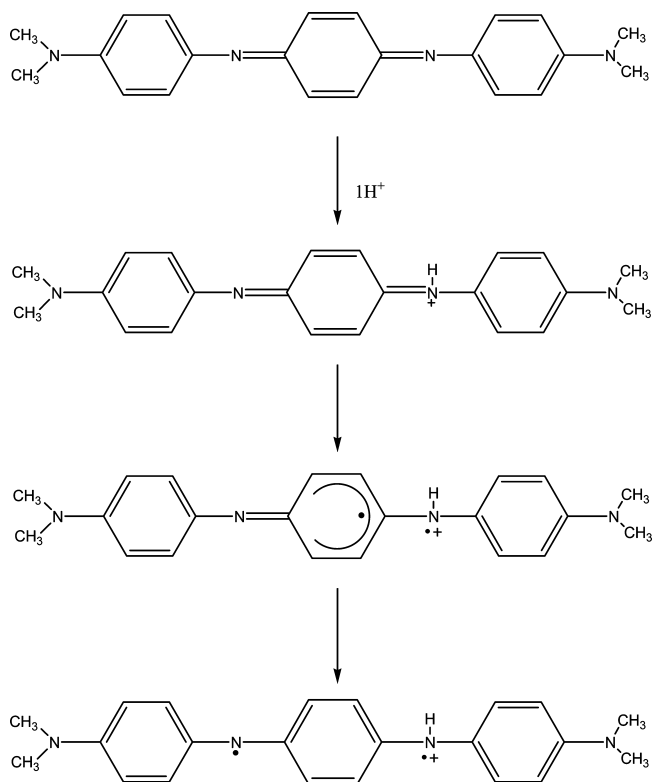
**Figure 1.** UV-vis-NIR spectra during the stepwise protonation (acid doping) of 0.1 mM TANI with DBSA in chloroform at ambient temperature: (a) TANI-EB titrated to doping level I, molar ratio DBSA/TANI from 0 to 1 (b) doping level I to II, DBSA/TANI molar ratio from 1 to 2 (c) Doping level II to III, DBSA/TANI molar ratio from 2 to 700.

corresponding to the exciton transition from the iminoquinone group, as in PANI-EB.<sup>22</sup> During the stepwise addition of DBSA, this peak gradually disappeared, and the band at 806 nm grew in intensity; this red-shifted band in PANI is defined as a  $\pi$ -to-polaron band. The solution turned from purple-blue to emeraldine green.

The shifts demonstrate the similarity between the PANI-EB to PANI-ES transition and the TANI-EB transition to doping level I. However, in the case of PANI, the polaron peak at around 800 nm reaches its maximum intensity only after the addition of 2 equiv of acid, while 1 equiv of acid gives the superposition of the exciton peak together with the polaron peak.<sup>22</sup> This indicates that only half of the total iminoquinone groups (2 imine nitrogens) are doped in PANI under such conditions.

Here, we found that 1 equiv of acid was sufficient to fully dope TANI to produce the first polaron, as evidenced by the complete exciton (597 nm) to polaron peak (806 nm) transition. The behavior observed for TANI had been explained using a disproportionation proton–electron exchange model.<sup>22</sup> However, the previously proposed model now seems to be unlikely for the behavior of TANI because it fails to explain the complete elimination of iminoquinone character revealed by UV-vis-NIR. The complete doping of TANI with the first equiv of DBSA will decrease its basicity, making further doping of the same molecule more difficult than the first doping step. The electronic change arises from elimination of the iminoquinone group, as the protonation of one of the two imine nitrogens leads to resonance structures with a delocalized charge/unpaired spin. (Scheme 2)

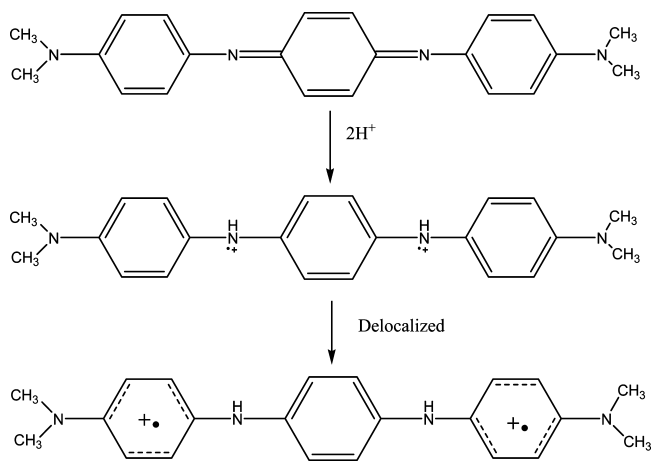
#### Scheme 2. The Protonation of TANI by First 1 equiv of DBSA (Level I)



Interestingly, a second equivalent of DBSA produced a new strong absorbance maximum at 957 nm together with several weak absorptions in the visible region and a loss of the 806 nm polaron peak, with the solution color changing to yellow-green. At this point (doping level II), each TANI molecule is doubly doped (protonated at two sites), and the iminoquinone nitrogens are assumed to have been converted into secondary

amine groups as in PANI (Scheme 3), and similar to the double-doping of other aniline oligomers.<sup>19,23</sup>

**Scheme 3. The Protonation of TANI by First 2 equiv of DBSA (Level II)**

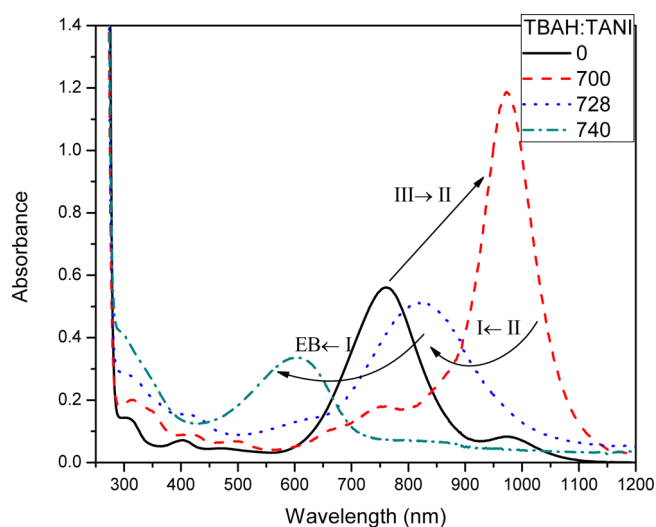


More surprisingly, with the addition of a large excess of DBSA (700 equiv), the 957 nm peak disappeared with a new peak appearing at 742 nm (doping level III; Figure 1c). The solution turned from yellow-green back to emeraldine green. This absorbance shift back to higher energy is likely from further protonation of one of the two middle amine nitrogens in level II-doped TANI. The dication species in the oligomer at doping level II is very difficult to protonate beyond this form such that very high acid concentrations were required for the third conversion. This result coincides with the descriptions of the protonation of amine nitrogen sites in PANI at high acid concentrations reported elsewhere.<sup>24–26</sup>

In order to exclude the possibility of irreversible chemical changes due to the large amount of acid, a dedoping process was initiated to neutralize the excess DBSA. A Brønsted base, TBAH, was used to deprotonate the TANI/DBSA complex starting from doping level III. TBAH was selected due to its solubility in chloroform. The protonation process was shown to be fully reversible such that the molar equivalents of TBAH required to recover the starting optical spectrum of TANI-EB was close to the equivalents of DBSA added (Figure 2). Therefore, it can be concluded that the shifts in UV–vis–NIR correlate with acid–base equilibria and not irreversible chemical reactions.

To further confirm these observations, other acids and aprotic solvents with different polarities were employed to study the doping of TANI (Table 1). We found the three-step protonation exists in other acid/solvent systems. HCl in MeOH was used due to the limited miscibility of aqueous HCl and chloroform.

Acids with different dissociation constants were employed, with a trend in  $pK_a$  values in water as follows:  $HCl < MSA < DBSA$ . In chloroform, doping level I and II can be readily achieved using stoichiometric equivalents of each of these acids. However, much more DBSA (700 equiv) and MSA (500 equiv) relative to HCl (200 equiv) was required to achieve doping level III, as expected. Similarly, in DMF, doping level II was achieved with fewer equivalents of HCl relative to MSA and DBSA.



**Figure 2.** UV–vis spectra of the follow-up stepwise deprotonation of 0.1 mM TANI and 700 equiv of DBSA mixture (doping level III) using TBAH in chloroform at ambient temperature.

Acid doping is considered more favorable in more nonpolar solvents due to increasing acid–solvent interactions in more polar solvents.<sup>27</sup> Here, 2.7 and 100 equiv of DBSA were required to achieve doping levels I and II in the most polar solvent DMF, which was in excess relative to the theoretical molar equivalents effective in toluene and chloroform. Additionally, further protonation was not achievable with large excesses of DBSA. Apparently, DMF possesses too high a polarity for the doping level II to level III transition to occur in it. Also, in strong acid the carbonyl oxygen atom of the DMF molecule could become the target of protonation, consuming acid equivalents. The same trend in achieving level III doping could be seen when HCl and MSA were used as dopant in DMF.

The acidity and solvent polarity effects are now considered the reasons why doping levels II and III were not seen in the previous study of TANI.<sup>22</sup> More dilute TANI/chloroform solutions had been used, in which the acidity was too low to trigger protonation even with the same DBSA/TANI molar ratios. Also, the more polar solvent (*N*-methyl-2-pyrrolidone) used previously also disfavored protonation of TANI.

The observations made using various dopant/solvent systems confirmed that the transitions observed in the optical spectra were from protonation-induced electronic changes, as other more complex behaviors would not be expected to be reproduced under the variety of conditions.

EPR measurements were undertaken to monitor the polaron evolution as a result of acid doping and for comparison to the optical experiments. Spin densities at different DBSA/TANI ratios were normalized to the spin density exhibited by the DBSA/TANI at 1:1 ratio (level I).

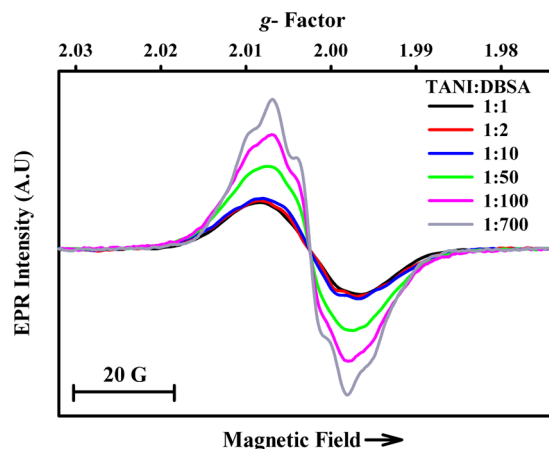
When 1 equiv of DBSA is added to 0.1 mM TANI in chloroform, an EPR singlet is found, characterized by a line width of  $\sim 21$  G (peak to trough) and a  $g$ -factor of 2.0026 (Figure 3). This spectrum lacks resolved hyperfine splittings and is assigned to a single structure with two unpaired electrons, one of which is a cation radical and the second is either a radical in the central ring or a neutral radical on the other bridging nitrogen (resonance forms given in Scheme 2). Both the neutral radical and the polaron (radical cation) of level



**Table 1.** The Acid/TANI Ratios for Doping Levels I, II, and III in 0.1 mM TANI Solution in Different Acid/Solvent Systems

doping levels	HCl			MSA			DBSA		
	I	II	III	I	II	III	I	II	III
toluene ( $\kappa = 2.38$ ) <sup>c</sup>	<i>a</i>	<i>a</i>	<i>a</i>	1	2	<i>a</i>	1	2	20
chloroform ( $\kappa = 4.81$ ) <sup>d</sup>	1	2	200	1	2	500	1	2	700
DMF ( $\kappa = 38$ ) <sup>c</sup>	2.7	50	<i>b</i>	2.7	100	<i>b</i>	2.7	100	<i>b</i>

<sup>a</sup>Can not be achieved due to the limited solubility of methanolic-HCl and MSA in toluene. <sup>b</sup>Doping level III does not occur. <sup>c</sup>Dielectric constant at 25 °C. <sup>d</sup>Dielectric constant at 20 °C.

**Figure 3.** Room-temperature EPR spectra of chloroform solutions of TANI (0.1 mM) with various molar equivalents of DBSA. All signals were centered at  $g = 2.0026 \pm 0.00005$ .

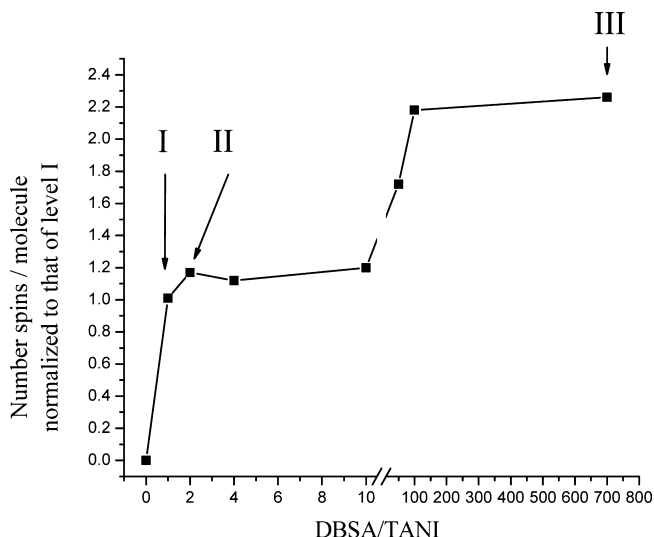
I-doped TANI (Scheme 2) are assumed to be delocalized such that no hyperfine structure was seen in the EPR spectrum.

Surprisingly, when an additional equivalent of DBSA was added, the spin concentration increased only marginally, while in the optical spectra, a complete conversion to a new species was apparent under the same conditions (Figure 1). Therefore, the EPR signal must also arise from a single new species. The EPR line shape remained an apparent singlet without hyperfine splittings again consistent with a delocalized spin system for two unpaired electrons in a diradical dication shown in one resonance form in Scheme 3. In this structure, a polaron pair (two weakly or noninteracting spins) and a bipolaron (coupled spins) can be in resonance. The potential resonance forms in the dication radical (Scheme 3) can place unpaired electron spin into the terminal rings and reduce the spin–spin interaction that would lead to complete loss of paramagnetism if the polaron (radical) centers were constrained close together. As the chain length of TANI is short, spins in partially coupled states are reasonable for the doubly doped species. This result is consistent with what Barlow et al. reported. They found the extent to which dication radicals couple with each other depends on the geometry and chain length of the molecules and can vary from 0 to 2.0 (which would correspond to a range of couplings from strong to completely noninteracting spins).<sup>10</sup>

The fact that only a single prominent polaron peak was seen at all three doping levels suggests the absence of any noteworthy intermolecular interactions such as dimerization, since the spin–spin interaction in dimers gives rise to energy level splittings and thus multiple  $\pi$ -to-polaron absorption peaks would be expected, which we do not observe.<sup>28,29</sup>

After a large excess of acid was added, the spin concentration increased to approximately twice the value for the structure at

doping level I (Figure 4 and Table 2). The level III doping is assumed to occur at one of the two central secondary amine

**Figure 4.** EPR signal intensity (expressed as spin per molecule relative to doping level I) of chloroform solutions of TANI (0.1 mM) with various molar equivalents of DBSA.**Table 2.** Unpaired Spin Per TANI Molecule Based on EPR Spectra of Chloroform Solutions of TANI (0.1 mM) with Various Molar Equivalents of DBSA

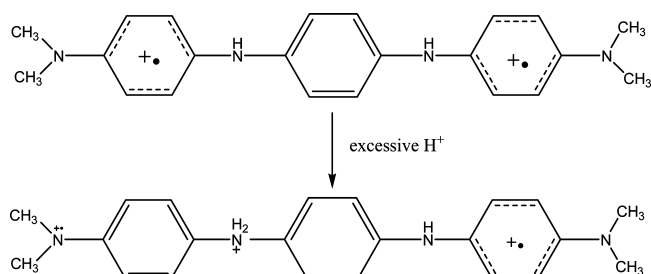
TANI/ DBSA	unpaired spin/TANI molecule normalized to that of doping level I
1:1	1.00 <sup>a</sup>
1:2	1.16
1:4	1.11
1:10	1.19
1:50	1.70
1:100	2.16
1:700	2.24

<sup>a</sup>All EPR signals were centered at  $g = 2.0026 \pm 0.00005$ .

groups, which are available in resonance forms of the level-II doped molecule. As a result, the ammonium cation  $-(C_6H_4)-NH_2^+-(C_6H_4)-$  segregates the polarons and prevents strong coupling of the unpaired spins (Scheme 4).

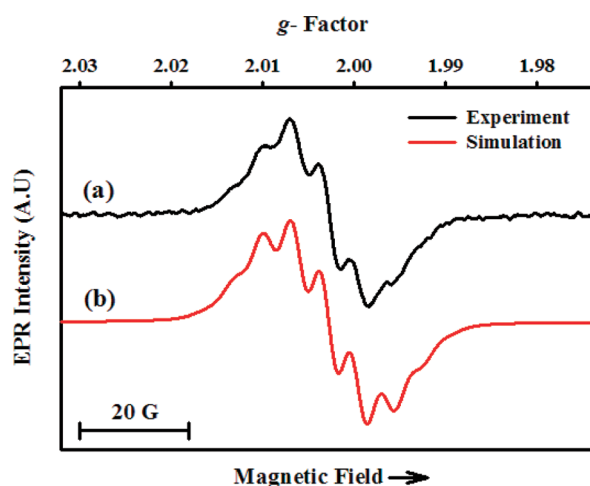
Interestingly, an apparent seven-line hyperfine pattern is resolved in the EPR signal with the addition of excess DBSA (Figure 3). This phenomenon could arise from the formation of a structure in which hyperfine interactions at a terminal dimethylamino group contribute to the EPR active species (Scheme 4 bottom structure). The newly formed ammonium cation at a bridging nitrogen limits delocalization within a

#### Scheme 4. Doping of Secondary Amine Group in TANI with Large Excess of DBSA (level III)<sup>a</sup>



<sup>a</sup>Radical cations formed at 2 equiv of acid were more stable at both ends, which left the secondary amine groups in the middle more susceptible to doping.

shortened conjugational length structure such that one unpaired spin now resides on a terminal dimethylamino nitrogen in the level III-doped molecule. A radical on the dimethylamino group was supported by simulating the multiline EPR spectrum using hyperfine splitting parameters for six equivalent hydrogens ( $A = 5.1$  G) and one nitrogen ( $A = 6.0$  G). These parameters are closely related to those reported for an isolated dimethylaniline radical (Figure 5b).<sup>30</sup> The



**Figure 5.** (a) Experimental EPR spectrum of chloroform solutions of TANI (2.5 mM) at doping level III. (b) Simulation assuming hyperfinecoupling interaction with 6H and 1N nuclei ( $A_{H(6)} = 5.1$  G and  $A_{N(1)} = 6.0$  G).

second unpaired spin is assumed to be delocalized away from the terminal dimethylamine groups (Scheme 4, bottom). Only poorly resolved hyperfine splitting is expected for this second unpaired spin. A three-step protonation sequence gives the structure we propose (Scheme 4) consistent with the EPR and optical observations.<sup>31</sup>

## CONCLUSION

The UV–vis–NIR and EPR spectroscopic measurements performed on TANI/chloroform solutions at three doping levels (I, II and III) with DBSA as dopant revealed different charge carriers as a function of protonation states of the two internal nitrogens and according to reasonable resonance forms of the doped species. The doping levels were proven to exist in different dopant and/or solvent systems with the acidity of dopants and polarity of solvents as controlling factors.

The polaron, partially coupled polarons, and two non-interacting polaron structures formed at different stages of doping gave deeper insight into the property of the intramolecular transport of various charge carriers in TANI. The chemical and electronic properties of the novel and interesting structural motifs may be useful in the development of new conjugated materials with applications in organic electronics.

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### Notes

The authors declare no competing financial interest.

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