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The effects of humidity on the electrical properties and carrier mobility of semiconducting polymers anion-exchange doped with hygroscopic salts

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ABSTRACT

To improve their electrical conductivity for various applications, semiconducting polymer films are often chemically doped to increase their equilibrium charge carrier density. Recently, a novel doping method involving anion exchange has provided control over the identity of the counterions that reside in such films, leading to increased stability under ambient conditions. In this work, however, we show that by ion-exchanging 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane-doped poly(3-hexylthiophene-2,5-diyl) films with hygroscopic salts like bis (trifluoromethane)sulfonimide lithium or $LiPF_6$, the doped film's electrical conductivity drops significantly when exposed to ambient humidity. The change in electrical conductivity depends directly on the degree of hygroscopicity of the counterion and can be over 50% with relatively modest changes in relative humidity (RH), and up to a factor of four between ambient and completely dry conditions. The film's humidity response is entirely reversible when adsorbed water is removed, potentially allowing the doped semiconducting polymer films to function as humidity sensors. Hall effect measurements show that the cause of the drop in conductivity with increasing RH is due to a decrease in carrier mobility and not due to de-doping. Our results emphasize that it is important to control the sample environment when making electrical measurements on anion-exchange doped semiconducting polymer films.

Thanks to their ease of processing, structural tunability, low intrinsic thermal conductivity, and biocompatibility, interest in using semiconducting polymers for applications such as biosensors or thermoelectric generators has grown steadily.[1–3] Due to their intrinsically low carrier density, conjugated polymers need to be electrically doped to meet the performance standards demanded by many applications. The most common way to do this is through chemical doping, a process that introduces a small molecule that can undergo a charge transfer reaction with the semiconducting polymer; since most conjugated polymers are *p*-type materials, oxidizing agents are chosen to create mobile hole charge carriers.[4–6] The extent of chemical doping depends mainly on the polymer's ionization energy and the dopant's electron affinity,[7] as well as the concentration of the dopant that is used.[8]

Recently, Yamashita and co-workers introduced a novel method referred to as anion-exchange doping,[9] which provides several advantages over conventional chemical doping. The method involves exposing a conjugated polymer film to a solution containing both a chemical dopant and a high concentration of electrolyte. The dopant oxidizes the polymer, and the dopant counterion is then exchanged out by mass action for the electrolyte anion from solution. This method not only provides control over the choice of counterion in doped semiconducting polymer films, but it also can achieve doping levels much higher than those reached via conventional doping: for example, Yamashita and co-workers were able to obtain nearly one carrier per monomer unit for the polymer poly(2,5-bis(3-tetradecylthiophen-2-yl) thieno[3,2-b]thiophene) (PBTTT) and the dopant 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F_4TCNQ) in the presence of different electrolytes.[9] The ability to choose the counterion inside the doped film can make doped films more stable under ambient conditions[9] and can also help tune the effect of coulomb interaction between the free carriers on the polymer backbone and its compensating charge, which is important for controlling carrier mobility.[9,10]

Because of all its advantages, multiple groups are now employing anion exchange doping when using semiconducting polymers in different applications. In the course of our exploration of anion exchange doping, however, we have discovered one potentially serious drawback: the typical electrolyte salts used in anion exchange doping, such as bis (trifluoromethane)sulfonimide lithium (LiTFSI), are generally highly hygroscopic, which means that the electrical behavior of anion-exchange-doped polymer films can be highly sensitive to the ambient humidity. In this work, we show that exposure of anion-exchange-doped polymer films to even moderate humidity can decrease the carrier mobility by over a factor of 3. This means that workers who study the properties of such films need to make sure they do so in a humidity-controlled environment.

There are of course previous studies on the influence of moisture on trap formation in semiconducting polymers.[11–17] Zuo and coworkers reported that the dielectric effect of water in nanovoids of semiconducting polymer thin films can create carrier traps that can be ~0.3 to 0.5 eV deep.[14] These traps can be mitigated by solvent annealing to reduce the number of nanovoids[14] or by filling the nanovoids with dopants that displace the water.[11,13,18] Another approach to mitigate the effects of water inhabiting nanovoids is to use conjugated polymers with denser side chain placement, such as regioregular poly(3-hexylthiophene-2,5-diyl) (P3HT),[17] which is a workhorse material in the field.

The aforementioned moisture studies were done on pristine or very lightly doped semiconducting polymer films used in either organic field-effect transistors or solar cells, and none of these studies examined the film's electrical conductivity or the effects of different doping methods. Here, we investigate the effect of humidity on the electrical conductivity, carrier density, and carrier mobility of both conventionally doped and anion-exchange-doped P3HT films. In particular, we study the effects of moisture on P3HT films doped via the anion-exchange method using LiTFSI and find a dramatic drop in electrical conductivity with increasing ambient humidity. We then use Hall effect measurements to show that the drop in conductivity with increasing humidity is primarily due to changes in carrier mobility and not due to dedoping. We also show that the effect of humidity on charge transport is quasi-reversible and that the electrical conductivity changes almost linearly with humidity. Thus, not only is care needed to control the humidity when studying these materials, but anion-exchange doped conjugated polymer films also could possibly serve a role as resistance-based humidity sensors.

In addition to exploring the effects of humidity on anion-exchange doped P3HT films, we also demonstrate the salt's hygroscopicity is key to the humidity-induced drop of electrical conductivity by comparing the properties of anion-exchange-doped P3HT films with LiTFSI to those exchanged with a less hygroscopic salt, lithium hexafluorophosphate ($LiPF_6$).[19–22] It is worth noting that anion hygroscopicity depends on the conditions being explored. For example, under conditions close to vacuum dry, the distinction of which ion is more hygroscopic may not be clear, as seen in the ionic liquid literature.[23,24] However, under typical ambient relative humidity conditions such as those studied here, it is generally well accepted that $TFSI^-$ is more hygroscopic than PF_6^-,[19–22] and indeed, we will show below that there are stronger humidity effects on the electrical properties of doped P3HT films with $TFSI^-$ than PF_6^-.

The overall goal of this study is to investigate the impact of humidity on conjugated polymer films doped both conventionally and with anion-exchange doping. To conduct this comparison, we start with 112-nm thick P3HT films spin-cast from a 2% w/v solution in *o*-dichlorobenzene. For the conventional doping method, we sequentially dope the P3HT films using different concentrations of F_4TCNQ dissolved in *n*-butyl acetate (*n*-BA). For the anion-exchange doping process, we follow the same procedure as for the conventional doping method, but with the addition of a high concentration of LiTFSI (30 mg/ml) or $LiPF_6$ (5 mg/ml) dissolved in the same solution as the F_4TCNQ. All of the processing steps were carried out in the inert atmosphere of a glovebox with effectively 0% relative humidity (RH). Details of the materials that we use and the casting and doping conditions are given in the supplementary material.

To investigate the effect that humidity plays on the electrical properties of doped conjugated polymer films, we chose dopant concentrations that resulted in similar electrical conductivity values with the two different doping methods (and thus with counterions with different degrees of hygroscopicity). The concentrations we focus on for anion-exchanged (AE) and conventional (Conv) doping were 0.1 mg/ml F_4TCNQ + 30 mg/ml LiTFSI, 0.1 mg/ml F_4TCNQ + 5 mg/ml $LiPF_6$, and 0.5 mg/ml F_4TCNQ, respectively; results with additional doping concentrations are given in the supplementary material. We note that the F_4TCNQ concentrations we use are low enough that there is no neutral F_4TCNQ present in the doped films, as confirmed by UV-Visible spectroscopy in Fig. S3 of the supplementary material.

After preparing doped P3HT films with these different processing conditions, we measured the films' electrical conductivities in three different environments with different RH levels. First, the conductivity was measured in the inert atmosphere of an Ar-filled glovebox (Ar Glovebox) with effectively 0% humidity. The samples were then transferred out of the Ar glovebox and exposed to ambient air for roughly 5 min before the conductivity was re-measured (Ambient Air). The air-exposed samples were then purged with Ar for 5 min prior to measuring the conductivity for a third time (Ar Purged). We chose a 5-min purge because the electrical conductivity of the samples no longer changed past that time.

Table I shows the electrical conductivities, measured via the van der Pauw four-point-probe method with electrodes placed at the corners of our 1.5 × 1.5 cm^2 samples, of 97% regioregular P3HT films doped using the conventional and anion-exchange methods in environments with different RHs. The conventionally doped samples have the same electrical conductivity in all three different environments within error. The anion-exchange-doped samples with both salts, however, show a significant drop in conductivity when taken from the inert, 0% RH environment of the Ar Glovebox and introduced to the ambient environment (~36% and ~40% RH for LiTFSI and $LiPF_6$, respectively). The drop in conductivity upon exposure to ambient humidity is quite significant, with the LiTFSI anion-exchanged sample showing a conductivity loss nearly a factor of 4. The samples anion-exchanged using $LiPF_6$ also exhibit a considerable reduction in conductivity, but the decrease is only about a factor of 2, despite the slightly higher RH for the $LiPF_6$-doped sample. This difference in the humidity-induced conductivity drop between $LiPF_6$ and LiTFSI makes sense in light of the fact that $LiPF_6$ is less hygroscopic,[20–22] indicating that the hygroscopicity of the anion plays a key role in the humidity-dependent electrical behavior. We also saw very similar results for P3HT samples created using different dopant concentrations and P3HT regioregularities, as demonstrated in Fig. S1 and elsewhere in the supplementary material, indicating that the humidity effect is not system specific.

The fact that the drop in conductivity is seen only with the anion-exchange doping method and not with conventional doping also lends support to our conclusion that the humidity effect involves the hygroscopic anions that were exchanged into the doped films. The

TABLE I. Electrical conductivities of anion-exchange-doped (AE) and conventionally doped (Conv) P3HT films measured under different environmental conditions. The dopant concentrations for AE were 0.1 mg/ml $F_4TCNQ + 30$ mg/ml LiTFSI and 0.1 mg/ml $F_4TCNQ + 5$ mg/ml $LiPF_6$, while the conventionally doped samples used 0.5 mg/ml F_4TCNQ. Exposure to humidity dramatically lowers the conductivity of anion-exchanged-doped samples, whereas conventionally doped samples show no conductivity change within error. Hall mobility and carrier densities were all obtained on the same set of samples. Unfortunately, due to logistical constraints, we are unable to perform Hall measurements inside the Ar glovebox.

	Environment	Conductivity (S/cm)	Hall mobility ($cm^2\ V^{-1}\ s^{-1}$)	Hall carrier density ($\times 10^{20}\ cm^{-3}$)
0.5 mg/ml conventional	Ambient	3.03 ± 0.20	0.029 ± 0.006	6.4 ± 0.94
	Ar Purged	2.98 ± 0.20	0.029 ± 0.005	6.3 ± 0.84
	Ar Glovebox	3.18 ± 0.16	N/A	N/A
0.1 mg/ml AE (LiTFSI)	Ambient	0.75 ± 0.15	0.014 ± 0.0004	3.3 ± 0.74
	Ar Purged	1.65 ± 0.14	0.042 ± 0.005	2.5 ± 0.51
	Ar Glovebox	2.88 ± 0.55	N/A	N/A
0.1 mg/ml AE ($LiPF_6$)	Ambient	3.66 ± 0.28	0.037 ± 0.003	6.1 ± 0.63
	Ar Purged	3.89 ± 0.24	0.040 ± 0.004	6.1 ± 0.65
	Ar Glovebox	6.74 ± 0.59	N/A	N/A

hygroscopic nature of LiTFSI and its effect on electronic transport is well-documented in the mixed organic/inorganic perovskite solar cell community, where LiTFSI is often employed as an additive to enhance the *p*-doping of 2,2′7,7′-tetrakis-(*N*,*N*-di-p-methoxyphenyl-amine)-9,9′-spirobifluorene (spiro-MeOTAD).[21,25–28] However, in the case of perovskite materials, the consequence of using LiTFSI is more severe than just the introduction of carrier traps, as adsorbed water can actually dissolve the material.[29]

To verify that it is water in the ambient environment that causes the large drop in conductivity for the anion-exchange-doped P3HT films, we attempted to restore the conductivity by flowing either dry air or argon gas into our ambient conductivity measurement setup; Table I shows that doing so yielded partial recovery of the conductivity. However, we were able to fully recover the original conductivity measured in the Ar glovebox by subjecting the films to a vacuum/purging process. This process involved four cycles where the films were placed under rough-pump vacuum for 5 min, followed by an Ar-gas refill (the green X in Fig. S2 in the supplementary material shows the fully recovered conductivity value for the 0.1 mg/ml LiTFSI-anion-exchanged sample after undergoing this process). All of this is consistent with the idea that an initially "dry" anion-exchange-doped sample readily absorbs water due to hygroscopic counterions upon exposure to moist air. Surface-level adsorbed water can easily be removed simply by purging with dry gas, resulting in partial restoration of the electrical conductivity. However, exposing the samples to the vacuum/purging process enables the complete removal of water from deeper within the films, leading to full recovery of the electrical conductivity.

It may not be surprising that for conventionally doped P3HT films, the non-hygroscopic F_4TCNQ dopants are not affected by humidity, but we were still intrigued to observe no moisture-related trap effects induced by water adsorption into nanovoids in these films.[17] We believe that this could be due to a combination of our use of 97% regioregular P3HT, which has densely packed side-chains, combined with the space-filling properties of the non-hygroscopic F_4TCNQ dopants,[11,17] which together mitigate water-related traps and their influence on electrical conductivity. Another possibility for the insensitivity of the conventionally doped samples to humidity could be due to left over neutral F_4TCNQ in the polymer films, as previous studies have indicated that neutral additives with strong electron-withdrawing nitrile groups can bind with water molecules and thus hinder the formation of water-induced traps.[30] As mentioned above, however, the relatively low doping concentration used in our experiments, along with the UV-Vis-NIR spectrum shown in the supplementary material (Fig. S3), confirm that our films do not contain any significant amounts of neutral F_4TCNQ. As a result, we believe that humidity-independent behavior of our conventionally doped films is most likely due to void-filling/repelling.

To understand the molecular-level causes of the conductivity decrease in anion-exchange-doped P3HT samples upon exposure to humidity, we also conducted Hall effect measurements on the same set of samples. Table I shows the Hall carrier mobilities and densities obtained both in ambient air and after argon purging; unfortunately, logistical constraints prevented us from placing our Hall effect set-up in the Ar dry-box where the samples were fabricated. The results indicate that the mobile carrier density remains unaffected within error by ambient humidity for both the anion-exchange- and conventionally doped samples; in other words, humidity does not cause de-doping. Indeed, the $TFSI^-$ and $PF_6{}^-$ anions are quite stable and thus not expected to react chemically or undergo any redox reactions in the presence of moisture.[9,31–34] Instead, the drop in electrical conductivity observed in the anion-exchanged samples upon exposure to humid environments primarily stems from a decline in carrier mobility. This agrees with previous studies suggesting that water can act as shallow traps in semiconducting polymer films.[11–17]

To further investigate the idea that the primary effect of humidity on anion-exchange-doped films is to reduce the carrier mobility, we utilized IR spectroscopy to investigate the trapping of carriers that results from humidity exposure. It is well-established in the literature that the degree of carrier delocalization, and thus, carrier mobility, is reflected in the position of the so-called "P1" polaron absorption band in the IR: less trapped or more delocalized polarons show a red-shifted P1 band, while trapped polarons that are more localized and have lower mobilities are associated with more blueshifted P1 bands.[10,35–37] Thus, we took the 0.1 mg/ml anion-exchange-doped (LiTFSI) and 0.5 mg/ml conventionally doped samples that had been exposed to ambient conditions and monitored their near-IR absorption as a function of time as the samples were purged with dry N_2 gas.

Figure 1(a) shows the results of this experiment, plotting the evolution of the blue side of the P1 absorption as the N_2 purging time increases for the humidity-exposed anion-exchange-doped P3HT sample; we chose to focus on the blue side because it better reflects the presence of more highly trapped polarons in the films,[10,35–37] and because the red side of the P1 band overlaps with the water O-H stretch near 2700 nm (see inset), making it hard to disentangle competing effects. The data show that with longer N_2 purging times, the intensity of the blue side of the P1 absorption diminishes, indicating a drop in the number of trapped polarons in the film. Moreover, despite the complication arising from the water O–H stretch, there is an observable isobestic point near 2900 nm (see inset) where the redder side of the P1 band increases with purging time. This shows that purging with dry gas causes the conversion of trapped polarons into more mobile polarons via the removal of moisture.

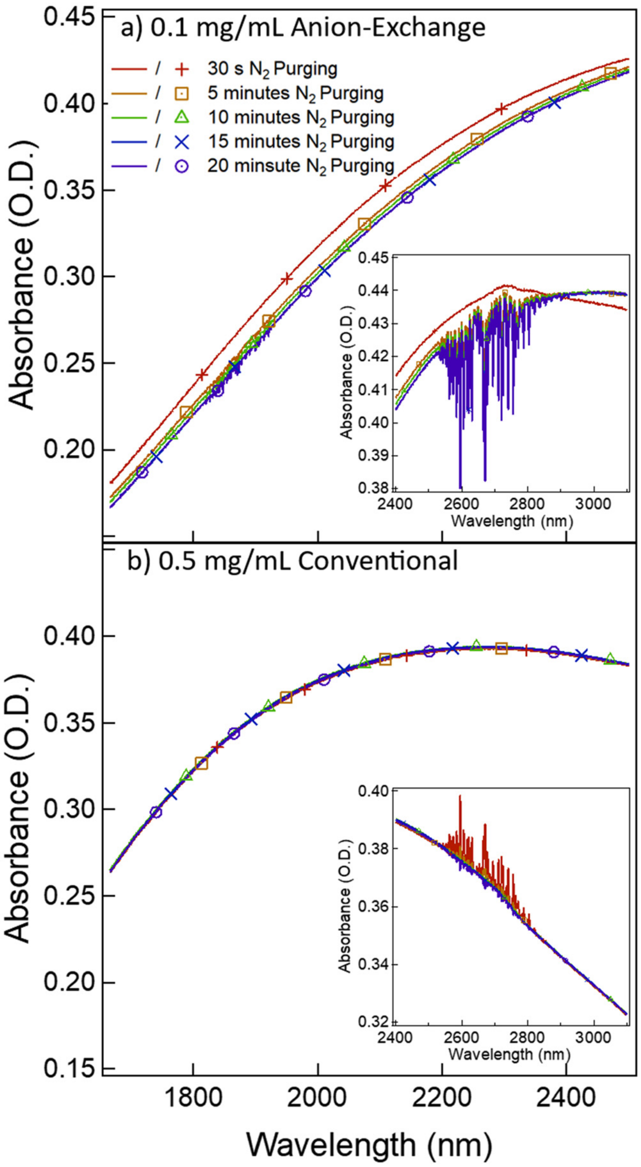

FIG. 1. UV Vis of 0.1 mg/ml $F_4TCNQ + 30$ mg/ml LiTFSI (AE) and 0.5 mg/ml F_4TCNQ (Conv) samples. The blue side of the P1 polaron absorption, which is associated with trapped carriers, for (a) an anion-exchange-doped P3HT film and (b) a conventionally doped P3HT film that had been exposed to ambient conditions as a function of time after purging with dry N_2. Purging clearly decreases the blue P1 absorption for the anion-exchange-doped sample while having no effect on the conventionally doped sample, consistent with the idea that humidity lowers the mobility of carriers in the anion-exchange-doped films [cf. (b)]. The insets in (a) and (b) show the same spectra extended deeper into the IR region, including the absorption of the water O–H stretch near 2700 nm (this absorption appears to go in opposite directions in the two panels because of the way the spectra were base-lined; see text).

In contrast, for the conventionally doped P3HT sample, shown in Fig. 1(b), there are no changes in the intensity of the P1 band with purging time, indicating that changing the humidity does not alter the trapping of polarons in conventionally doped P3HT films; both results are consistent with the way the carrier mobility changes in response to humidity, as shown in Table I. We note that because of the way we performed the baseline (either under ambient conditions for the anion-exchange-doped sample or after N_2 purging for the conventionally doped sample), the water absorption feature near 2700 nm appears to go in opposite directions in the two panels of Fig. 1.

Finally, to verify that the decrease in conductivity in anion-exchange-doped P3HT samples is specifically caused by humidity rather than other ambient gases such as O_2, we performed a set of measurements in ambient conditions under controlled RH. This was accomplished by placing 0.1 mg/ml anion-exchange-doped samples using both LiTFSI and $LiPF_6$ inside an air-filled desiccator containing drierite to control the humidity, and then measuring the electrical conductivity as a function of RH. The results are presented in Fig. 2, which shows a remarkably linear relationship between the change in electrical conductivity (relative to that measured at 15% RH, the lowest we could achieve with this set-up) and relative humidity for the air-exposed anion-exchange-doped films. We note that for RH lower than ~20%, the linear relationship between conductivity and RH appears to lessen relative to what is observed at higher RH. This is because, as with the purging experiments described above, drierite is not capable of removing water from deep within the film. However, even with some trapped water, the nearly linear relationship between RH and conductivity depicted in Fig. 2 suggests that anion-exchange-doped films employing hygroscopic salts can possibly serve as viable materials for resistance-based humidity-sensing applications.

It is worth mentioning that the trend observe in Fig. 2 is similar to that seen in humidity sensors based on organic field-effect transistors (OFETs).[38,39] Even though OFET-based humidity sensors typically utilize pristine conjugated polymers rather than doped ones, the underlying sensing mechanism is basically the same in that adsorbed water acts as a trap leading to a decrease in charge carrier mobility. We note that although our doped films may be slightly less sensitive to humidity than OFETs, our resistance-based humidity sensing approach offers a significant advantage in terms of simplicity of production.

The data in Fig. 2 also show that the slope of the relative change in conductivity vs RH for LiTFSI-exchanged samples (green squares) is considerably higher than that of $LiPF_6$-exchanged samples (blue triangles), consistent with the idea that $TFSI^-$ is a more hygroscopic

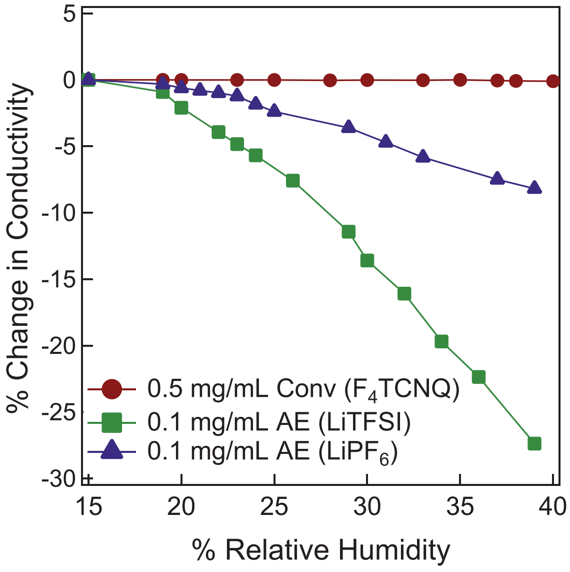

FIG. 2. Electrical conductivity of conventionally (0.5 mg/ml F_4TCNQ, red circles) and anion-exchange-doped (0.1 mg/ml F_4TCNQ with 30 mg/ml LiTFSI, green squares, and 0.1 mg/ml F_4TCNQ with 5 mg/ml $LiPF_6$, purple triangles) P3HT films as a function of percent relative humidity in air. The ordinate plots the relative change in conductivity compared to that measured at 15% RH, the lowest we could obtain with our set-up. The conductivity change is highly linear down to ∼20% RH, suggesting that the doped polymer films anion-exchanged with LiTFSI could possibly be used as resistance-based humidity sensors.

anion than PF_6^-.[19–21] The conventionally doped samples (red circles) show no response to changes in humidity within error, as discussed above, consistent with the idea that hydrophobic F_4TCNQ prevents water from interacting with the charge carriers in doped P3HT.[21,28] These observations further confirm our hypothesis that exposure the anions to water vapor is what is responsible for the observed decline in conductivity, rather than the infiltration of water into the void spaces of the film.

Although ions like $TFSI^-$ and PF_6^- are generally chosen for their electrochemical stability, the fact that they are hygroscopic is often overlooked. The hygroscopicity of these ions depends on how water molecules bind around them, a factor defined as water sorption capacity per ion pair.[40] Several studies have demonstrated that under ambient temperature and humidity conditions, $TFSI^-$ possesses a higher capacity to absorb water than PF_6^-.[19–22] The extent of water absorption by different ions also is connected to both the relative basicity of the anions and the ratio of hydrophobic F atoms to the total number of atoms within the anions.[19,21,22] In combination, doped P3HT films with $TFSI^-$ not only have a stronger affinity for water but also tend to accommodate more water, explaining why these films show a more significant humidity-induced drop in conductivity than films containing PF_6^-.

In summary, our study has demonstrated a high sensitivity of the electrical properties of conjugated polymer films anion-exchange-doped with hygroscopic salts, such as LiTFSI, to humidity. Given that one of the advantages of anion-exchange doping is that it creates more air-stable samples, our results show that it is crucial to consider the impact of the environment, and particularly RH, to make accurate measurements and interpretations. We verified that it is the hygroscopic nature of anions like $TFSI^-$ that is responsible for the change in electrical behavior with RH by showing that less hygroscopic anions like PF_6^- show a smaller conductivity change with RH, and that non-hygroscopic dopants like F_4TCNQ show no changes with RH at all. Through Hall effect measurements and IR spectroscopy, we established that the decrease in electrical conductivity caused by humidity is a result of water-induced trapping affecting the transport of charge carriers; exposure to moisture does not appear to affect the doped carrier density. The effects of humidity on the conductivity of anion-exchange films are reversible, as long as sufficient efforts are made to remove deeply trapped water from within the doped films by using a combination of vacuum and humidity-free gas purging. Finally, it appears that the decrease in electrical conductivity shows a roughly linear relationship with relative humidity, suggesting that anion-exchange-doped conjugated polymers hold potential for humidity-sensing applications.

See the supplementary material for a detailed description of the experimental methods and a presentation of additional related results.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Quynh M. Duong and Diego Garcia Vidales contributed equally to this work.

Quynh M. Duong: Conceptualization (equal); Data curation (equal); Investigation (equal); Methodology (equal); Writing – original draft (equal). **Diego Garcia Vidales:** Conceptualization (equal); Data curation (equal); Investigation (equal); Methodology (equal); Writing – original draft (equal). **Benjamin J. Schwartz:** Conceptualization (equal); Funding acquisition (lead); Supervision (lead); Writing – review & editing (lead).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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