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Modifying field-effect transistor response in a conjugated polymer upon the addition of radical dopants

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ABSTRACT

As open-shell moieties are increasingly integrated into organic electronic devices, there remains a need to establish the interactions that occur between these oxidation–reduction-active (redox-active) radical species and commonly-used conjugated polymers. In this report, we show that the addition of the stable radical galvinoxyl to the conjugated polymer poly(3-hexylthiophene) (P3HT) alters the thin film transistor response from semiconducting to conducting as well as modestly enhances the electrical conductivity. This interaction is not seen with other radical species. While an increase in charge carrier concentration is observed, the interaction does not seem to be otherwise consistent with a simple charge-transfer doping mechanism, due to the mismatched reduction and oxidation potentials of the two species. Additionally, no freeze-out of charge carriers is observed at lower temperatures. It is also not due to parallel conduction through the radical fraction of the bulk composite, as the radical species is non-conductive. Hole mobility is enhanced at lower concentrations of the radical, but it decreases at higher concentrations due to the reduced fraction of conductive material in the polymer bulk. Despite the increase in mobility at lower concentrations, the activation energy for charge transport is increased by the presence of the radical. This suggests that the radical is likely filling trap states within the P3HT for the composite thin film while not affecting their energetic distribution.

1. Introduction

Conjugated small molecules and polymers are the leading classes of materials in organic electronic devices. In fact, an impressive range of molecular architectures have been tailored for applications including organic field-effect transistors (OFETs) [1,2], organic photovoltaics [3–5], organic light-emitting devices [6], and thermoelectric modules [7,8]. However, conjugated materials are not always the optimal materials choice for every application, and many organic electronic technologies have yet to capture a significant share of the commercial market. For this reason, there is interest in developing alternative classes of materials that can complement the strengths of conjugated systems.

One such class is comprised of stable organic radicals [9–11]. These moieties show excellent charge transfer properties, making them well-suited for organic battery applications [12], and their open-shell nature makes them useful in spin-manipulation applications [13–17]. Beyond their usage as small-molecule dopants [18,19], polymers containing radicals have shown promise as interfacial modifying layers in organic electronic devices [20–22], and proper molecular design allows for impressive intrinsic electronic conductivity values to be had [23]. Additionally, conjugated molecules with covalently-linked radical moieties have been developed for use in battery applications [24–31], as well as to protect the conjugated moiety from degradation by manipulating the excited state dynamics [32–37]. With their potential as next-generation electronic materials, determining how open-shell molecules interact with oft-used conjugated materials in thin films is of prime importance to guide future applications.

The interaction of radicals with materials in their excited states, observed primarily through fluorescence quenching, has been well-documented in the literature [33,38–45], and our previous work has established the excited-state interactions between a common conjugated polymer, poly(3-hexylthiophene) (P3HT), and three distinct stable organic radicals [46]. Despite finding a clear pattern in the excited state interactions, similar considerations have not been given to the interactions in the ground state. Of course, for most organic electronic applications, the ground state interactions are more relevant. Thus, to elucidate the potential effects of introducing open-shell functionalities into thin films of conjugated polymers, the full scope of the interactions between these classes of materials must be established in a

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complete manner.

One means to examine ground-state interactions that is particularly relevant to device applications is to evaluate the charge transport properties of one material, and how these properties are affected by the presence of another species in thin films. Changes in the electronic structure of the host material, and even formation of charge-transfer complexes, lead to significant changes in the electrical properties even with small quantities of additive [47], and this molecular principle is often exploited to develop functional devices (e.g., chemical sensors) [48,49]. A useful device geometry for measuring these charge transport properties is the OFET. OFETs allow the charge carrier concentration in the material to be modulated through application of a gate voltage, and evaluation of the subsequent response and transfer curves allows for the carrier concentration and mobility values to be determined. Here, we report an interaction between P3HT and the galvinoxyl radical (Gx), which causes a shift from semiconducting to conducting behavior. This is not seen with the other radical species evaluated here, and the P3HT-galvinoxyl radical interaction does not appear to be caused by an increase in free charge carriers, as seen with many other oft-reported molecular dopants in organic electronics [47,50,51]. In addition to hinting at the possibility of synergistic interactions between the two classes of material, these results underscore potential pitfalls of incorporating radical functionality into organic electronic devices, and they highlight the need to control the chemistry of the open-shell group in a careful manner when thin film composite considerations are being made. Because many of the potential applications of radicals in conjugated hosts are primarily concerned with either manipulating excited-state behavior of the conjugated material or aim for the electronic properties of the closed- and open-shell components to be decoupled, interactions that alter the electronic structure and semiconducting character of the host material may lead to reduced efficacy in an actual device context. Thus, this work provides the first step in clear molecular design considerations as open-shell materials are further incorporated into conjugated polymer matrices for high-performance organic electronic devices.

2. Experimental details

2.1. Materials

The galvinoxyl (Gx) and 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) (97%) radicals, hexamethyldisilazane (HMDS) (99%), and anhydrous 1,2-dichlorobenzene (DCB) (99%) were purchased from Sigma-Aldrich. The 2-phenyl-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide (PTIO) radical (98%) was purchased from TCI America. P3HT (regioregular electronic grade, M_n ~60 kg mol^{-1}) was purchased from Rieke Metals. Gold (99.99%) and titanium (99.7%) were purchased from Kurt Lesker. Acetone (99.5%), chloroform (99.8%), and isopropanol (99.5%) were purchased from Fisher. Silicon wafers were purchased from Silicon Valley Microelectronics. These metallic silicon wafers were degenerately p-doped with boron and coated with a 300 nm thermally-grown silicon dioxide layer. Poly(galvinoxylstyrene) (PGSt) was synthesized according to a previously reported procedure [52]. All materials were used as received.

2.2. OFET fabrication

Silicon wafers were diced into 13.6 mm × 15.6 mm chips. These substrates were cleaned by sonication for 10 min each in acetone, chloroform, and isopropyl alcohol, in a sequential manner, and dried with compressed nitrogen. The substrates were then loaded into a spincoater. Liquid HMDS was added to the substrate and allowed to rest for 30 s. After this time, the sample was spun at 3000 rpm for 30 s, followed by heating on a hot plate at 100 °C for 30 min under ambient conditions. Then, 10 nm of titanium, followed by 80 nm of gold, were thermally evaporated onto the oxide side of the substrates through a shadow mask to form the source and drain contacts. These contacts formed a channel with a width of 10 mm and a length of 0.1 mm. Afterwards, the active layer solution was spun-coat on the substrates at a rate of 1500 rpm for 60 s within an inert atmosphere glovebox. The active layer solutions consisted of P3HT and different open-shell dopants blended to give a total solids concentration of 25 mg mL^{-1} in DCB, and these solutions were stirred overnight at 50 °C prior to being used as active layer coating solutions. The devices did not undergo a thermal annealing procedure as the galvinoxyl radical is unstable at standard annealing temperatures for P3HT thin films (i.e., >100 °C).

After fabrication, the devices were tested using a Lakeshore Cryotronics Model TTPX vacuum probe station for room temperature measurements, and a Lakeshore Cryotronics Model CRX-VF for variable-temperature measurements. Keithley 2400 SourceMeters, controlled using in-house Labview programs, were used to gather the current-voltage response data for room-temperature measurements, and Keithley 2450 SourceMeters were used for variable-temperature measurements. A diamond-tipped scribe pen was used to remove the oxide, revealing the metallic silicon gate that allowed for contact to be made with the back electrode. Output curves were obtained by sweeping the drain-source voltage from +10 V to −100 V in 2.5 V increments while the gate-source voltage was held constant for a given sweep and stepped from +10 V to −100 V in 10 V increments. Transfer curves were obtained by sweeping the gate-source voltage from +10 V to –100 V in 2.5 V increments and holding the drain-source voltage constant at –100 V. Conductivity responses were obtained by disconnecting the gate electrode and sweeping the drain-source voltage from –50 V to +50 V in 0.5 V increments.

3. Results and discussion

P3HT is an oft-used organic semiconductor, and it demonstrates a typical response when incorporated into a field-effect transistor (FET) geometry (Fig. 1a,c). However, upon blending with the galvinoxyl radical, a shift in behavior is seen, where the output characteristics no longer saturate at the measured drain-source voltages (Fig. 1b,d). This also results in the transistor no longer reaching an OFF state. To verify that this is not due solely to the open-shell nature of the compound, two other radical species are blended at a similar molar ratio.

Doping the P3HT OFET with PTIO or TEMPO radicals does not show the same behavior as the galvinoxyl radical (Fig. 2). One potential explanation for this behavior is that the galvinoxyl radical is doping the P3HT polymer through an integer charge-transfer reaction. In other words, an electron is transferred from the highest-occupied molecular orbital (HOMO) of a P3HT segment to the singly-occupied molecular orbital (SOMO) of a galvinoxyl molecule. For the sake of comparison, the TEMPO and PTIO radicals were chosen to select a wide range of preferred redox behaviors. Whereas the galvinoxyl radical is an n-type radical, meaning that it is preferentially-reduced to form a stable anion, the TEMPO radical is p-type, meaning that it is preferentially-oxidized to form a stable cation, and the PTIO radical is ambipolar, meaning that it can undergo both oxidation and reduction reactions in a facile manner (Fig. 3).

The galvinoxyl radical, unlike the TEMPO radical, can be reduced to form a stable anion, and its reduction potential of –4.7 eV relative to vacuum [53], is significantly lower than that of the PTIO radical, with a reduction potential of –4.1 eV [54]. However, the oxidation potential of P3HT is –5.0 eV [19], which is 0.3 eV below the reduction potential of the galvinoxyl radical. This energy difference is significantly greater than the thermal energy available to the system. Furthermore, our previously-reported UV–Vis light absorbance spectra of P3HT-galvinoxyl radical blends indicated no evidence that any free charge carriers or supramolecular complexes, such as charge transfer complexes, were formed [46]. By contrast, charge-transfer dopants such as 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane show a significant change in the absorbance spectrum due to the formation of polarons

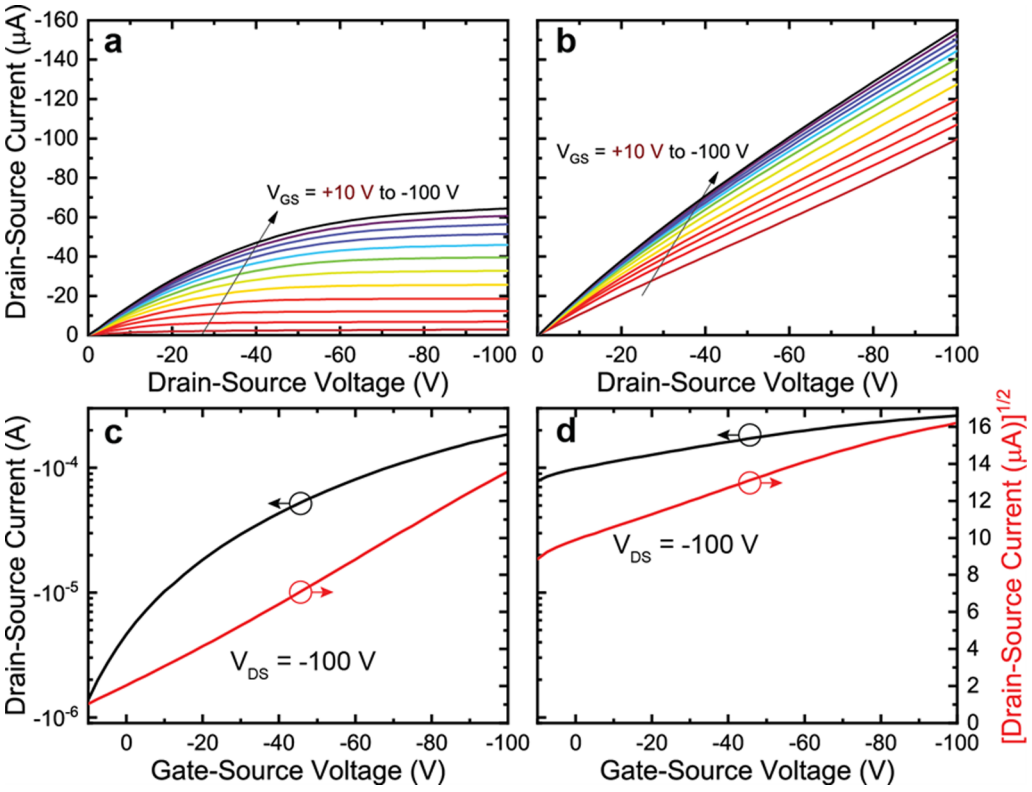


Fig. 1. Output curves for (a) pristine P3HT transistor and (b) a P3HT-Gx blend transistor with a 5% galvinoxyl (by weight) loading. The corresponding transfer curves are shown in (c) and (d). In the pristine film, the current saturates at high voltage, and the saturation point increases with gate voltage. In the doped film, the current is roughly linear with voltage, and the conductivity dependence on gate voltage is reduced. The differing scale between (a) and (b) vs. (c) and (d) is due to hysteresis.

[47,50,55]. Therefore, a charge-transfer interaction is unlikely.

To further establish the nature of the P3HT-galvinoxyl radical interaction, the charge transport properties were investigated at higher loadings of the radical (Fig. 4). While lower loadings can utilize the galvinoxyl radical as a small molecule, higher loadings with a small molecule dopant result in poor film quality. To ensure that the observed behavior at higher loadings was not due to film quality issues, we incorporated the galvinoxyl radical into a macromolecular form. By creating a polymer blend composed of P3HT and the polymer species poly(galvinoxyl styrene) (PGSt), high-quality film formation was observed on a consistent basis. Importantly, the same change in behavior is observed when PGSt is incorporated into the P3HT active layer thin films as was observed with the small molecule galvinoxyl radical; this suggests that the presence of the polymer backbone does not affect the

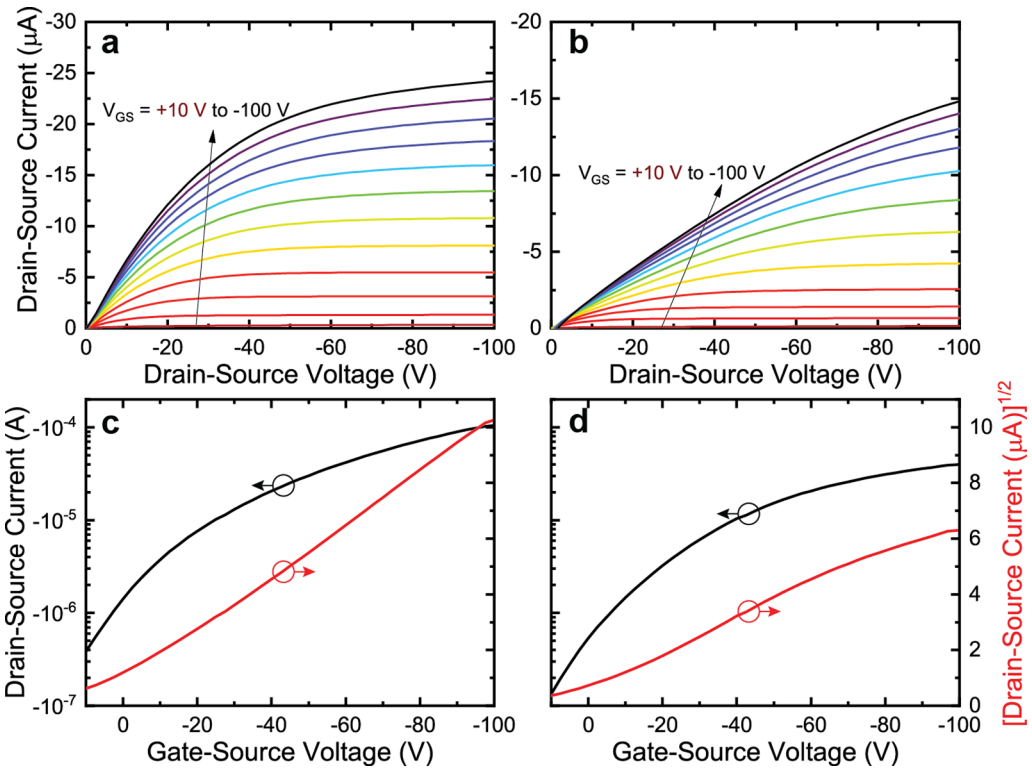


Fig. 2. Output curves for P3HT transistors with loadings of 2.5% (by weight) of the (a) PTIO and (b) TEMPO radicals. The corresponding transfer curves are shown in (c) and (d). These loadings were selected to have approximately the same molar concentration as the galvinoxyl radical-containing device shown in Fig. 1b. The qualitative shift in behavior is not observed for these radicals, which contrasts with what was observed for the galvinoxyl radical.

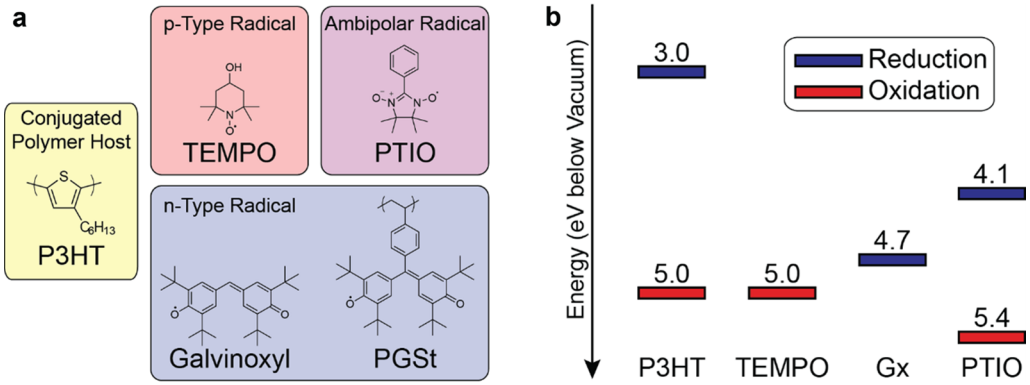


Fig. 3. (a) Chemical structures of the conjugated polymer (P3HT), radical polymer (PGSt), and small molecule open-shell materials implemented in this work. Radicals are classified according to whether they preferentially reduce (n-type), preferentially oxidize (p-type), or are capable of being oxidized or reduced under normal conditions (ambipolar). (b) Oxidation (red) and reduction (blue) potentials of all molecular species implemented in this work. For P3HT these values are identified with the HOMO and lowest-unoccupied molecular orbital (LUMO) energy. For the radical species, these are identified with the SOMO energy. This identification is ambiguous for ambipolar species, such as the PTIO radical; thus, both its oxidation and reduction potentials are shown.

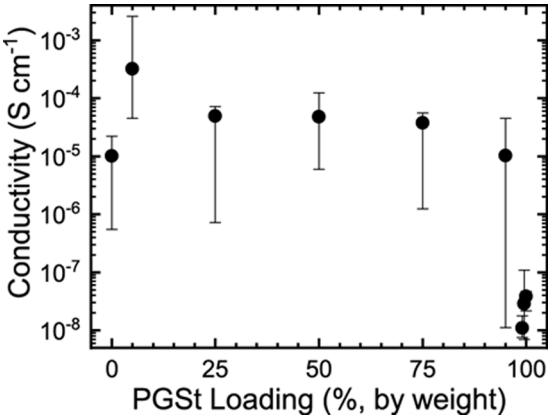


Fig. 4. Electronic conductivity of the P3HT-PGSt blends (i.e. blends of two macromolecular materials including the open-shell species) as a function of the PGSt loading. Though an increase is seen from 0 to 5% PGSt loadings, the conductivity does not change for loadings from 25% to 75%. No conductivity is observed for blends with extremely high PGSt loadings.

observed charge transport behavior. Because the response of the device active layers remained linear, we extracted the electrical conductivity values of the P3HT-PGSt composite films, and we observed a marked increase in conductivity upon radical polymer doping. In fact, a large increase in electrical conductivity is seen going from 0 to 5% PGSt (by weight). The conductivity then decreases upon increasing the loading to 25% PGSt (by weight), and its value levels at even higher loadings. At the highest loadings (i.e., when the active layer film is almost completely composed of PGSt), the conductivity drops dramatically. This is because PGSt is not a good electrical conductor, and these data suggest that a minimum loading of between 1 and 5% P3HT (by weight) is needed for charge transport to occur readily.

Utilizing the FET geometry allows for the contributions of the charge carrier mobility and charge carrier concentration to the conductivity of the material to be decoupled from one another. If the device is far from saturation, then the charge carrier concentration should be modulated linearly with changes in gate voltage, which will allow for the mobility to be extracted, according to the following equation.

$$I_{DS} = \mu_{lin} C_{ox} \frac{W}{L}\left(V_{DS} V_{GS} - \frac{{V_{DS}}^2}{2}\right) \quad (1)$$

Here, μ_{lin} is the linear regime mobility, C_{ox} is the capacitance per unit area of the gate dielectric, W is the channel width, and L is the channel length. For the saturation regime, the formula is expressed by Eq. (2).

$$I_{DS} = \mu_{sat} C_{ox} \frac{W}{L}\left(\frac{{V_{GS}}^2}{2}\right) \quad (2)$$

Here, μ_{sat} is the saturation regime mobility. To extract the mobility from the transfer curves measured at V_{DS} = –100 V, Eq. (1) was used for the doped OFETs (as these devices never saturated), and Eq. (2) was used for the pristine P3HT devices. Representative fits are shown in Fig. 5. At low loadings of the galvinoxyl radical and the open-shell PGSt macromolecule, the mobility increases with greater radical doping (Fig. 6a). However, at loadings beyond ~10%, the mobility decreases (Fig. 6b). This is likely due to an increased fraction of the bulk composite being non-conductive. Decreased crystallinity of the P3HT due to the dopant impurities could also play a role; however, our previous results suggest that the crystalline packing of P3HT is unaffected by the

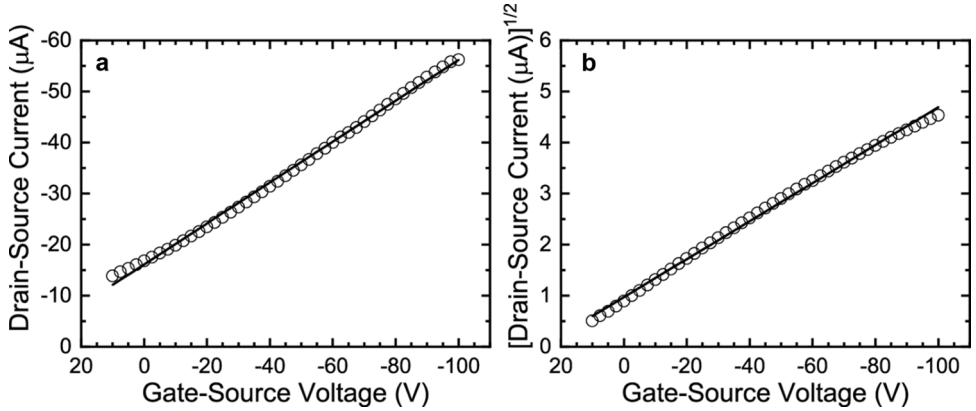


Fig. 5. Representative fits for Eqs. (1) and (2). (a) Transfer curve of a P3HT OFET doped with 5% PGSt (by weight) fit with Eq. (1). (b) Transfer curve of an undoped P3HT OFET fit with Eq. (2).

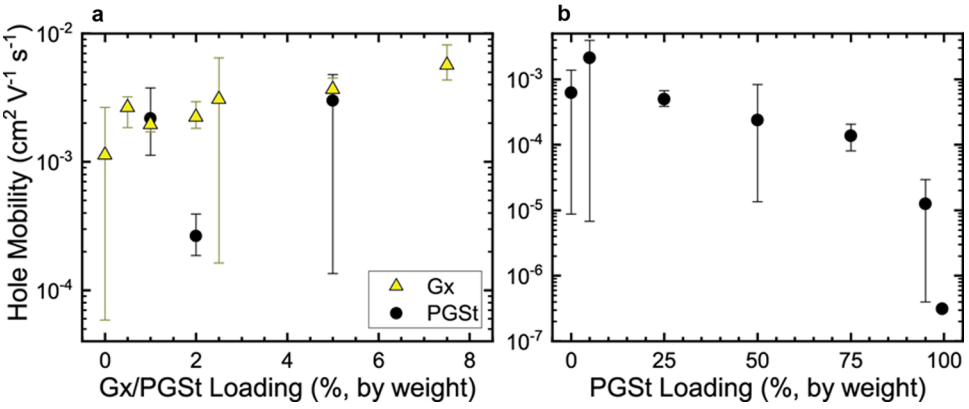


Fig. 6. Mobility as a function of the galvinoxyl moiety loading, ranging from 0 to 100% loading (by weight). (a) Results for low loading where the samples using the small molecule galvinoxyl are shown in yellow, samples using the macromolecular species in black). (b) Results for loadings used in Fig. 4. The mobilities were extracted from the transfer curves assuming saturation for 0% loading and linear regime for higher values. The mobility can be seen to increase slightly at low loadings but decrease at high loadings. At the highest loadings, the mobility decreases dramatically.

galvinoxyl radical at a loading as high as 22% by weight (10% on a molar basis) [46]. Note that a similar trend in both the small molecule and radical polymer cases is had because the interaction is with the radical moiety, and the presence of the backbone does not affect the change in mobility.

The charge carrier concentration can be calculated based on the following equation.

$$\sigma = \mu n_h q \tag{3}$$

Here, σ is the conductivity, μ is the mobility, n_h is the concentration of charge carriers, and q is the absolute value of the electron charge. The greater conductivity at intermediate radical loadings implies that the charge carrier density is enhanced by the presence of the radical species (Fig. 7), despite the fact that a simple charge transfer doping mechanism would be energetically unfavorable.

As integer charge transfer doping, morphology changes, and conduction through the galvinoxyl bulk are unlikely mechanisms, the other possibility is that the galvinoxyl radical is facilitating charge transport within the P3HT domains. Charge transport in conjugated polymers such as P3HT is often described using a thermally-activated charge transport model [56]. Here, charges spend much of their time in shallow trap states, which are those whose energies are within a few k_BT of the transport energy. The slow step in charge transport is therefore the release of charges from those states, with some activation energy related to the distribution of trap energies. Deep trap states (i.e., those whose energy is far greater than k_BT away from the transport level) also affect the charge transport by capturing charge carriers for longer timescales. With this in mind, we speculate that the galvinoxyl radical may be acting to reduce the number of trap sites within the polymer film. Shallow trap sites are thought to affect the mobility, while deep trap sites are thought to affect the carrier concentration [57], and thus, a decrease in the number of traps can potentially explain both trends in the data (Fig. 6 and Fig. 7). A number of mechanisms for trap passivation have been identified in the literature [58], and while our previous results suggest that morphological changes do not occur, exclusion of water [59] and integer charge transfer from the dopant to the trap states are also observed [60,61]. This last one is of interest; while charge transfer from P3HT to the galvinoxyl radical is unfavorable, trap states with energies greater than 0.3 eV would be expected to spontaneously transfer, and some shallow trap states may be close enough for the transfer to occur.

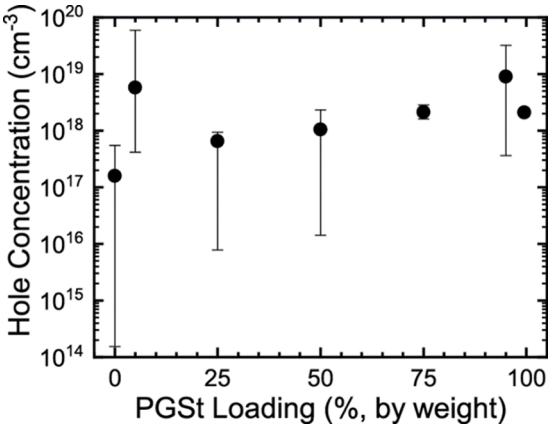


Fig. 7. Charge carrier concentration found by dividing the conductivity by the mobility as a function of the PGSt fraction. A modest increase is seen at higher loadings.

To further examine this point, the temperature dependent behavior of the P3HT-galvinoxyl blends is shown in Fig. 8a. As expected, the conductivity decreases with decreasing temperature. However, the ON−OFF ratio of the doped device stays nearly constant as temperature is lowered (Fig. 8a). If the shift in behavior were due to integer charge transfer doping, lowering the temperature would result in insufficient thermal energy to ionize the conjugated polymer, which would cause the device to behave as an undoped transistor at lower temperatures. As this is not observed, this is further evidence against integer charge transfer doping. The mobilities and ON-currents of the devices are well-described using an Arrhenius law (Fig. 8b, Fig. 8c, and Table 1). A slight increase in the activation energy can be seen comparing the doped to the undoped transistors. As the activation energy is related to the distribution of shallow trap energies[57], this suggests that distribution is unaffected by the presence of the radical. However, if the radical fills all shallow traps equally, or preferentially fills those on the shallower end of the distribution (i.e. those closer to the transport level), then an increase in activation energy would be expected to accompany the increase in mobility. While the exact specifics of which traps are filled is not completely clear, it is still reasonable to conclude that the radical improves charge transport by reducing the number of trap states in the polymer.

4. Conclusions

In summary, the addition of the galvinoxyl radical causes a shift in behavior for P3HT from semiconducting to conducting. This interaction is not observed for two other radical species tested. Previous reports suggest that no supramolecular complex is formed in thin films containing both P3HT and galvinoxyl [46], yet the qualitative shift in transistor behavior is clear evidence that an interaction is occurring. The addition of small amounts of the galvinoxyl radical appear to enhance charge carrier concentration and mobility, though mobility decreases at the highest loadings as the conductive fraction of the blend decreases. Despite the increase in apparent carrier concentration, the measured redox potentials of P3HT and the galvinoxyl radical suggest a simple charge transfer is unfavorable, and measurements at lower temperatures do not lead to a freeze-out of carriers. While the

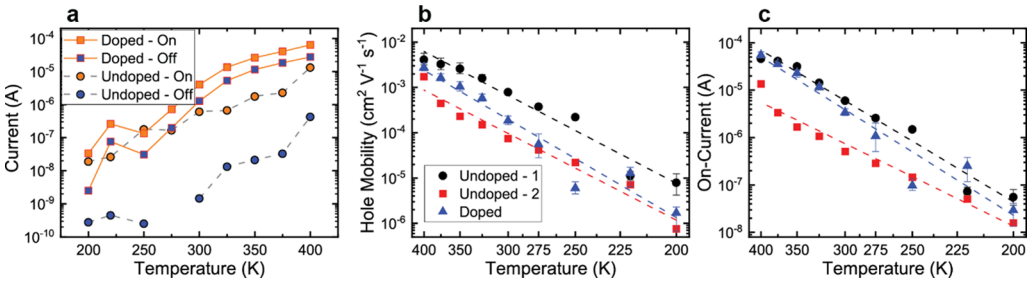


Fig. 8. (a) Plot of on (orange) and off (blue) currents of a pristine P3HT OFET (circles) and a P3HT OFET blended with 5% PGSt by weight (squares). The current decreases with temperature, but the qualitative behavior does not change. Arrhenius plots of (b) mobility and (c) ON current for undoped P3HT OFETs from two separate batches of devices (black circles and red squares) and a P3HT OFET blended with 5% PGSt by weight (blue triangles). A similar slope can be seen for both undoped devices, despite the difference in magnitude, while the doped device shows a slightly greater slope.

Table 1
Arrhenius fitting parameters for undoped P3HT OFETs from two batches of devices and a P3HT OFET doped with 5% PGSt by weight.

Sample	$\mu - E_A$ (meV)	$I_{ON} - E_A$ (meV)
Undoped – 1	230	250
Undoped – 2	230	210
Doped	260	270

galvinoxyl radical does not catalyze the charge transport mechanism, its presence improves the charge carrier mobility, likely by reducing the number of trap sites. As composites of conjugated materials with radicals become more prevalent in the literature, these results underscore the importance of understanding all the interactions that take place between these classes of materials.

CRediT authorship contribution statement

Daniel A. Wilcox: Conceptualization, Investigation, Writing - original draft, Visualization. **Bryan W. Boudouris:** Conceptualization, Writing - original draft, Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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