

Evidence of the Controlled Interaction between PEDOT and PSS in the PEDOT:PSS Complex via Concentration Changes of the Complex Solution

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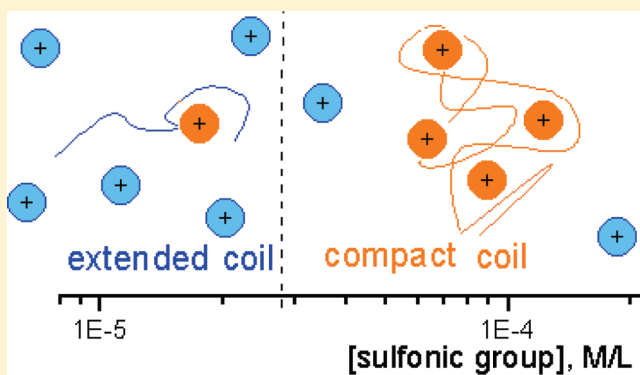
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S Supporting Information

ABSTRACT: Photoluminescence, electronic absorption, and pH studies of a poly(ethylene-3,4-dioxythiophene):poly(styrenesulfonic acid) (PEDOT:PSS) dispersion as a function of the PEDOT:PSS concentration are shown to provide a better understanding of the effect of PSS on the intramolecular conductivity of PEDOT chains. Particularly, concentration changes of PEDOT:PSS were found to be accompanied with different extents of dissociation of protons in the solution and different charge states of PSS chains, respectively, which affect the electrostatic interaction between PSS and PEDOT and intramolecular conductivity in the PEDOT backbone.



INTRODUCTION

Poly(ethylene-3,4-dioxythiophene) (PEDOT) is an important polythiophene derivative that was developed by Bayer AG research laboratories in the 1980s. In addition to its relatively high conductivity (10^{-5} – 10^2 S/cm), films of this polymer were found to be almost transparent in the oxidized state.¹ Insolubility or poor solubility of this polymer in conventional solvents is a serious drawback which has been overcome by the development of a poly(ethylene-3,4-dioxythiophene):poly(styrenesulfonic acid) (PEDOT:PSS) complex^{2,3} which forms a dispersion of the polymer nanoparticles in water and, therefore, allows one to process this polymer as a conductive film. PSS serves not only as a dispersant of PEDOT but also as a charge-compensating counterpolyanion for the positively charged PEDOT backbone, yielding on a molecular level a primary PEDOT:PSS structure⁴ (Figure 1). The secondary as well as tertiary structure of this complex consists of charged oligomers (about 6–18 repeating EDOT units) distributed along a high-molecular PSS chain with the necessary quantity of sulfonic group anions; such a structure has been proposed by Kirchmeyer et al.¹

The suggested hierarchical PEDOT:PSS complex structure (Figure 1) helps one to understand two possible ways to improve the conductivity of PEDOT:PSS particles which concern, on the one hand, the optimal morphology of the particles and their interparticle arrangement and, on the other

hand, reduction of the intrinsic disorder within PEDOT:PSS particles themselves.

So far, addition of solvent molecules, such as tetrahydrofuran, dimethylformamide, dimethyl sulfoxide, etc., to the PEDOT:PSS blend was one of the widely used methods to improve the conductivity of PEDOT:PSS films.⁵ Addition of an organic solvent as a secondary dopant to the PEDOT:PSS films is known to improve film conductivity;⁶ however, the mechanism of this improvement is the subject of discussions which gave rise to different models. For example, Jonsson and coauthors reported the effect of reduction of the thickness of the excess PSS layer which surrounds the conducting PEDOT:PSS grains, resulting in an increased and improved connectivity between these grains as the main mechanism responsible for the conductivity increase.^{7,8} Other models propose breaking of the bonds between PEDOT and PSS counterparts and their increased phase segregation,^{9–12} increased mobility of the charge carriers,¹³ swelling of the polymer molecules,¹⁴ and conformational changes of PEDOT chains^{15–17} as well.

Here for the first time we show that PEDOT and PSS interaction can be controlled without any additives in the blend, by simply changing the PEDOT:PSS concentration in the

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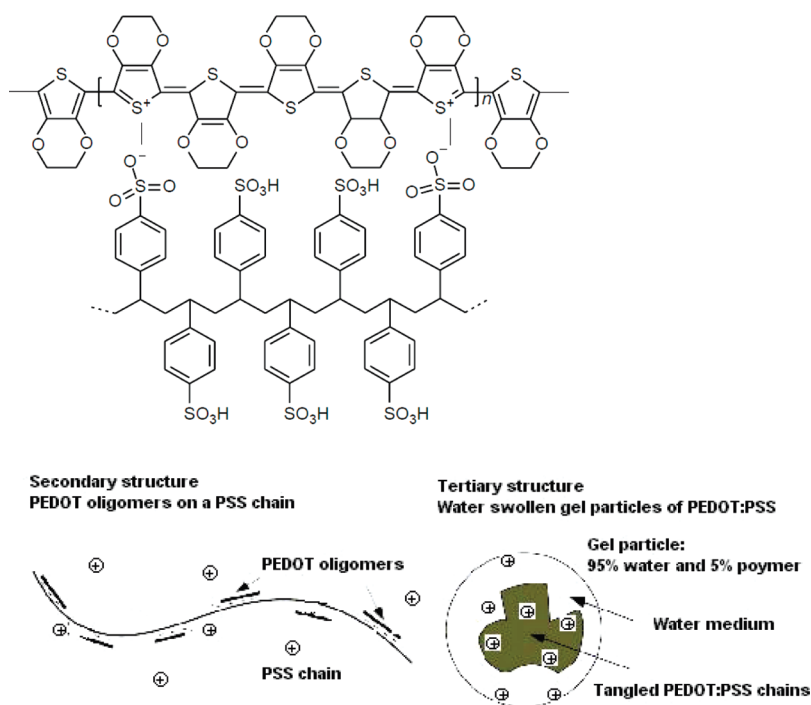


Figure 1. Hierarchy of the PEDOT:PSS complex structures: primary (at the top), secondary, and tertiary. Protons in the lower chart are shown by the positive circles. Adapted from ref 1.

aqueous dispersion, and that such an intermolecular interaction is responsible for the change in intramolecular conductivity of the PEDOT chain itself. To show this, we have performed comprehensive studies of proton behavior, electronic absorption, and photoluminescence spectra of the PEDOT:PSS aqueous dispersion as a function of the polymer concentration.

EXPERIMENTAL SECTION

The PEDOT:PSS aqueous dispersion (1.3 wt %) was purchased from Aldrich. The weight ratio of PEDOT to PSS in the polymer complex was ca. 0.5:0.8 wt %. This initial stock dispersion was diluted by distilled water to prepare the necessary concentrations of the aqueous polymer dispersion. Reference PSS solutions (0.1 wt %) were prepared by passing the sodium salt of PSS (Aldrich) solution through a KU-2 cation exchange membrane. Molar concentrations of both PSS and PEDOT:PSS were calculated with respect to sulfonic groups only.

Electronic absorption spectra were measured using a SPECORD M40 dual-beam spectrophotometer, with the distilled water as a reference sample. The measurements of sample solutions were conducted using the same cuvette. The spectra were additionally corrected for the slight difference in absorption of the cuvettes and/or nonequivalence of light pathways between the reference and the sample channels.

The homemade setup¹⁸ was used to measure photoluminescence (PL) spectra. The emission was excited by nitrogen laser radiation ($\lambda_e = 337$ nm) whose pulse width was 9 ns, the power of pulse emission 5 kW, and the pulse repetition rate 70 Hz. PL was registered through a MDR-12 grating monochromator equipped with a photomultiplier tube counter, an amplitude discriminator, and a coincidence circuit. The final spectra were corrected for the spectral sensitivity of the registering system.

The pH of the solutions was measured using a pH tester (pHep model, HANNA instrument). The accuracy of the

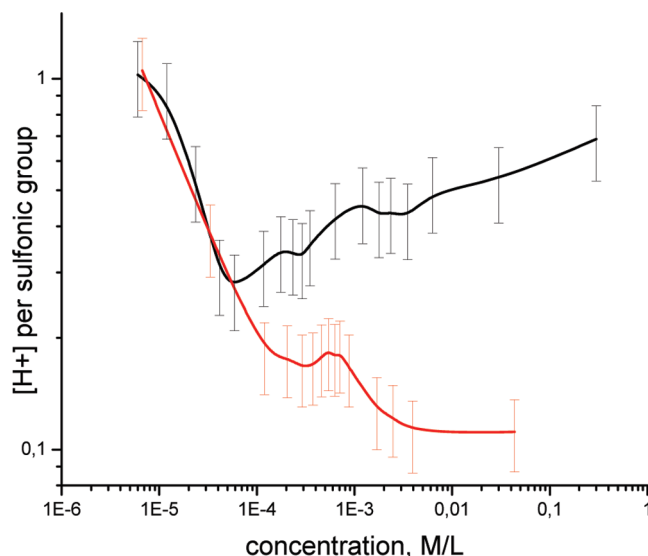


Figure 2. Amount of protons per sulfonic group versus concentration of the sulfonic groups in aqueous solutions originating from the net PSS (black curve) and PEDOT:PSS (red curve). The vertical bars show the measurement error.

measurements was 0.05 pH. The concentrations of protons in the solutions were calculated by the determined pH values. In order to escape systematic errors of the pH measurements, aqueous toluenesulfonic acid was taken as a reference solution, to which all other measurements have been reduced.

RESULTS AND DISCUSSION

Studies of the pH of PEDOT:PSS aqueous dispersions revealed nontrivial behavior of the proton concentration in the

solution as a function of the polymer concentration (Figure 2). The acidity of the solution originates from PSS, and the nonlinear behavior of the proton concentration versus polymer concentration is, therefore, due to the polyelectrolyte character of the acid. It was found that both the PEDOT:PSS complex and pristine PSS display similar trends in the proton concentration behavior. Namely, they show, first, that protons are not completely dissociated in the solution because the average measured amount of dissociated protons is less than one proton per sulfonic group and, second, the relative amount of dissociated protons per sulfonic group depends on the polymer concentration in the solution.

Two regions of proton concentration changes can be roughly distinguished. The first region concerns very low concentrations of the polymer, below $\sim 5 \times 10^{-5}$ M for PSS and below $\sim 5 \times 10^{-4}$ M for PEDOT:PSS, where the relative amount of dissociated protons per sulfonic group decreases with the increasing polymer concentration. Such a tendency is consistent with a similar trend obtained for poly(vinylsulfonic acid) solutions by Sumaru et al.¹⁹ The situation in the first region looks like a proton release from PSS macromolecules would be suppressed that contradicts with the well-known fact that strong polyelectrolytes, like PSS, are completely dissociated in water solutions.²⁰ The contradiction can be withdrawn if we consider the PSS solution of low concentration as a discrete medium being a sum of weakly interacting microvolumes containing stretched highly charged macroanions, thus surrounded by a strong electrostatic field immobilizing the released protons. As a result of the approaching polymer chains and increasing electrostatic repulsion between the macroanions, the chains tend to adopt a coil conformation with the occasional capture of protons to equilibrate the negative charges on the backbone (see the scheme for the tertiary structure in Figure 1).

The second region, observed at higher polymer concentrations, shows a tendency to saturation of the relative amount of dissociated protons per sulfonic group or even a reverse increase of this amount for PSS. Although this effect cannot be explained in detail at the moment, its origin could be due to interaction of the approaching polymer coils which results in their disturbance and a partial release of the earlier captured protons, respectively. The PEDOT:PSS dispersion displays a similar $[H^+]$ -concentration behavior but with some lag naturally due to both the smaller quantity of free sulfonic groups and net negative charge of the initially ionized anions electrostatically bound to the positively charged PEDOT chains.

Further evidence that the polymer molecules vary in the chain–chain distance and interaction, respectively, comes from photophysical studies of the polymer solutions. PL spectra of the PEDOT:PSS aqueous dispersion (Figure 3a) revealed qualitative changes as a function of concentration of PEDOT:PSS. It has been found that small concentrations of the PEDOT:PSS aqueous dispersions (10^{-3} to 2×10^{-2} wt % or 3.3×10^{-5} to 6.7×10^{-4} M, respectively) possess a weak emission in the visible region, with the bands located at ~ 460 and 416 nm and an increasing emission below 380 nm to the UV (Figure 3a, curve 1). The qualitative changes in PL spectra were clearly observed in the concentration range 10^{-1} – 10^{-2} wt % (3.3×10^{-3} to 3.3×10^{-4} M). Upon increasing concentration, the PL spectra showed a development of the band at 460 nm and its increasing contribution to the spectrum, while contribution of the UV emission below 370 nm was relatively decreasing with simultaneous merging of the emission features in the 370 – 420 nm

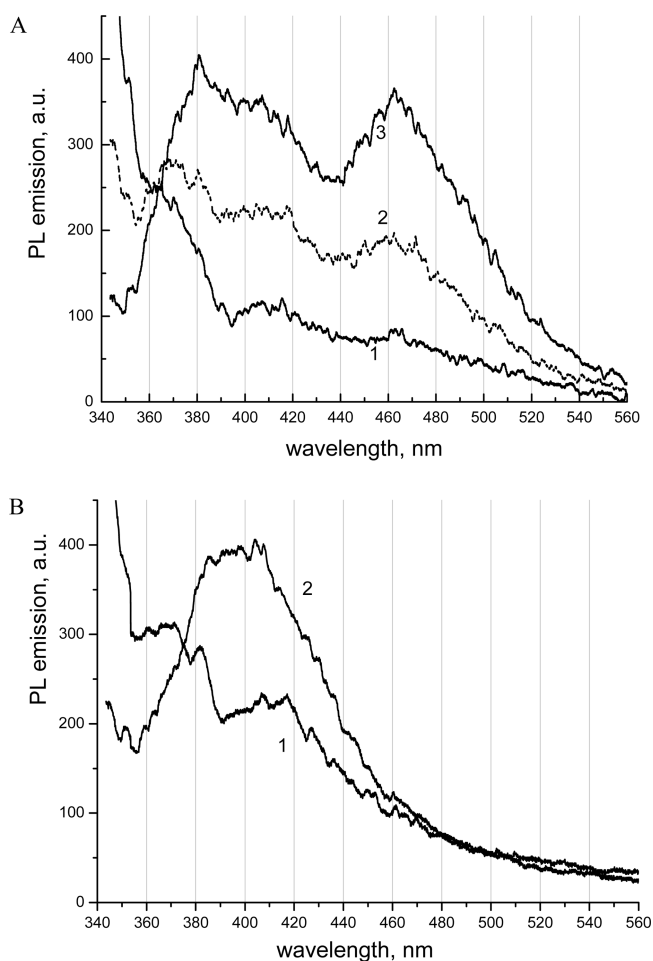


Figure 3. (a) Change in PL emission of the PEDOT:PSS aqueous dispersion as a function of the polymer concentration (calculated per sulfonic group): (1) 6.69×10^{-4} M; (2) 1.67×10^{-3} M; (3) 3.34×10^{-3} M. (b) Change in PL emission of the PSS aqueous solution with a concentration of (1) 5.43×10^{-5} M and (2) 5.43×10^{-4} M (calculated with respect to sulfonic groups).

(Figure 3a, curves 2 and 3). An isoemissive point at ~ 365 nm suggests that there are two states of the PEDOT:PSS complex which are mutually converting one into another as the polymer concentration changes.

In order to clarify the contribution of the components, i.e., PEDOT and PSS, to the emission of the polymer complex, PL emission of the aqueous PSS solution as a function of its concentration has been studied, since only PSS can be dissolved in water. PL emission of the PSS solution at low concentration (5×10^{-5} M) revealed an increasing band below 360 nm followed by structural features at ~ 372 and 415 nm (Figure 3b) which can be interpreted as vibronic overtones that accompany a major emission band. These overtones are separated by ~ 3100 cm^{-1} which is indicative of the C–H stretching vibration of the aromatic ring of PSS. The same features are present in PL spectra of PEDOT:PSS at low concentration (Figure 3a, curves 1 and 2), which allows us to assign the bands at ~ 370 and 415 nm to those of the PSS component. At higher concentrations, PL emission of PSS shows, however, restructuring of the spectral features into a single wide and featureless band at ~ 400 nm which is typical of the excimer emission. Such an excimer can arise as a result of approaching polymer chains due to the flexible character of PSS

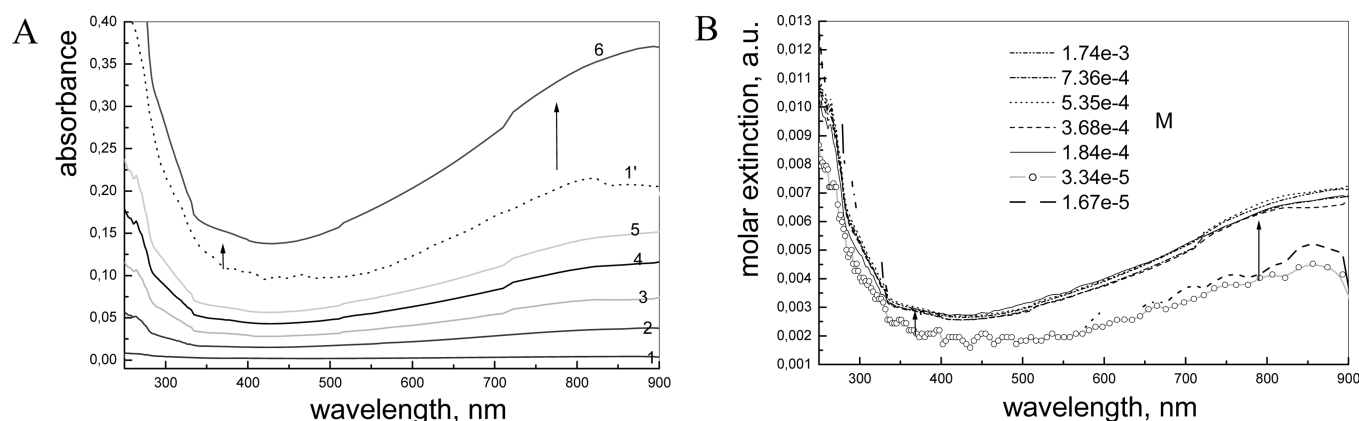


Figure 4. (a) Absorption spectra of the PEDOT:PSS aqueous dispersion in a 10 mm cuvette as a function of the polymer concentration (in terms of the PSS groups): (1) 1×10^{-3} wt % (3.34×10^{-5} M); (2) 5.5×10^{-3} wt % (1.8×10^{-4} M); (3) 1.1×10^{-2} wt % (3.7×10^{-4} M); (4) 1.6×10^{-2} wt % (5.3×10^{-4} M); (5) 2.2×10^{-2} wt % (7.3×10^{-4} M); (6) 5.2×10^{-2} wt % (1.7×10^{-3} M); (1') curve 1 multiplied by a factor of 52. (b) The same curves presented as molar extinction of PEDOT:PSS; concentration values (with respect to the sulfonic groups) are indicated.

chains and their increasing concentration in the solution. For PEDOT:PSS, the featureless band at ~ 400 nm appears at far higher concentration of the sulfonic groups in the solution. This result is consistent with the more stiff nature of the PEDOT:PSS chains, which hampers the approach of PSS chains in the PEDOT:PSS molecule and their intramolecular chain–chain interactions and requires also more molecules for the intermolecular chain–chain interaction to occur. One can observe also an additional band at 460 nm for the PEDOT:PSS dispersion (Figure 3a, curve 3). The band at 460 nm should be related either to PEDOT–PEDOT or stronger PEDOT–PSS interactions due to approaching polymer chains upon increasing their concentration. It is debatable to assign this band directly to the charged PEDOT chains, since it is expected that this conductive polymer possesses very poor emission, if any, normally like other highly conductive polymers.²¹ For example, Park et al.²² have shown that the PL emission of charged PEDOT chains doped with 1-butyl-3-methylimidazolium hexafluorophosphate is significantly suppressed as compared with the neutral dedoped form of PEDOT. These authors reported that the PEDOT–dopant complex possesses a weak emission band at ~ 541 nm under excitation at 488 nm; however, the emission of the dopant alone has not been identified/separated from that of the complex.

Behavior of the electronic absorption spectra with the increasing polymer concentration shows that a quantitative increase in the absorption is accompanied with the qualitative changes in spectra (Figure 4). In order to better observe these changes, Figure 4b is introduced to show a molar extinction coefficient (i.e., absorption per sulfonic group) to compare the behavior of the curves. The most distinctive changes appeared above a concentration of $\sim 3 \times 10^{-5}$ M, i.e., a shoulder around ~ 370 nm as well as an increasing tail in the near-IR region; these changes are shown by arrows in Figure 4. Since the absorption of PSS is practically absent above 310 nm in the whole range of concentrations used (see the Supporting Information), the above changes should be attributed to either PEDOT chains or a cooperative effect of interactions in the PEDOT:PSS complex. Since the absorption increase in the near-IR correlates with the conductivity increase in PEDOT:PSS films, as shown in our separate work,¹⁴ a similar increasing absorption in the near-IR region in the solution can be obviously assigned to the increase in intramolecular conductivity of PEDOT chains. Moreover, these

spectral changes in the near-IR which accompany the increase in intramolecular conductivity are quite similar to spectral changes in other conductive polymers, for example, polyaniline upon its doping by protonic acids.^{23–25}

The above results strongly indicate that interaction between PEDOT and PSS chains also varies with the PEDOT:PSS concentration. There are a few arguments in favor of this suggestion. First, the above-mentioned different degree of electrostatic screening of the pendant free sulfonic anions by protons, which depends on the complex concentration, leads to changes of total (net) electrostatic charge on the PSS chains and thus results in variation of strength of the electrostatic attraction of the PEDOT and PSS counterparts. Specifically, as mentioned above, this is displayed as variation in the measured amount of dissociated protons per sulfonic group of the polymer solutions. Second, a varied interaction between PEDOT and PSS chains at different concentrations can be deduced also from electronic absorption spectra (Figure 4). Specifically, the shoulder at ~ 370 nm in the absorption spectra (Figure 4a) above the concentration of $\sim 5 \times 10^{-4}$ M, most probably, corresponds to the enhanced interaction of the charged EDOT and benzene-sulfonate moieties of the PEDOT and PSS, respectively. Appearance of such a shoulder at the long wavelength side with respect to the major absorption band is one of the features of the molecule–molecule association.²⁶ Intramolecular chain–chain interaction in the PEDOT backbone is hardly possible, since this polymer has a planar structure,¹ i.e., it is not flexible, and such an interaction is also hindered by the surrounding PSS chains. Chain–chain interactions in PSS, if any, are not observed in the above spectral range (Figure 4 and Figure S1 in the Supporting Information), as expected, probably because of the stretched conformation of polyanion chains in the low concentration region. Therefore, the most plausible assignment of the above spectral changes is due to PEDOT–PSS interactions. Third, the progressing increase of the PL band at ~ 460 nm as compared with the bands in the 360–420 nm region with increasing polymer concentration can be explained by the formation of an exciplex as a result of stronger interaction and approach of the PEDOT and PSS counterparts.

The above results also evidence that the degree of electrostatic interaction of dissociated protons with the PSS chain and corresponding interaction of the positively charged PEDOT

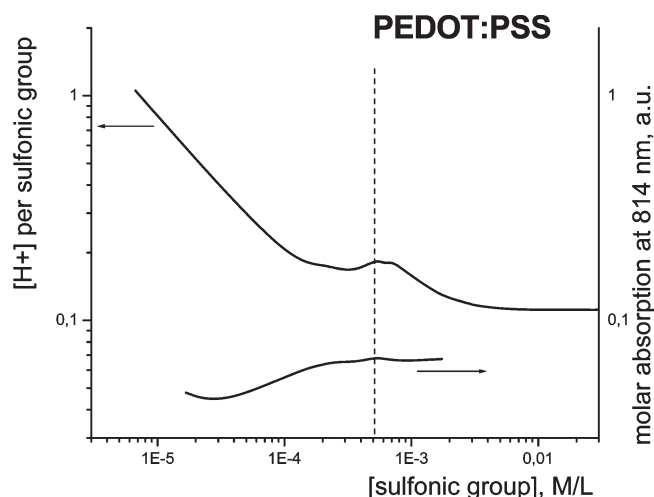


Figure 5. Dissociated protons amount per sulfonic group (upper curve) and molar absorption at $\lambda = 814$ nm (lower curve) of PEDOT:PSS versus polymer concentration (with respect to sulfonic groups) in the aqueous dispersion.

units with anionic units of PSS influences the intramolecular conductivity of PEDOT itself. Specifically, the maximum of dissociated protons per sulfonic group at concentrations below 3×10^{-5} M favors electrostatic interaction of negatively charged PSS and positively charged PEDOT counterparts, which corresponds to the smallest contribution of the near-IR absorption tail to the spectrum (Figure 5). Vice versa, a reduced interaction of PEDOT and PSS due to the increased amount of protons associated with PSS chains results in the increase of this near-IR band. The relative intensity of this band correlates with the chain conductivity, as discussed above.

It is also known that the PSS backbone is flexible and its fractal dimension can vary from 1.5 to 2.7 depending on the ionic strength of the solution.²⁷ The larger amount of protons associated with PSS chains better equilibrates the negative charge on the PSS backbone and, therefore, weakens its interaction with the positively charged PEDOT. Such an effect leads, in turn, to smaller distortion of the planar PEDOT backbone and, therefore, to easier electron transfer along the PEDOT chain. Better release of protons from PSS chains at small polymer concentrations leads to enhanced electrostatic attraction between more negatively charged PSS chains and the positive PEDOT backbone. Such an attraction may, in turn, affect the planarity of the PEDOT backbone and decrease its intramolecular conductivity, respectively, which correlates with the decrease in the near IR absorption (Figure 5). It is interesting to note that a compulsory removal of protons from PEDOT:PSS solution by NaOH addition leads to a similar decrease in electronic absorption in the near-IR²⁸ and was interpreted by Kok et al. as a partial dedoping of the polymer.

CONCLUSION

It was found that qualitative changes in PL emission, electronic absorption, and proton dissociation in PEDOT:PSS aqueous dispersions induced by the polymer concentration changes lead to the varying interaction between PEDOT and PSS counterparts in the PEDOT:PSS complex. This interaction is controlled by the amount of dissociated protons from the PSS chains. Dissociation of protons from the polymer chain results in more

tight interaction between PSS and PEDOT which can be registered through changes in PL and electronic absorption spectra. On the other hand, association of protons with the PSS coil weakens the electrostatic interaction between PSS and PEDOT and leads to a smaller distortion of the planar PEDOT structure, respectively. The latter, in turn, favors better intramolecular conductivity in the PEDOT molecule. This result yields a better understanding of the effect of PSS on the intramolecular conductivity of PEDOT chains in the PEDOT:PSS complex.

ASSOCIATED CONTENT

S Supporting Information. Figure showing absorption spectra of the PSS aqueous solutions. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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