Tuning the Dedoping Process of PEDOT:PSS Films using DBU-Solvent Complexes

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Abstract

In this study, we report a successful simple technique to dedope pristine PEDOT:PSS films at room temperature by dipping the films into 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) mixes with different solvents such as dimethyl sulfoxide (DMSO), acetonitrile (MeCN) and deionized (DI) water. The treated PEDOT:PSS films presented a strong π-$\pi*$ absorption band centered at 630 nm, which indicated that the PEDOT chains were being reduced to their neutral state. The dedoping efficiency of the PEDOT chains depended on the used DBU complex, the DBU concentration in the mixture as well as the immersion time, which was quantified comparing the relative intensities between the π-$\pi*$ and the polaronic (centered around 900 nm) bands. The best dedoping efficiencies of PEDOT:PSS films were obtained using MeCN/DBU or DI water/DBU complexes, as the polaronic band almost disappeared, whereas using DMSO/DBU complex the polaronic band was always present. This difference was mainly related to the degree of basicity of the DBU complexes and solubility extent of PEDOT:PSS in the various solvents. Finally, thick dedoped PEDOT:PSS films showed a strong yellow emission when they were excited with a 488 nm laser. The encapsulated dedoped thick films endured up to 50 mW of laser power without impacting their luminescent and physical properties.

1. Introduction

Conjugated organic polymers have attracted great interest because of their potential applications in corrosion resistance coatings [1], electromagnetic shielding [2] and development of organic electronic devices [3-8]. In particular, the polymer poly(3,4-ethylenedioxythiophene doped with the polymeric counteranion poly(styrenesulfonate) (PEDOT:PSS) has acquired high relevance owing to the various and increasing uses that include for photographic films, electrochromic devices [9], organic field effect transistors [10], light emitting diodes [11] and photovoltaic cells [12]. The particular properties in the oxidized state of PEDOT [13], as well as its very high electrochemical stability and easy-to-process, are due to the PSS counterion that acts as the source for the charge balancing [14,15] and keeps the PEDOT segments dispersed in the aqueous medium. The oxidized state (*p*-doped) of PEDOT is one of the most studied; in contrast, although significant efforts were devoted to obtain dedoped (reduced, neutral) PEDOT segments, this has been scantly investigated. Some reports show that PEDOT:PSS can be dedoped by using reducing agents [16-19] resulting in changes in the electrical, thermoelectric, and optical properties [16-20]. In particular, one of the possible applications, of dedoped PEDOT in organic electronics, is their use in organic batteries as anode [17,21]. Previously, we reported a partial reduction of PEDOT:PSS to its neutral state by a simple process consisting in the addition of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, $C_9H_{16}N_2$) to the aqueous PEDOT:PSS dispersion. In addition, these dedoped samples in aqueous dispersion as well as encapsulated films showed a strong yellow emission using a 10 mW laser power [22].

In the present work, we have prepared a series of DBU complexes, i.e. DBU was mixed with different solvents in order to create a molecular entity formed by a weak association between a DBU molecule and a solvent molecule [23-25]. This allows us to study the effect of degree of basicity on the dedoping process of PEDOT:PSS. DBU is a neutral, strong, organosuperbase used as reagent and catalyst in organic synthesis [23-25]. In general, DBU is considered non-nucleophilic strong base, but some authors have shown that DBU can also act as nucleophiles [25,26]. The advantages of this base are their commercial availability and relatively low cost [27]. The most interesting physicochemical property of neutral organosuperbase is their exceptional basicity associated with a high kinetic activity in proton exchange reactions. It has been reported in literature that DBU basicity has been measured using several solvents, such as deionized (DI) water, acetonitrile (MeCN, CH_3CN), dimethyl sulfoxide (DMSO, $(CH_3)_2SO$), indicating that its conjugate acid pK_a values depend on the used solvent; the conjugate acid pK_a value of the DBU in MeCN is pK_a=24.33, in DMSO is pK_a=13.9 and in DI water is pK_a = 13.5 [23,28]. Furthermore, an important and beneficial characteristic of a superorganic base such as DBU is the ability of recycling its use in repeated action, in which reversible proton transfer occurs between the base and a substrate, an acidic counterpart.

DMSO is a polar organic solvent that when is added into an aqueous solution of PEDOT:PSS enhances the conductivity of PEDOT:PSS films [29-34] due to a partial phase separation of the PSS excess [29,34]. MeCN has been also used for enhancing the PEDOT:PSS conductivity. However, no conductivity enhancement or remarkable changes have been observed in PEDOT:PSS films when they are only MeCN treated; it is necessary to mix it with DI water for enhancing their conductivity, due to a preferential solvation of the hydrophobic PEDOT and

hydrophilic PSS chains with cosolvents [35]. Recently, a partial dedoping process of PEDOT:PSS using DMSO-hydrazine solution over-coating has been reported [16]. In the present work, we report a simple dedoping process based in dipping the PEDOT:PSS films into DBU complexes. The effects of mixing DBU with DMSO, MeCN and DI water on the dedoping process and emission of PEDOT:PSS films were studied. Using this simple dedoping process, it is possible to control the dedoping level of PEDOT:PSS films. Additionally the films with the best dedoping level showed an intense yellow emission coming from the neutral PEDOT chains when they were excited with a 488 nm blue laser.

2. Experimental method

The solutions were prepared using an aqueous dispersion of PEDOT:PSS (Clevios P), which was previously filtered through a 1 μm syringe filter. The square of Dow corning glass substrates (2.5 cm in length) were successively ultrasonically cleaned in acetone, methanol and isopropyl alcohol for 20 min each time. Immediately, after evaporation of the solvents, the substrates were maintained in a UV-ozone ambient for 45 min. Thin films of PEDOT:PSS solution were deposited on these glass substrates by spin-coating (1870 rpm for 5 s, followed by 40 s at 2500 rpm) and then dried at 100 °C for 15 min. After deposition, the dipping method was performed by immersing the dried PEDOT:PSS films into a solution made of DMSO (1 ml = 14.08 mmol) and DBU (1 ml = 6.68 mmol) (DMSO/DBU), at room temperature and at two different v/v ratios: 2:1 v/v ratio corresponding to 4.2:1 molar ratio (MR) and 10:1 v/v ratio (21:1 MR). The mixtures were stirred during 30 min before their use. The films were immersed at different times (10, 20 and 30 min). Subsequently, the substrates were placed in vertical position for 30 min to

drain most of the dedoping solution. Finally, these samples were dried under reduced pressure (70 kPa) at 110 °C for 35 min. The same procedure was performed on the PEDOT:PSS films immersed into MeCN (1 ml = 19.5 mmol) in mixture with DBU (MeCN/DBU) and into DI water (1 ml = 55.56 mmol) in mixture with DBU (DI water/DBU) at 2:1 v/v (5.8:1 MR MeCN/DBU, 16.6:1 MR DI water/DBU) and 10:1 v/v (29:1 MR MeCN/DBU, 83:1 MR DI water/DBU) ratios and immersion times of 10, 20, 30, 60 and 120 min. Using the same volumetric amount of DBU in the experiments allows fixing the number of DBU molecules regardless of the solvent used. In order to elucidate the effect of the amount of protonated DBU molecules in the dedoping process, i.e the amount of formed solvent-DBU complexes, we have additionally prepared solvent/DBU mixtures with a 1:1 MR (DMSO/DBU 1:2.1 v/v, MeCN/DBU 1:2.9 v/v, DI-water/DBU 1:8.3 v/v) and with a 25:1 MR (DMSO/DBU 11.9:1 v/v, MeCN/DBU 8.6:1 v/v, DI-water/DBU 3:1 v/v). These solvent/DBU mixtures were stirred during 40 h. The first case, 1:1 MR solvent/DBU, was prepared for considering the possibility of having the same amount of formed complexes, in the case of a complete DBU protonation, independently of the solvent used. The second case, 25:1 MR solvent/DBU, was used due that a complete switch of DBU molecules to their protonated form has been reported when DBU is mixed with DI water in this MR using a protonation time of 2 h [25].

Film thicknesses of pristine (ca. 70 nm) and immersed PEDOT:PSS samples were obtained for averaging six measurements made on each sample using an Alpha Step 500 surface profiler along two parallel scratches going from center to edge of the films. The average roughness of treated PEDOT:PSS films were estimated using a NanoScope E (Digital Instruments/Veeco Metrology Group) atomic force microscope (AFM). Absorption

measurements were performed with an UV-Vis-NIR Varian Cary 5E spectrophotometer. Raman spectroscopic measurements were carried out using a micro-Raman Renishaw spectrometer equipped with a 633 nm excitation laser source and power of 2.5 mW. Photoluminescence (PL) spectra were measured at room temperature using an Ar-ion laser emitting at a wavelength of 488 nm. In the experimental setup, an optical long-pass filter with a wavelength cut-off of 530 nm was used and a selective amplifier tuned at a frequency of 100 Hz. The conductivities of the obtained films were determined by four-point probe measurements. Surface analysis by X-ray photon spectroscopy (XPS) was performed using a Physical Electronics Ulvac Phi Versa Probe II spectrometer employing an Al Kα (hν=1486.6 eV) X-ray source operated at 15 kV and 25W with a take-off angle of 45° and typical operating pressures at ~1x10^{-9} Torr.

3. Results

Normalized absorbance spectrum of the pristine PEDOT:PSS film (Fig. 1) shows the same features previously reported [36,37]. In contrast, the measured normalized Vis-NIR absorption spectra of the PEDOT:PSS films immersed into DMSO/DBU and MeCN/DBU mixtures, at v/v ratio of 10:1 (Fig. 1(a)) and 2:1 (Fig. 1(b)) and at different treatment times, show an absorption band around 630 nm and another one around 900 nm. The first band at 620-639 nm is related to the neutral state in PEDOT [38,39] and attributed to π-π* transition. The second one is assigned to the polaronic band [36,37,40-43], which is a characteristic of the oxidized state. It is observed clearly from figure that the intensity of the π-π* band is relatively greater than the polaronic band, indicating that a large number of PEDOT:PSS chains in the treated films were dedoped [38,39,43]. Moreover, the dedoping efficiency of the PEDOT:PSS films strongly depends on the

amount of DBU in the immersion mixture, but weakly at the immersion time. Specifically, the π-π^* band becomes relatively more intense when MeCN is used instead DMSO in the dedoping mixture, whereas the band at 900 nm begins to decrease at low DBU concentration in the mixture, such as is observed in Fig. 1(a). This indicates that the PEDOT chains in the films are being dedoped but they are still not completely reduced. In contrast, at high concentration of DBU in the mixture, PEDOT:PSS films immersed into DMSO/DBU mixture show that the intensity of the polaronic band is considerable decreased and almost disappears when the PEDOT:PSS films were immersed into MeCN/DBU mixture. In addition, the normalized absorption spectra of the PEDOT:PSS films immersed into MeCN/DBU (2:1 v/v) mixture show the π-π^* band with two well-defined shoulders arising from the vibronic structure (Fig. 1(b)) [44], which are evident compared with those observed at low DBU concentration. In contrast, films immersed into both DMSO/DBU mixtures do not present well-defined vibronic structures.

Fig. 2 presents normalized absorption spectra of PEDOT:PSS films immersed into DI water/DBU complex at ratio used of 10:1 v/v at two different times, 10 and 20 minutes. The spectra show that even in low DBU concentration in DI water, it is possible to observe a similar effect that in the case of a high DBU concentration in MeCN, i.e. well defined vibronic shoulders as well as a red-shift of the maximal π-π^* absorption band. Similar two well-defined shoulders have been reported in PEDOT films synthesized by electropolymerization using propylene carbonate (PC) as solvent [44] whereas those electropolymerized using MeCN as solvent, the UV-vis-NIR spectra do not show these vibronic shoulders [45-47]. The presence of the vibronic shoulders in the absorption spectra in electropolymerized PEDOT films has been correlated with film smoother structures. However, we found that the dedoped films immersed into MeCN/DBU

(2:1 v/v) mixtures are rougher in comparison with those films immersed into DI water/DBU

mixtures (2:1 v/v). Based on the AFM data, the average roughness was ~10.1 nm in MeCN/DBU

(2:1 v/v) treated PEDOT:PSS films, while the corresponding value for DI water/DBU (2:1 v/v)

treated film was ~2.3 nm. These data correspond very well with those obtained using a

profilemeter, the average roughness was ~19 nm in MeCN/DBU (2:1 v/v) treated PEDOT:PSS

films and the value for DI water/DBU (2:1 v/v) treated film was ~3 nm. Thus, the average

roughness of films dedoped with MeCN/DBU is generally around 5 times greater than films

immersed into DI water/DBU. However, the average roughness of films immersed into

MeCN/DBU (2:1 v/v) was smaller than the electropolymerized PEDOT films prepared in MeCN

as solvent, which showed an average roughness of 152.5 nm [47]. Furthermore, the immersion

time was prolonged, using 30, 60 and 120 min, for the PEDOT:PSS dipped into DI water/DBU

and MeCN/DBU mixtures in order to compare the effect of using a polar protic solvent and polar

aprotic solvent (Fig. 3) in the optical properties. From figure we observe that λ_{max} of the

absorption band is red-shifted at 644 nm for the DI water/DBU mixture whereas for the

MeCN/DBU mixture the maximal of the absorption band is at 637 nm. Additionally, the films

treated with DI water/DBU mixture show two maxima in the normalized absorption spectra

whereas the films treated with MeCN/DBU mixture only show a wide maximum. The red

shifting in the normalized Vis-NIR spectra is remarkable for DI water/DBU immersion mixture

at the two v/v ratios used, 10:1 (Fig. 3) and 2:1 (Fig. 4), in comparison with that obtained using

10:1 v/v MeCN/DBU mixtures. A similar red-shifting in the normalized absorption Vis-NIR

spectra have been reported in electropolymerized PEDOT films using PC as solvent compared

with those electropolymerized using MeCN; these red shifting have been correlated with

differences of solubilities of EDOT oligomers in these solvents [44]. In our case, these differences in the optical properties can be partially related to difference in solubility of PEDOT and PSS in DI water as well as in MeCN. Other important factors that play a key role in these differences in the absorption spectra will be explained later. Moreover, it was observed that using small volumetric amounts of DBU in the mixtures, with MeCN and DI water, and increasing the immersion time we could almost get the disappearance of the polaronic band. The effect of the different DBU solvent complexes in the dedoping of PEDOT chains can also be observed as a color change in the films. Inset of Fig. 4 shows a comparison of the coloration between the pristine film and film immersed into DI water/DBU (2:1 v/v) mixture. This typical color change of the oxidized and reduced film is in good agreement with reports using electrochemical doping/dedoping process [48]. Thus, the evidence shows that the type of solvent used, solvent/DBU v/v ratios and the immersion time are important parameters to tune the dedoping level of PEDOT:PSS films.

One advantage of using organic neutral superbases is their exceptionality basicity and the possibility of recycling their use in repeated action. For these reasons, the MeCN/DBU and DI-water/DBU solutions were reused and pristine PEDOT:PSS films were immersed in these mixtures. The normalized absorption spectra of these PEDOT:PSS films (Fig. S1) does not present visible changes after reusing the solutions. Additionally, the effect of using different DBU complexes on the conductivities of the PEDOT:PSS films were measured. Table I represents the average of least three conductivity measurements in different areas of the films. The conductivity of the DMSO/DBU and MeCN/DBU treated PEDOT:PSS films with low concentration of DBU (10:1 v/v) showed the larger conductivities than that measured for the

pristine films, even when the treatment time was 30 min. This indicates that DMSO/DBU and MeCN/DBU treatments remove the excess of PSS, decreasing in this way the insulating barriers between the conductive PEDOT grains. The increase of film thickness in these treated films is probably related with an increase of film roughness, indicating that the size of the conductive domains grows due to PSS partial phase segregation. PEDOT:PSS treated films using a high concentration of DBU in DMSO, DMSO/DBU (2:1 v/v), showed a decrease in their conductivities as a function of treatment time, which is related to an increase of PEDOT chains dedoping. As the treatment time is increased, DMSO/DBU complex begins to remove the PSS-anions doping the PEDOT backbone, thus, the conductivity of the PEDOT:PSS film is decreased. The films treated with DI water/DBU showed the bigger thickness and the conductivity was only possible to measure for films with small treatment time. The films treated with DI water/DBU were very rough and for long treatment time the film conductivity was below the detection limit of the measuring device. This is due to PSS is soluble in water, thus, the great amount of DI water used in the mixture (10:1 v/v DI-water/DBU) as well as the treatment time create discontinuities and non-uniformity in the film precluding the conductivity measurements.

Using the same v/v solvent/DBU ratio in the treatment mixtures, we are setting the number of DBU molecules used in the dedoping process, regardless of the number of the solvent molecules. Basicity of a base B in a solvent S is defined as [28]:

$$H^+B + S \Leftrightarrow B + HS^+ \qquad (1)$$
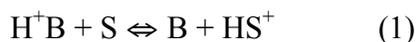
$$K_a = a(B)a(HS^+)/a(HB^+) \qquad (2)$$

where the activity (*a*) is proportional to the concentration of the specie and, in dilute base concentration, the solvent S is taken as a constant. Note that K_a is the equilibrium constant, thus, the different pK_a values for the different solvent/DBU mixtures are only valid for systems in thermodynamic equilibrium. Basicity is expressed as the dissociation constant of the conjugated acid HB^+ of the base B or its negative logarithm pK_a [28]. Thus, a larger pK_a value means a large concentration of protonated DBU molecules implying that, although DI-Water/DBU pK_a = 13.5 < DMSO/DBU pK_a =13.8 < MeCN/DBU pK_a = 24.3, dedoping efficiency is not directly related to the amount of formed solvent$^-$-DBU$^+$ complexes. Another possibility is that the DBU molecules not forming part of the complex, i.e. non-protonated DBU molecules, are responsible for the dedoping process; DBU molecules have nucleophilic properties, i.e they are donors of an electron pair. However, this also cannot fully explain the great differences in the dedoping efficiency between the films treated using DI water/DBU with those treated using DMSO/DBU mixtures. Since the amount of non-protonated DBU molecules are expected to be similar, then, it is reasonable to expect similar dedoping efficiency. In contrast, in the films treated using DI water/DBU is expected to show differences in the dedoping efficiencies with those treated using MeCN/DBU, where the amount of non-protonated DBU molecules is expected to be quite different. Part of the explanation can be obtained from the differences in molar ratios of the immersion mixtures as well as different solvation of PEDOT and PSS in the cosolvent used. For the case of solvent/DBU 2:1 v/v, we have 4.2:1 MR, 5.8:1 MR and 16.6:1 MR for DMSO/DBU, MeCN/DBU and DI water/DBU, respectively. From here, we observe that there are approximately 4 times more water molecules than DMSO molecules in the immersion mixtures. It is known that PEDOT is insoluble in almost all the common solvents whereas PSS is highly

hydrophilic. Additionally, the chemical reduction of $PEDOT^+$ to $PEDOT^0$ chains eliminates or weakens their electrostatic interactions with the PSS^- anions. Therefore, excess water molecules in the treating mixtures will more easily remove the excess of PSS as well as less reduced PEDOT:PSS conductive grains compared to the other solvents, effectively increasing in this way the dedoping processes observed in the DI water/DBU PEDOT:PSS films.

To study the role played by the formation of the $solvent^-$-DBU^+ complexes, we have prepared solvent/DBU mixture with a 1:1 MR between solvent and DBU. These mixtures were stirred for 40 hours in order to protonate the largest amount of DBU molecule, thus giving rise to the formation of the $solvent^-$-DBU^+ complexes. If all the DBU molecules were protonated, independently of the solvent used, then all the DBU molecules will form part of the complexes and will present Bronsted basic properties. Therefore, the dedoping properties of the different treating mixtures should be basically the same, regardless of the solvent used. In Fig. 5, we present the normalized absorption spectra for two immersion times, 10 min (Fig. 5a) and 30 Min (Fig. 5b). From figure, we observe that the dedoping process almost does not depend on the mixture used as well as on the immersion time. These little differences in dedoping levels mean that probably all DBU molecules are protonated. However, it has been reported that when the DBU is in a 1:1 MR with DI-water [25] a small amount of DBU molecules are protonated, independent of protonation time, which suggests that the complexes probably play a negligible role in the dedoping process, at least by 1:1 MR DI-water/DBU treatment mixture. In the figure is also shown the normalized absorbance spectrum of PEDOT:PSS film only treated with DBU solution. The comparison between the normalized absorption spectra of PEDOT:PSS films treated with solvent/DBU mixtures and with that PEDOT:PSS film only DBU treated shows that

the main difference between them, it is the presence of a well defined absorption band at ~600 nm in the normalized absorption spectra of the PEDOT:PSS films treated with solvent/DBU mixtures.

Even more, the normalized absorption spectra of PEDOT:PSS films treated with a 2:1 v/v solvent/DBU mixtures (Fig. 1b and Fig. 4) as well as 1:1 MR solvent/DBU mixtures (Fig. S2), all these mixtures were only protonated during 30 min before being used for the dedoping process so what is not expected a great amount of protonated DBU molecules, were compared with those normalized spectra of PEDOT:PSS films treated with a 1:1 MR solvent/DBU mixtures and underwent a protonation process for 40 h (Fig. 5). From this comparison, we notice that the normalized absorption spectra of treated PEDOT:PSS films using solvent/DBU mixtures with short protonation time are more similar to that of the PEDOT:PSS films only treated with DBU solution. Thus, the formation of solvent/DBU complexes plays a role in the dedoping process.

To understand the importance of the role played by the formation of the $solvent^-$-DBU^+ complexes due to the protonation of the DBU, we prepared mixtures with a 25:1 MR solvent/DBU: a) DMSO/DBU (11.9:1 v/v), b) MeCN/DBU (8.6:1 v/v) and c) DI water/DBU (3:1 v/v). It has been reported that a complete switch of DBU molecules to their protonated form when they are mixed with DI-water using a protonation time of 2h [25]. Then, these mixtures were stirred for 40 h in order to protonate all the DBU molecules, at least those mixed with DI water, obtaining the complete formation of the $solvent^-$-DBU^+ complexes. In Fig. 6, we present the results of the dedoping process using these treatment mixtures for two immersion times. We

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observe that the dedoping efficiencies are practically the same for a given solvent/DBU mixture regardless of the immersion time, which indicate that the mixtures have reached their state of thermodynamic equilibrium, i.e. the maximum number of protonated DBU molecules. We also observe that in the case of the MeCN/DBU and DI water/DBU mixtures, basically the same normalized absorption spectra are obtained, in which we observe the presence of two maxima, one at ~ 600 nm and the other one at ~ 640 nm, while the polaron band around 900 nm almost disappears. Particularly, in the case of PEDOT:PSS film treated with 25:1 MR MeCN/DBU mixture, its normalized absorption spectrum shows a well-defined band at 600 nm, which is difficult to obtain using short protonation time, although large molar concentrations of DBU in the treating mixtures are used (Figs. 1b and S2). The comparison of both normalized absorption spectra, previously discussed, with the normalized absorption spectrum of PEDOT:PSS films only DBU treated (Fig. S3) corroborates that the well-defined band at 600 nm is related to the formation of solvent$^-$:DBU$^+$ complexes. This implies that the complexes play an important role in the dedoping process indicating that there are two possible routes for charge transfer and, consequent, chemical reduction of PEDOT$^+$ chains: (a) PEDOT$^+$:PSS$^-$ + solvent$^-$:DBU$^+$ $\rightarrow$ PEDOT^0 + DBU$^+$: PSS$^-$ + solvent, (b) PEDOT$^+$: PSS$^-$ + DBU $\rightarrow$ PEDOT^0 + DBU$^+$: PSS$^-$. The amount of charge transferred to the PEDOT$^+$ chains will depend on each of the dedoping routes. Consequently, the electrostatic interactions between partially reduced PEDOT$^+$, PSS$^-$ anions and the DBU$^+$ cations will be related to each of the routes of charge transfer, which is reflected in the different vibronic structure observed in the absorption spectrum [49,50]. For the DMSO/DBU mixture only a wide absorption band around 610 and the polaron band around 900 nm are observed. This is related to the fact that DMSO also acts as a secondary dopant.

Raman spectroscopy was performed to further confirm the dedoped state of treated PEDOT:PSS films. This technique is frequently used for the characterization of the oxidized and reduced state of PEDOT chains. Fig. 7 shows the Raman spectra of the pristine film and the PEDOT:PSS films immersed into DMSO/DBU, MeCN/DBU and DI water/DBU using an excitation wavelength of 633 nm with a 2.5 mW laser power. The main band between 1400 and 1500 cm^{-1}, which corresponds to the $C_\alpha=C_\beta$ symmetric stretching on PEDOT chains, is observed in all the spectra. However, this peak in the pristine PEDOT:PSS film is less intense compared with those observed in films immersed into DBU complexes. Moreover, the peak in treated PEDOT:PSS films is narrower and a little red shifted, located at 1425 cm^{-1}, compared with that of pristine film, located at 1434 cm^{-1} [43]. This red shifting in the $C_\alpha=C_\beta$ symmetric stretching is associated with an increase of benzoid structure in the PEDOT chains and as consequence a dedoping process. Furthermore, the remarkable intensity of $C_\alpha=C_\beta$ symmetric vibration in treated films compared with that of pristine film was also observed in our previous report, using an 514 nm excitation wavelength [22]. The use of laser wavelength close to the $\pi-\pi*$ transition energy produce intense and well-defined Raman resonant peaks in the neutral state of PEDOT whereas in a doped state PEDOT structure their intensities are less intense and not well defined [43]. The obtained results indicate the dedoping of PEDOT:PSS films using DBU-solvent complexes. Note that the signal intensities of the films immersed in DI water/DBU mixtures are the most intense while the less intense are obtained using DMSO/DBU mixture, which implies that the use of DI water is more reliable for the dedoping process compared with DMSO.

From the results obtained using Vis-NIR absorption, conductivity measurements and Raman, it is inferred that the dedoping process carried out on the PEDOT:PSS films is more efficient when they are immersed in MeCN/DBU or DI water/DBU complexes than when they are immersed in DMSO/DBU complex. These differences in dedoping efficiency can be explained considering that DMSO also works as a secondary dopant in the PEDOT:PSS that increase its conductivity [29]. It is well established in literature that DMSO eliminates the excess of PSS and weakly interacts with the PSS- anions doping the PEDOT chains, thereby decreasing the thickness of the insulating barriers between the conductive grains PEDOT [29,34,51]. In order to study the effect of immersing the PEDOT:PSS films in the different DBU complexes, the surface chemical composition of these films was analyzed using X-ray photoelectron spectroscopy (XPS). The information provide by XPS measurements comes from atoms on the sample surface up to 10 nm within the bulk of the sample, depending of the experimental condition and the material being studied. Both PEDOT (with S-C bonds) and PSS (with S-O and S=O bonds) contain one sulfur (S) atom in their monomer unit, which are in different chemical environments in PEDOT (thiophene ring) that in PSS (sulfonate group). Due to differences in chemical environments of S atoms in the PEDOT and PSS monomers, their binding energies (BE) are different [51-53] allowing in this way to quantify the effect of DBU solvent complex treatments on PEDOT:PSS films. From the area of the S(2p) signal of XPS spectra coming from PEDOT (A_{PEDOT}) and PSS (A_{PSS}), it is possible to quantify the molar ratio of sulfonate to thiophene monomer unit ($R_{S/T}=A_{PSS}/A_{PEDOT}$) located on the surfaces and in the first layers of the PEDOT:PSS treated films. Furthermore, the effect of doping and the partial localization of charge carrier in PEDOT chains can be identified at the XPS spectra as an asymmetric tail at

higher side binding energy of S(2p) PEDOT component. Fig. 8 shows S(2p) spectra coming from PEDOT:PSS pristine films as well as those treated with different DBU complexes. These PEDOT:PSS films were treated with the DBU complexes (10:1 v/v solvent/DBU) during 10 min. The molar ratio of the Clevios P aqueous dispersion, according to the manufacturers, is $R_{S/T}$ = 1.9, which corresponds to a weight ratio of 2.5:1 PSS to PEDOT, indicating that PSS is used in excess in its synthesis [14,15]. Calculation of the area under the S(2p) peak of PEDOT:PSS pristine films shows a $R_{S/T} \approx 4.0$ ratio, which is approximately 2.1 larger than that of the aqueous dispersion. This shows that when the Clevios P aqueous dispersion is deposited on a glass substrate to fabricate pristine PEDOT:PSS films, a large proportion of PSS excess is on the surface of the film, which facilitates their removal by washing or dipping in solvents. For all the treated PEDOT:PSS films were observed a decrease in their molar ratio: $R_{S/T} \approx 1.2$ for MeCN/DBU complex, $R_{S/T} \approx 1.1$ for DMSO/DBU complex and $R_{S/T} \approx 1.5$ for DI water/DBU complex. From this analysis, we observe that the bigger amount of the PSS removal is performed when films are treated with DMSO/DBU complex, because in this case the complex takes out the PSS- anions doping the PEDOT chain, consequently modifying PEDOT optical, chemical and electrical properties (see Fig. 1 and Table I), while the excess of DMSO in the mixture washes out the PSS chains on the film surface. Furthermore, part of the S(2p) spectrum for S=O bonds and C-S bonds may come up from DMSO molecules remaining in the film. In contrast, when the films are immersed in the MeCN/DBU complex, the S(2p) spectrum can be very well fitted using only Gaussian Lorentzian (GL) curves and it is not necessary to use an asymmetric tail to produce a good fit in the PEDOT contribution ($\chi^2 = 1.81$ using an asymmetric tail, $\chi^2 = 2.0$ using GL curves), which clearly shows that a dedoping process was performed at the PEDOT chains.

Moreover the MeCN/DBU mixture does not contain S atoms, such as PEDOT or as PSS, and the whole signal of the S(2p) spectrum only comes from PEDOT and PSS. These results are in good agreement with the Vis-NIR absorption spectra of PEDOT:PSS films treated with the different DBU complexes. The N(1s) spectra of treated PEDOT:PSS films show the presence of DBU molecules on their surfaces (Fig. S4). N(1s) spectra can be well-fitted using Gaussian curves. It is also observed that the N(1s) spectrum is dependent of the solvent used; pyrrolelike (BE ~ 400.5 eV) to pyridinelike (BE ~ 398.4-399.0 eV) ratio for MeCN/DBU complexes is bigger than DI water/DBU and DMSO/DBU complexes. This binding energy shifting could be related to the stronger attraction between DBU molecules and H^+ ions ($DBUH^+$) from the MeCN solvent in comparison with the other solvents, in consequence related with the basicity, or related to different interaction strengths between PSS^- anions with DBU^+ cations due to the dedoping routes. Consequently the chemical environment of the N atom in the DBU molecule is modified due to changes occurring in C=N-C bond. O(1s) spectra for the pristine and MeCN/DBU treated PEDOT:PSS films are presented in Fig. S5. MeCN/DBU complex does not contain oxygen atoms so the data of the XPS measurement only comes from O(1s) of PEDOT and PSS monomeric units. The peak at ~532 eV comes from the S=O bonds of PSSH while the peak at ~533.5 eV comes from the S-O-H bonds of PSSH as well as C-O bonds of PEDOT. From figure, it is observed that the peak area at ~533.5 eV increases when the PEDOT:PSS films are treated with the MeCN/DBU complex, corroborating that mainly PSS is being removed from films. On the other hand, the peak at ~532 eV is shifted to lower binding energies regions [20], which can be related to an interaction between PSS^- anions with DBU^+ cations resulting from the dedoping

process. This effect is also observed for all PEDOT:PSS films treated with the other DBU complexes.

Finally, the emission of the dedoped films under excitation of a 488 nm laser was measured. The emission coming from dedoped thin films (~80 nm) was not observed at naked eye. In order to have a stronger emission, thick pristine PEDOT:PSS films were deposited by dropping PEDOT aqueous dispersion onto the glass substrate and dried at 120 °C. The thick PEDOT:PSS films were immersed into the DBU complexes and dried at 120 °C during 1 hour. The photoluminescence measurements were only performed on the PEDOT:PSS samples treated with DMSO/DBU (10:1 v/v) and MeCN/DBU (10:1 v/v) because they present different dedoping efficiency. After this treatment, the PEDOT:PSS films treated with MeCN/DBU complex showed strong emission in the visible range on each point of the sample surface, with a maximum emission peak at 630 nm, whereas those treated DMSO/DBU complex show a weak emission in the same spectral range and this emission was only possible to observe at some point on the sample surface. When the MeCN/DBU treated PEDOT:PSS films were encapsulated, it was possible to obtain the same emission spectrum at very high laser power without inducing a visible damage on the films, and the luminescence was observed with the naked eye, using a optical filter to reduce/remove Raleigh scattering (Fig. S6). The thick treated PEDOT:PSS films endured up to 50 mW of laser power whereas in our previous work [22] the dedoped PEDOT:PSS thin films showed also strong emission, but the films did not endure 10 mW of laser power, which is related to differences in the film thickness, treating procedure and dedoping efficiency of both methodologies. In our previous work [22], the aqueous dispersions of PEDOT PSS were mixed with DBU using a stirring hotplate, before the film fabrication. This

allowed a homogenization between the PEDOT:PSS chains and DBU molecules, which were homogenously distributed in the PEDOT films. In the present work, the pristine PEDOT:PSS films were immersed into DBU/solvent solutions, which allows the presence of DBU layer on the film surface, such as it is observed from the XPS spectra (Figure S4). Therefore, DBU molecules on the surface protect the film from the laser power, besides obstructing the oxygen ingress from the atmosphere hindering the reoxidation of PEDOT^0 chains. Moreover, the fabrication of thick PEDOT:PSS films makes that although the degraded PEDOT^0 chains in the top layers of films do not contribute to the PL emission, those PEDOT^0 chains in the bottom layers of thick films, that have not suffered laser damage or being reoxidaded, continue to emit.

4. Conclusions

In this work, a simple process for dedoping PEDOT:PSS films is implemented, which consists in the immersion of PEDOT:PSS films into mixtures of DBU with different solvents such as DMSO, MeCN and DI water. The treated PEDOT:PSS films showed a strong absorption band at 630 nm (π-π*), indicating a dedoping of the PEDOT chains, whereas the intensity of the polaron band (~900 nm) depended of the used DBU complex, the concentration of DBU in the mixture as well as the immersion time. The best dedoping efficiencies were obtained using MeCN/DBU or DI water/DBU complexes; the polaron band almost disappeared and the conductivity of treated PEDOT:PSS films decreased compared with the pristine one and, under certain experimental conditions, it was below the detection limit of the measuring device. In contrast, when the PEDOT:PSS films were treated using DMSO/DBU mixtures, under all experimental conditions, the absorption spectrum always showed the polaronic band, the conductivity was each time

possible to measure and, generally, the conductivity of the treated films was always greater than the pristine film. The difference between using MeCN/DBU and DI water/DBU complexes with respect to the DMSO/DBU complex is related to (i) solubility differences of PEDOT:PSS in the solvents, (ii) the basicity of the various DBU complexes, $pK_a = 24.3$ in MeCN, $pK_a = 13.9$ in DMSO, $pK_a = 13.5$ in DI water, (iii) the protonation percentage of DBU molecules in the different solvents. Finally, thick films of treated PEDOT:PSS showed strong yellow emission when they were excited with a 488 nm laser, with a maximal emission peak around 630 nm, which confirms that PEDOT chains are being dedoped by the DBU complexes. In addition, these films endured up to 50 mW of laser power without suffering any evident impact in their luminescent properties and any apparent physical damage.

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Table 1. Thicknesses and conductivities of PEDOT:PSS films treated with different DBU complexes.

Treated PEDOT:PSS film	Thickness (nm)	Conductivity (S/cm)
DMSO/DBU (2:1)-10 min	69	0.75
DMSO/DBU (2:1)-20 min	64	0.50
DMSO/DBU (2:1)-30 min	58	0.44
DMSO/DBU (10:1)-10 min	69	1.6
DMSO/DBU (10:1)-20 min	72	2.5
DMSO/DBU (10:1)-30 min	74	2.8
MeCN/DBU (10:1)-10 min	85	1.1
MeCN/DBU (10:1)-20 min	83	1.5
MeCN/DBU (10:1)-30 min	76	1.2
DI water/DBU (1:1)-10 min	84	0.14
DI water/DBU (10:1)-20 min	88	-
DI water/DBU (10:1)-30 min	92	-
Pristine	70	0.19
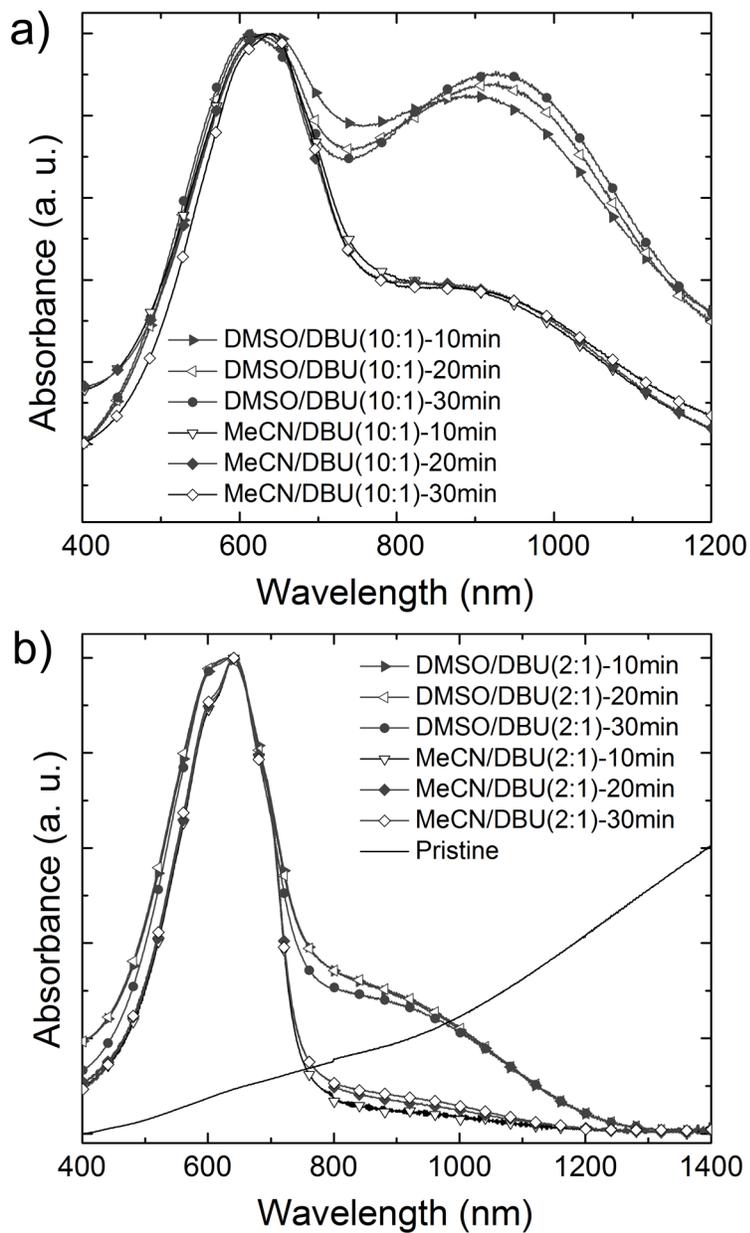
Figure 1. Normalized absorbance spectra of pristine and treated PEDOT:PSS films with DMSO/DBU and MeCN/DBU mixtures at v/v ratio of a) 10:1 and b) 2:1 at different times of immersion.
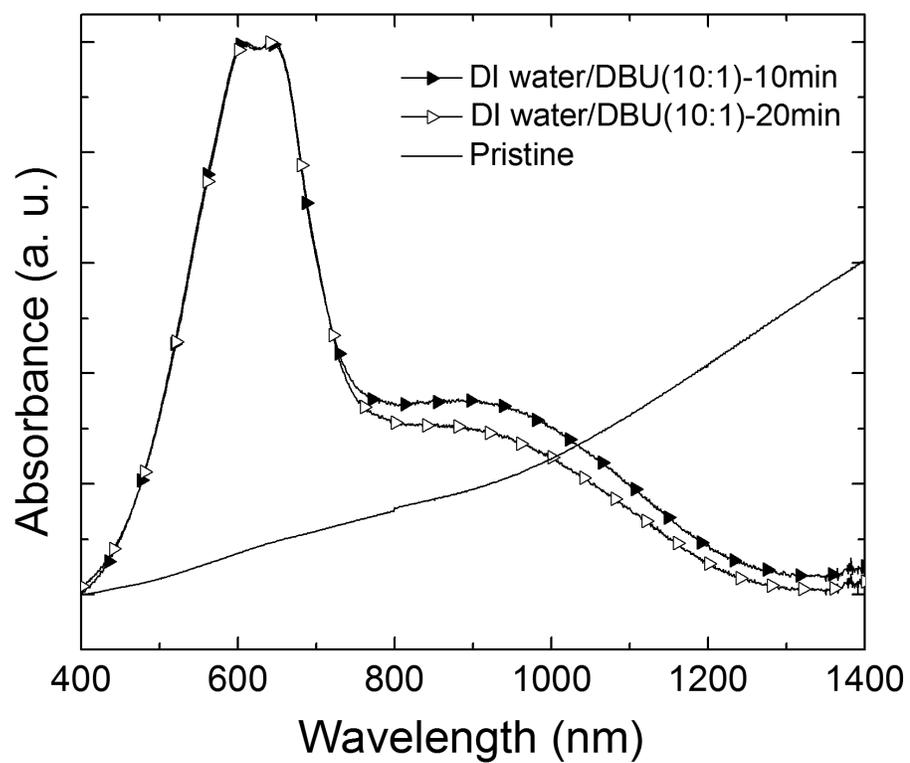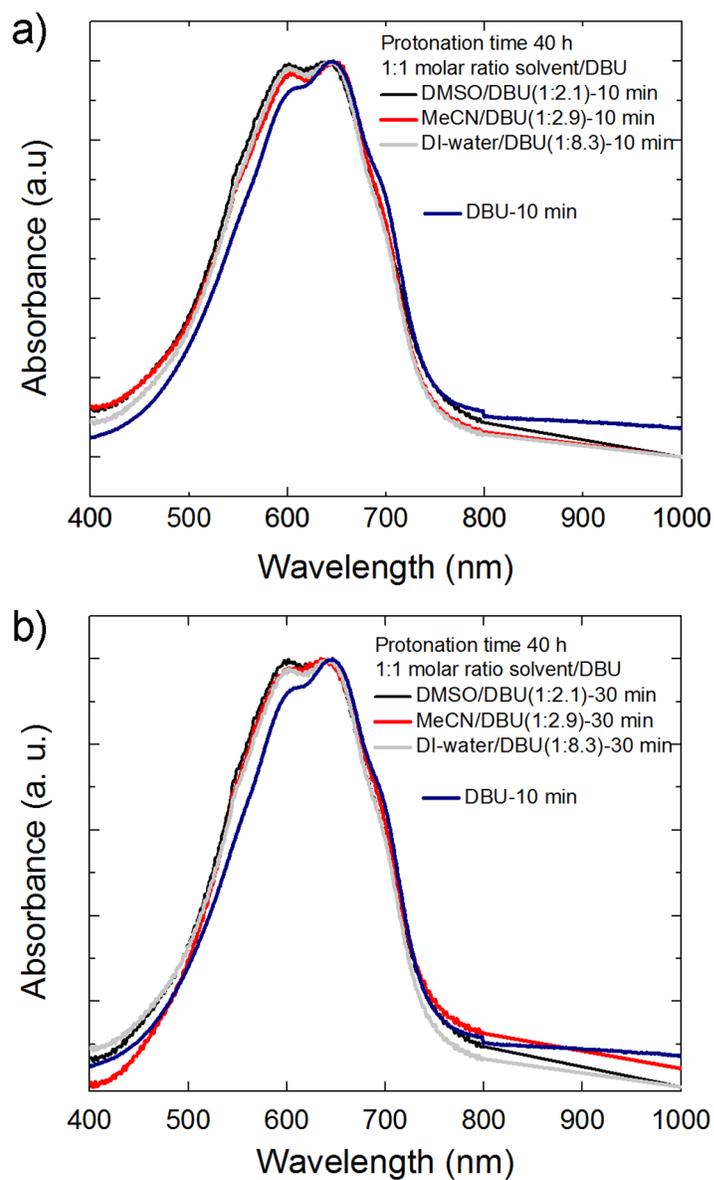
Figure 2. Normalized absorbance spectra of treated PEDOT:PSS films with DI water/DBU mixture at 10:1 volume ratio for two different times of immersion.
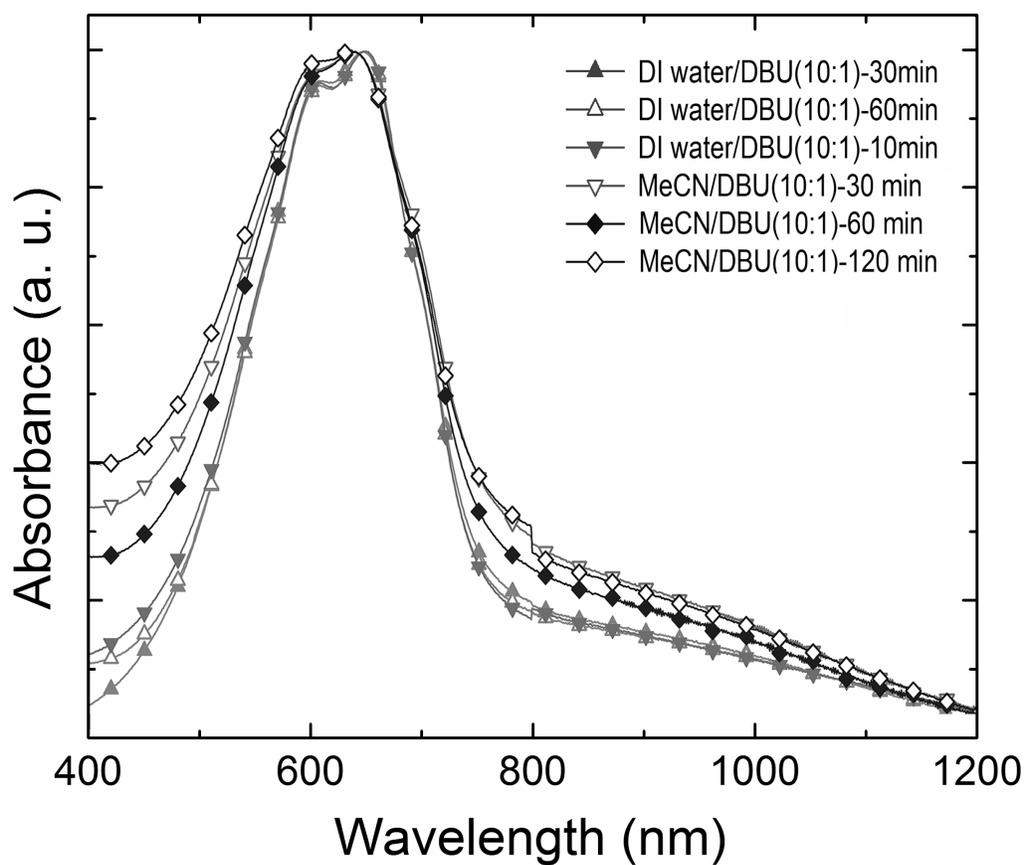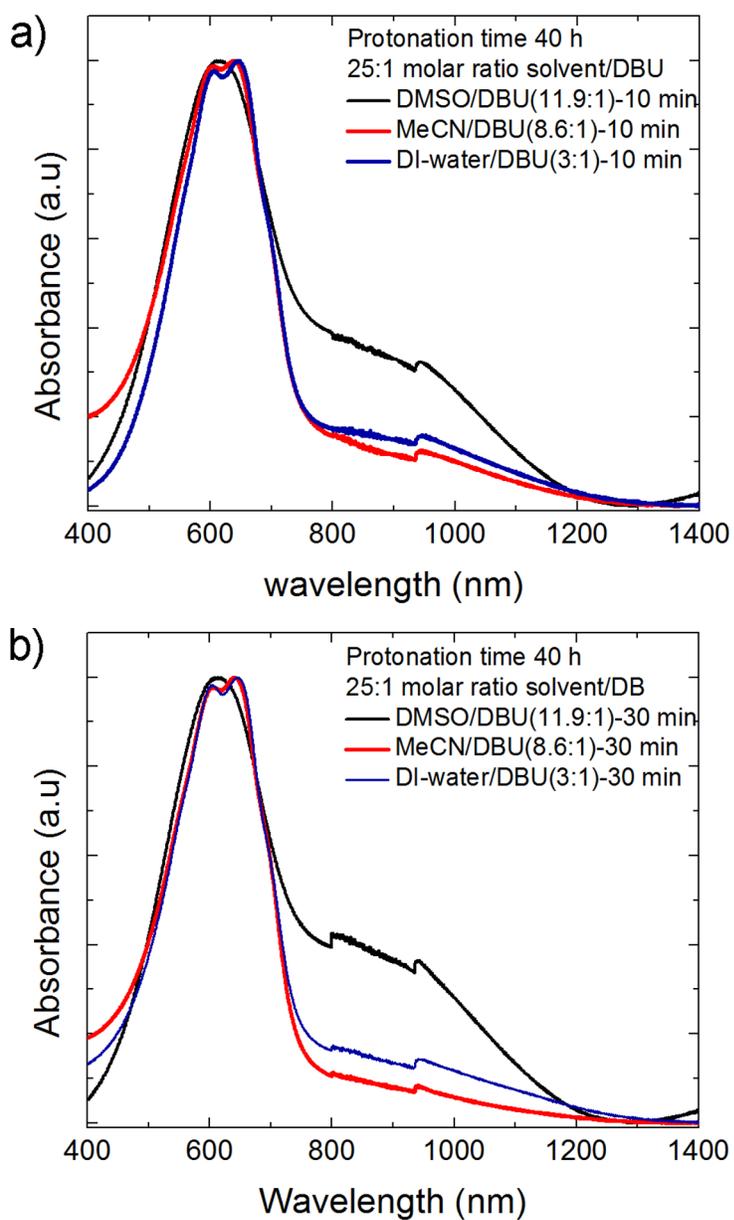
Figure 3. Normalized absorbance spectra of treated PEDOT:PSS films with a) DI water/DBU and b) MeCN/DBU mixtures at v/v ratio of 10:1 at 30 min, 60 min and 120 min of immersion.
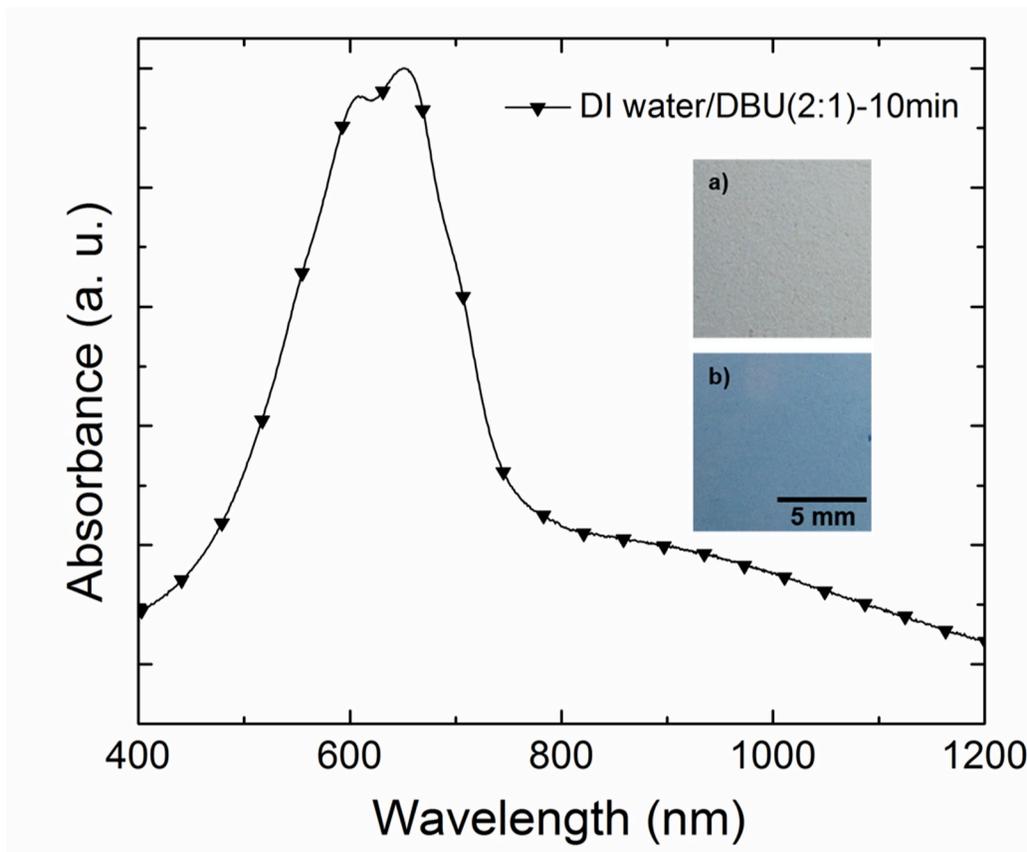
Figure 4. Normalized absorbance spectrum of treated PEDOT:PSS film with DI water/DBU mixture at 2:1 volume ratio for 10 min of immersion. The inset shows photographic images of PEDOT:PSS film before and after their treatment.

Figure 5. Normalized absorbance spectra of treated PEDOT:PSS films with a 1:1 molar ratio solvent to DBU and two different immersion times. The mixtures were stirred during 40 h to allow the maximum protonation of DBU molecules. For comparison, we are showing a PEDOT:PSS film treated only with DBU.

Figure 6. Normalized absorbance spectra of treated PEDOT:PSS films using solvent/DBU mixtures stirred during 40 h with a 25:1 molar ratio, to allow a complete switch of DBU molecules to their protonated form, at least for DI-water/DBU mixtures.
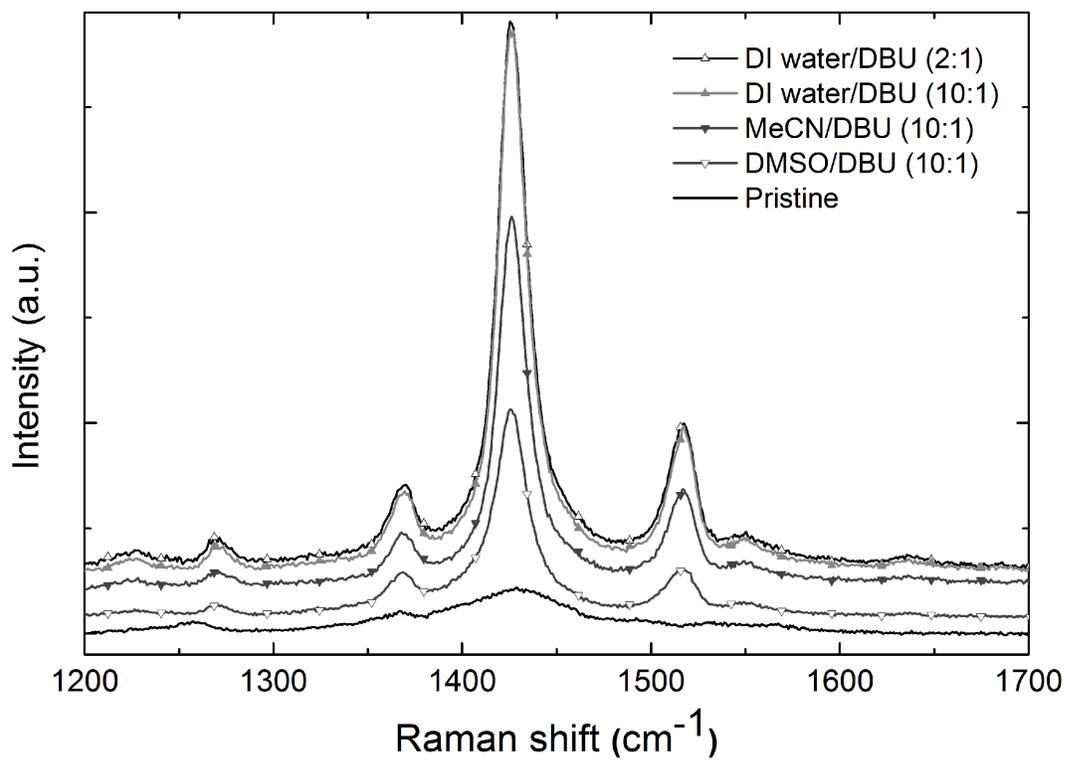
Figure 7. Raman spectra of the pristine film and treated PEDOT:PSS films with DMSO/DBU, MeCN/DBU and DI water/DBU mixtures at the volume mixing ratio of 10:1 and of 2:1 for the treated film with DI water/DBU mixture.
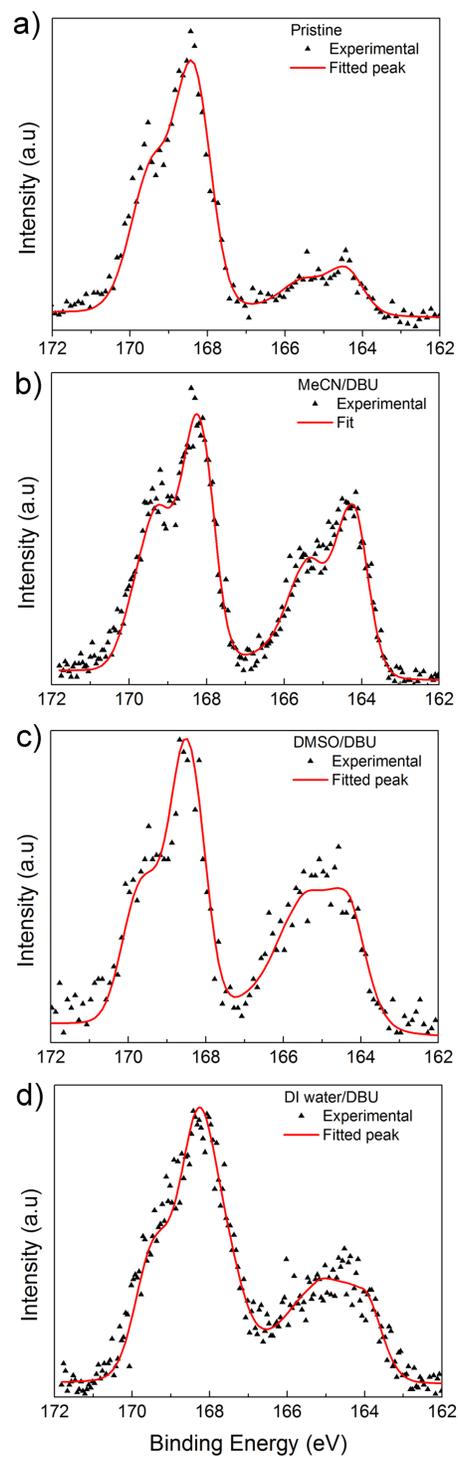
Figure 8. S(2p) XPS spectra of a) pristine film and treated PEDOT:PSS film with b) MeCN/DBU (10:1 v/v), with c) DMSO/DBU (10:1 v/v) and with d) DI water/DBU (10:1 v/v) mixtures.