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High operational and environmental stability of high-mobility conjugated polymer field-effect transistors achieved through the use of molecular additives

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Due to their low-temperature processing properties and inherent mechanical flexibility conjugated polymer field-effect transistors (FETs) are promising candidates for enabling flexible electronic circuits and displays. Much progress has been made in recent years on materials performance; in several donor-acceptor copolymer systems field-effect mobilities above 1 cm²/Vs have been demonstrated. However, there remain significant concerns about operational

and environmental stability, particularly in the context of applications that require a very high level of threshold voltage stability, such as active-matrix addressing of organic light-emitting diode (OLED) displays. Here, we report a detailed study of the physical mechanisms behind operational and environmental degradation of high mobility, p-type polymer FETs and demonstrate an effective, novel route to dramatically improve device stability. We show that water incorporated in nanometer sized voids within the polymer microstructure is the key factor in charge trapping and device degradation. By inserting molecular additives into these voids that displace water it is possible to increase the stability as well as uniformity to a high level sufficient for demanding industrial applications.

The longstanding materials research efforts to discover high-mobility organic semiconductors have resulted in several families of materials that exceed the mobility performance of common thin-film inorganic semiconductors, such as amorphous silicon.^{1,2,3} With polycrystalline molecular semiconductors the key challenge is now to achieve the required device uniformity for large-area applications, such as displays. With conjugated polymers that show high field-effect mobilities $> 1\text{cm}^2/\text{Vs}$ in nearly amorphous microstructures^{4,2,5}, device uniformity over large-areas can be excellent but the reduced crystallinity and the associated faster diffusion of extrinsic species such as oxygen or water makes these materials prone to environmental and operational degradation⁶. The presence of water has been shown to cause strong electron trapping in n-type organic FETs⁷ and diodes⁸. Water at the interface has also been identified as a cause of threshold voltage shifts in p-type organic FETs upon application of a long-term bias stress⁹; however a full analysis of how the presence of water affects the performance and environmental and operational stability of high-mobility polymer FETs has not been reported yet.

The use of small, molecular additives mixed into conjugated polymer films has been explored in several previous studies. Molecular additives have been used to generally improve the microstructural order of the polymer films during solution processing^{10,11} or more specifically as nucleation agents¹² to accelerate the polymer crystallization kinetics. Some groups have investigated p-type or n-type electrical

doping of conjugated polymers through the addition of charge-transfer dopant molecules. For p-type doping a molecule is required with a lowest unoccupied molecular orbital (LUMO) level deeper than the highest occupied molecular orbital (HOMO) level of the host conjugated polymer¹³. Such charge transfer doping leads to better contact injection and may even improve device stability by pre-emptying electrons from filled trap states in the tail of the density of states of the highest occupied molecular orbitals (HOMO)¹⁴. However, it also leads to an inevitable, undesirable increase of the FET OFF current. Here we investigate the influence of molecular additives on the environmental and operational stability as well as uniformity of polymer FETs based on high-mobility donor-acceptor polymers. Surprisingly, we have found that a wide range of molecular additives that do not act as charge transfer dopants for the polymer can dramatically improve the device stability, contact resistance and device uniformity without leading to undesirable increase in OFF current. We present a detailed study of the mechanism by which this stability improvement occurs.

We fabricated polymer FETs in standard bottom-contact, top-gate configuration with a wide range of high-mobility conjugated donor-acceptor co-polymers and exposed them to various environments. One of the systems we studied in depth is an indacenodithiophene-co-benzothiadiazole copolymer (IDTBT), a near amorphous polymer with a low degree of energetic disorder^{4,15} (Supplementary Section 1). Neat IDTBT FETs without additive exhibit significant environmental instabilities and the device characteristics depend strongly on the atmosphere in which the device is operated. The as-prepared devices fabricated in a N₂ glove box had poor performance exhibiting a shallow rise of the current with increasing gate voltage and an overall low ON current (black curve in Fig. 1(a), left panel). When operating the devices after 24-h storage in air (blue curve), we observed much better performance with lower threshold voltage, steeper rise of the current with increasing gate voltage, and higher ON current. However, when the devices were returned to a N₂ atmosphere, performance started to degrade again (red curve); this degradation was found to accelerate by annealing the device in N₂ at a low temperature of 70°C (green curve). Such dependence of characteristics on the operating atmosphere

constitutes a fundamental limitation for the applicability of these polymers. For example, in an OLED display package, the transistor backplane needs to operate reliably in a strictly inert, oxygen-free atmosphere to avoid OLED degradation. Surprisingly, we found that the addition of 2 wt.% of the small molecule tetracyanoquinodimethane (TCNQ) to the polymer solution results in near perfect environmental stability (Fig. 1(a), right panel). Even after annealing at 70°C for 12 hours in N₂, the characteristics retain their ideal behavior, indistinguishable from the characteristics measured after fabrication or those measured in air. This invariance to environments can also be seen in the output characteristics, which are textbook-like and show no evidence for contact resistance (Fig. 1(b)); on the other hand, the output characteristics of devices without TCNQ additive depend strongly on operating environment and exhibit contact resistance limitations in the linear regime, particularly for devices operated in N₂ (Supplementary Fig. S1). We observed similar improvements for other additives, such as tetrafluoro-tetracyanoquinodimethane (F4TCNQ) and 4-aminobenzonitrile (ABN, Supplementary Fig. S2, S3). In the case of F4TCNQ the electron affinity of the additive is large enough to induce some ground-state electron transfer leading to charge transfer doping, this manifests itself as an increase of the FET OFF current. However, for TCNQ and ABN, which have too low an electron affinity to dope IDTBT with an ionization potential of 5.3 eV (Fig. 1(c)), no increase in OFF current is observed compared to neat films.

A further benefit of additive incorporation is a significant reduction in contact resistance. We extract the contact resistance from Transmission Line Method (TLM) measurements as a function of channel length. The contact resistance of a neat IDTBT transistor is high (27.1 kΩcm) when measured in N₂ after fabrication and is reduced to 7.1 kΩcm upon prolonged exposure to an ambient air environment (blue to black in Fig. 1(d)). With all the molecular additives the contact resistance is below 5 kΩcm independent of environment. With TCNQ or ABN we do not see any evidence for an increased bulk conductivity or OFF current suggesting that the improved contact resistance may reflect a reduction in the trap density in the bulk of the polymer film. The TLM measurements also reveal that devices with the same

channel length exhibit a significantly smaller spread in resistance for films with additives than those without. Most notably, the spread in resistance values measured by the standard deviation (n=11 FETs on 3 different substrates) is reduced by a factor of 20-30 upon incorporating 2 wt.% of F4TCNQ, TCNQ or ABN into the polymer film.

Of most critical importance for OFET applications is the operational stability over prolonged periods of time. This was tested using constant-current stress measurements, that mimic the mode of operation in an active matrix addressed OLED display (see supplementary information section 1 for details of stress procedure)¹⁶. Here we focus on stress measurements performed under N₂ that represent most directly the stress conditions that would be present, for example, in an OLED package (stress measurements in air were also performed and are shown in supplementary section 1). We observed a pronounced improvement in the threshold voltage shift (ΔV_T) stability through incorporating the molecular additive into the semiconducting film at a concentration of 2 wt.% (Fig. 1(e)), by up to a factor 12 in the case of F4TCNQ and ABN compared to that observed in neat IDTBT devices. The threshold voltage shift was reduced to less than 1V after a day of constant current stress under conditions that are representative for OLED applications. The subsequent recovery period furthermore shows that an IDTBT transistor with additive recovers almost completely, with almost half of the threshold voltage recovery happening within the first hour. This is better than the threshold voltage stability of amorphous silicon transistors¹⁷, comparable to that of amorphous oxide TFTs¹⁸, and meets the requirements for OLED applications.

In the following we investigate the physical mechanism for this surprising, additive-induced improvement in device performance and stability. First, we establish that molecular charge transfer doping is not responsible for the performance improvement. This distinguishes our work from previous studies that reported doping to improve stability at the expense of an undesirable increase in OFF current¹⁴. Using ultraviolet photoelectron spectroscopy (UPS), we confirm that IDTBT and TCNQ undergo no charge transfer (Fig. 2(a)), as indeed expected from the

energy level diagram. Both the onset of secondary electron emission and the edge of the HOMO band are not changing with increasing concentration of TCNQ from 0 to 20 wt.%. Hence, the position of the Fermi energy remains unchanged upon addition of TCNQ (Fig. 2(b)). This finding is in line with the FET data presented in Fig. 1, where addition of TCNQ does not lead to an elevation of the OFF-current that would be expected if charge transfer (i.e. doping) was taking place. In contrast, for the F4TCNQ additive, a small level of charge transfer does take place (Supplementary Fig. S7). This results in a small shift of the Fermi-level, which is consistent with the observed increase in OFF current. This is in line with the fact that, in contrast to TCNQ, the lowest unoccupied molecular orbital (LUMO) of F4TCNQ is slightly larger than the ionization potential of IDTBT. However, since similar enhancements in stability are observed for ABN, TCNQ, and F4TCNQ, which have a large range of electron affinities (Fig. 1(c)), this suggests that even in the case of F4TCNQ the additive-induced stability improvement is not in fact a consequence of shallow doping as suggested by Kahn et al.¹⁹ The UPS results are confirmed by sub-bandgap absorption measurements using photothermal deflection spectroscopy (PDS), a high-resolution absorption spectroscopy technique to detect sub-band gap states in organic molecules²⁰. Here, we find that the weak charge transfer seen in IDTBT films with 5 wt.% of F4TCNQ leads to a clear signature of an F4TCNQ anion at 1.1 eV²¹ and an associated IDTBT polaron-induced absorption band between 1.2-1.6eV⁴. However, for pure IDTBT films, air exposed IDTBT films and, in particular, IDTBT films with 5 wt.% of TCNQ added, additive-induced absorption features lack entirely (Fig. 2(c)). This is further evidence that charge transfer between the additive and the polymer cannot be responsible for the observed improvements in FET stability and performance.

Alternatively, one could hypothesize that the additive may improve stability by undergoing charge transfer with some environmental species that would otherwise cause traps in the film. To investigate the interaction between the additive and the environment, we measured infrared (IR) absorption in the C-N stretching region of TCNQ where peaks at 2227 and 2215 cm⁻¹ correspond to neutral TCNQ and those at 2213 cm⁻¹ and 2193 cm⁻¹ correspond to TCNQ anions²². Initially we could not detect

any TCNQ anions for an IDTBT film with 5 wt.% of TCNQ measured in air; only after 7 days of air exposure do we see traces of TCNQ anions which, however, come from less than <1 % of all TCNQ molecules (Fig. 2(d)). For F4TCNQ, on the other hand, a clear formation of anions is observed after air exposure (Supplementary Fig. S10). We emphasize that the fact that such interaction is not observed for TCNQ suggests that charge transfer to an environmental species is unlikely to be the reason for the observed stability enhancement.

Inspired by these results, we then investigated a wider range of molecular additives. In fact, the simplest method to incorporate a molecular additive is to leave residual solvent in the polymer film. Residual solvents are even less likely to electronically interact with the polymer. Whilst in all previous preparations the films were annealed at 100°C for 1 hour after fabrication to remove residual solvent, for these experiments neat IDTBT films were intentionally annealed for less than 2 minutes at 100°C to leave some residual solvent that can act as a molecular additive in the films (central panel of Fig. 3(a)). Surprisingly, a similar improvement in performance and stability was observed. For IDTBT films with residual dichlorobenzene (DCB) solvent, the transfer characteristics are significantly steeper and reach higher ON-current (Fig. 3(a)) and the threshold voltage stability is significantly better than for films in which the residual solvent has been removed by annealing for 1 h. Also the current-stress induced threshold voltage shift is significantly lower than in films without residual solvent (Fig. 3(b)). To confirm that this effect is not related to the lower voltages that need to be applied to the device with residual solvent to maintain a constant current of 2.5 μA , we also stressed the device at a much higher current (100 μA), and even under these aggressive conditions the threshold voltage shift is smaller than that of a device without residual solvent stressed at 2.5 μA . Solvent additives improve performance and stability in similar way as solid additives; however, in contrast to TCNQ or F4-TCNQ they do not impart long-term stability as they evaporate from the films on the timescale of a month (see Figure S13/S14).

We have observed the beneficial effect of residual solvents not only in IDTBT, but also for a wide range of high-mobility polymers. For instance, in diketopyrrolo-

pyrrole (DPP) polymers, such as diketopyrrolo-pyrrole-dithienylthieno[3,2-b]thiophene (DPP-DTT)^{23,24} or in polyfluorene polymers, such as poly(9,9-dioctylfluorene-alt-benzothiadiazole) (F8BT), we have observed similar improvements in performance (Fig. 3(a)) and stability (Fig. 3(b)) upon leaving residual solvents as additives in the film. In fact, with our novel preparation method, we were able to extract a gate voltage independent hole mobility of $1 \times 10^{-2} \text{ cm}^2/\text{Vs}$ for F8BT which to the best of our knowledge is among the highest hole mobility reported for this widely investigated material.

To better understand the molecular requirements for an additive to provide this beneficial effect on stability, we investigated different solvent molecules. This is possible because IDTBT, in particular, is highly soluble in a wide range of solvents. We find that many chlorinated and non-chlorinated aromatic solvents, but also non-aromatic solvents, such as chlorocyclohexane, are capable of providing this effect (Supplementary Fig. 11); a summary list is provided in Fig. 3(c). However, interestingly, some solvents, such as tetralin and 2-methylnaphthalene, only produce a limited effect or no improvement. We attribute this lack of effect to either the larger size of these molecules and/or a less favorable interaction of these solvents with the polymer, which manifests itself as an observed lower solubility of the polymer in these two solvents (Supplementary Section 5).

We have attempted to quantify the amount of residual solvent that remains in the film using two independent techniques, variable angle spectroscopic ellipsometry (VASE) and quartz crystal microbalance measurements. VASE measurements were performed on IDTBT films with the DCB solvent deliberately left in the film and after annealing the same films at 100°C for an additional hour (Supplementary Section 6). By fitting the data with an effective medium approximation (EMA) model that assumes a certain fraction of voids in the polymer network that are filled with a medium of refractive index n , we could significantly optimize the fits to the experimental data (Supplementary Tab. S4, Fig. S17). Optimized fits for a range of values for n , resulted in void fractions of around 1 %. Interestingly, QCM measurements on identical IDTBT films also gave a consistent value of 0.9% for the

amount of residual solvent left in the film (Supplementary section 7). Assuming a void fraction of 1%, we therefore fitted the refractive index n of the void before and after driving the residual solvent out of the film. Here, films with residual solvent could be fitted best with the void's refractive index of $n=1.55$ (Fig. 4(a), middle panel). This is consistent with the voids being filled by DCB which has a refractive index of 1.55. In contrast, after annealing the same film at 100°C for an additional hour, the fitting of the experimental data resulted in a lower refractive index of $n=1.2$ for the voids (Fig. 4(a), bottom panel). The VASE and QCM results therefore suggest that there is a void fraction on the order of 1% in the polymer films that is largely filled with solvent after film deposition. After prolonged annealing the solvent molecules are removed from the voids which then become filled with a medium of lower refractive index, possibly a mixture of air/ N_2 and water. Interestingly, the minimum concentration of TCNQ, F4TCNQ and ABN that needs to be added to the films to observe a significant improvement in performance was also on the order of 1-2 wt.%; for lower concentrations, the observed improvement in performance dropped off rapidly. We were also able to correlate the void fraction to the degree of device instability when comparing the device performance of IDTBT polymers with different side chains that exhibit different void fractions (Supplementary Fig. S19). This suggests a direct correlation between the filling of voids and device stability: As long as the voids are filled with a small molecular additive, FET performance and stability are high.

The question then arises as to the nature of the species and the physical mechanism that causes the device degradation, when the voids are not filled by a molecular additive. Under such conditions significant hole trapping clearly occurs in the device: Both shallow hole traps that manifest themselves in reducing the sub-threshold slope and steepness of the transfer characteristics as well as deep traps that cause the current-stress induced threshold voltage shift, somehow become active when the voids are not filled by a molecular additive. To understand the mechanism by which this occurs, we investigated the role of water in the films⁹. Water is omnipresent in organic semiconductor films, even when device fabrication is performed under inert atmosphere conditions. By exposing an IDTBT FET to humid

nitrogen and dry air in an isolated cryostat, we confirmed that intentional water exposure can indeed cause similarly poor device characteristics as observed in neat IDTBT films without additive under conditions where no oxygen is present (Supplementary Fig. S20). Exposure to O₂ is able to alleviate the adverse effect of water. To study the performance of neat IDTBT films without additive in strict absence of water, we stored the devices in an inert glovebox atmosphere with only ppm levels of H₂O, but placed the device near a powder of cobalt(II) chloride, which acts as a strong desiccant (Fig. 4(b) and Supplementary section S8). Importantly, FETs exposed to CoCl₂ performed significantly better than reference FETs prepared in identical conditions but kept in the same glovebox away from CoCl₂ (Fig. 4(c)). The performance of the CoCl₂ exposed devices is as good as that of devices comprising an additive such as F4TCNQ, TCNQ, ABN, or a residual solvent; also their stress stability is much better than that of devices that were not exposed to CoCl₂ (Supplementary Figs. S21, S22). These experiments show that even in the absence of additives, good device performance can be obtained if very careful precautions are taken to remove water from the films. Under normal processing conditions, however, even if all device processing steps are carefully performed in an inert atmosphere glovebox, trace amounts of water become incorporated during film and device processing into the small, nanometer-sized voids within the film, when these are not filled with an additive. These water molecules are nearly impossible to remove completely by low-temperature annealing and are responsible for the poor device performance and stability of devices without molecular additive.

The formation of water-induced deep traps involved in long-term operational stress and threshold voltage shifts has been investigated previously⁹; the formation of shallow traps has mainly been studied for small molecule systems^{25,26}, but not yet for high mobility polymer systems. In order to gain an understanding of the molecular mechanism by which water may create shallow hole traps in the polymers, we performed electronic-structure calculations (at the optimally tuned ωB97X-D/6-31G(d,p) level of theory^{27,28}) of the interactions between water molecules and the polymer backbone (for further computational details, see Supplementary Section 9). We present here results on IDTBT since it is the polymer

most extensively studied in our experimental work (results on DPPDTT and F8BT are shown in supplementary section 9). The calculations involve an oligomer containing two donor-acceptor polymer repeat units; we consider its interaction with a single water molecule in two hydrogen-bonding configurations (see Fig. 5(a)), one in which the water molecule acts as an electron acceptor / H-donor (Fig. 5(a) top panel) and the other as electron donor / H-acceptor (Fig. 5(a) bottom panel). The results show that the presence of water has a strong effect on the potential energy profile for the torsion of the bond connecting the IDT and BT subunits. In the absence of water (black curve in Fig. 5(b)), the torsion potential is steeper than in the presence of the water molecule, particularly for the case of water acting as H-donor (red curve). The decreased potential energy barrier induced by water causes a marked decrease in the system order. In the presence of water, there occur a much wider distribution of torsion angles and a broader distribution of HOMO energies over *ca.* 200 meV (Supplementary Information Table S6). As a result, shallow trap states appear for the positively charged hole carriers. This is consistent with our previously reported finding that in poorly crystalline but high-mobility polymer systems the low degree of energetic disorder that is responsible for the high carrier mobilities reflects a narrow, well-defined distribution of torsion angles.⁴ We expect the electrical performance of this type of polymers to be highly sensitive to any mechanism that widens the distribution of torsion angles and thus creates a distribution of shallow trap states, which is in line with the poor performance of devices without additive.

There are other potential mechanisms by which water molecules can cause charge trapping: We have considered the solvation of a positive polaron by the polar water molecules (Fig. 5(c)) and have found that the polarization interaction energy of the polaron per water molecule is comparable, though of slightly smaller magnitude, than the interaction energy between the neutral chain and a water molecule that we discussed in the previous paragraph (supplementary section 9). Therefore, solvation effects are not likely to be a dominant, but could be a contributing factor to shallow trap formation. In terms of deep trap formation the production of protons H⁺ by the electrochemical reaction of holes (h⁺) on the polymer with water molecules $2\text{H}_2\text{O} + 4\text{h}^+ \rightarrow 4\text{H}^+ + \text{O}_2$ has been suggested as the main mechanism for bias-stress induced

threshold voltage shift in organic FETs⁹. In our calculation there is no indication that water (or an H₂O-O₂ complex) can transfer an electron to a hole (positive polaron) on the polymer chains (the ionization potential of water or water-O₂ being much larger than the electron affinity of a positive polaron on the backbone). However, the situation becomes different in the case of formation of a hydroxyl anion (leaving behind a proton or hydronium cation). The calculations show that a hydroxyl anion has an ionization potential that is sufficiently low that it can readily transfer an electron to a positive polaron, as illustrated in Fig. 5(d), which leads to the loss of the polaron. The resulting OH radical can be expected to be amenable to further reactions to eventually generate oxygen and additional protons. Thus, this electrochemical mechanism is likely to play a role as well provided that some hydroxyl anions from the water dissociation reaction are present within the voids of the polymer. Though our calculations do not allow us to identify a single dominant mechanism they make it very clear that there are several potential mechanisms by which water can be expected to degrade device performance and stability.

In terms of the mechanism for the additive-induced improvements in stability we propose two hypotheses: (i) the additives interact with the polymer in such a way that they restore the steepness of the torsion potential; and/or (ii) they simply displace water molecules from being in direct contact with the polymer and in this way prevent any of the trap formation pathways discussed above or render them less effective. To investigate these mechanisms we also performed electronic-structure calculations in which both a water molecule and an additive molecule interact with the polymer; however the conformational space that needs to be considered at the electronic-structure level becomes so vast that it would be difficult to identify with certainty the relevant, low-energy configurations (Supplementary Information Section 9). The fact that oxygen appears as well to have a beneficial, “water-passivating” effect, can be related to the formation of hydrogen-bonded water-oxygen complexes (such as (H₂O-O₂) or ([H₂O]₂-O₂))⁸ that could similarly prevent water from interacting directly with the polymer chains.

Experimentally, the molecular configurations within the small voids are very difficult to probe, as the relevant concentrations of water involved are low while at the same time water is an omnipresent species in most experiments. In any case, our work has clearly demonstrated the significant benefit that molecular additives exert on the performance and stability of state-of-the-art polymer FETs. It provides a practical and manufacturable technique to resolve a long-standing challenge in the field of polymer electronics; the operational and environmental stability that we have achieved through the addition of molecular additives will enable a wider range of applications for polymer electronics, including advanced OLED and liquid crystal displays, as well as FET sensors that should be sensitive only to the analyte to be detected but not to changes in the atmosphere and conditions in which they are operated. Our simple additive-induced trap removal technique is also likely to benefit other applications of organic semiconductors such as charge transport in light-emitting diodes or solar cells.

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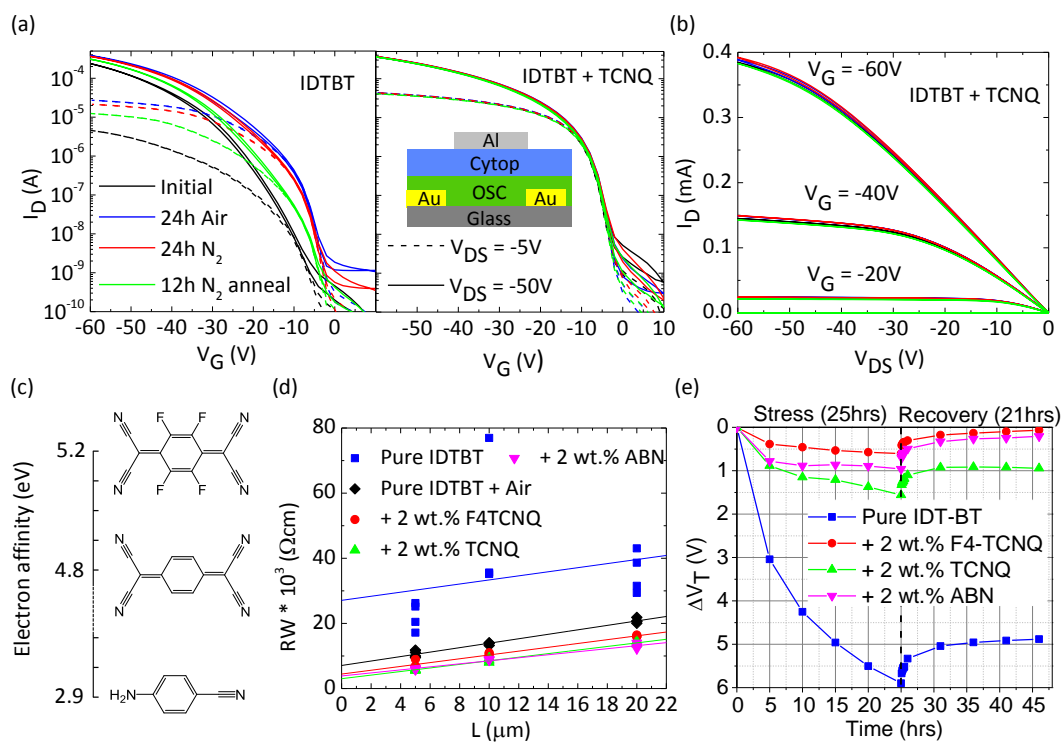


Figure 1 Improving polymer FET performance and the environmental and operational stability through the use of molecular additives (a) Linear (dashed lines) and saturation (solid lines) transfer characteristics of IDTBT OFETs with (right panel) and without (left panel) 2 wt.% of TCNQ additive. Measurements were taken successively for the as-prepared device, after 24 hours exposure to first air and then nitrogen environments and after a 12 h anneal in nitrogen. The device structure is shown as an inset (channel length $L = 20 \mu\text{m}$, channel width $W = 1 \text{mm}$); (b) Output characteristics of an OFET with 2 wt.% of TCNQ additive; (c) Electron affinity of the F4TCNQ, TCNQ and ABN additives used; (d) Transmission line measurements of the normalized channel resistance as a function of channel length for FETs comprising IDTBT, IDTBT after air exposure and IDTBT with 2 wt.% of TCNQ or F4TCNQ. The contact resistance can be extracted from an extrapolation to zero channel length; (e) Constant current-stress measurements at $2.5 \mu\text{A}$ and room temperature comparing the threshold voltage shift of neat IDTBT OFETs with and without additives, in nitrogen. The recovery kinetics after removing the current stress are also shown.

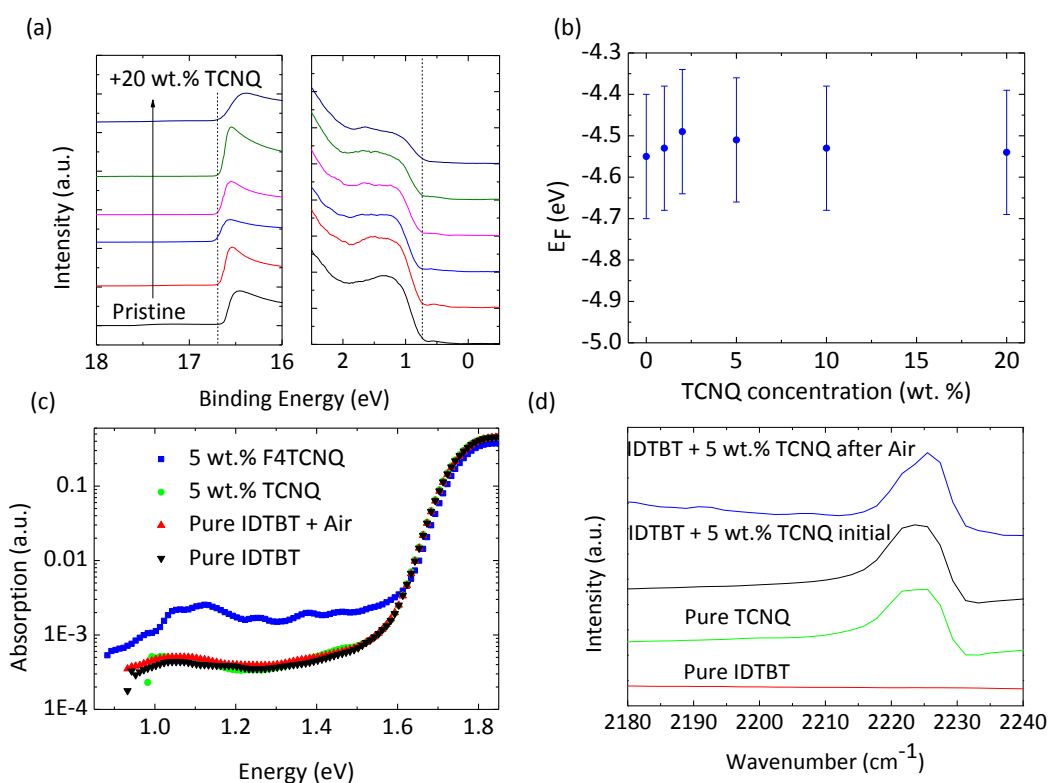


Figure 2 Investigation of potential electronic interactions between additives, the polymer and the environment (a) UPS measurements near the cut-off for secondary electron emission (left) and near the HOMO edge (right) for IDTBT films with 0,1,2,5,10,20 wt.% of TCNQ; (b) Extracted Fermi-level position from the secondary electron cut-off; (c) PDS spectra of IDTBT with and without 5 wt.% of F4TCNQ and TCNQ. The spectrum of a neat IDTBT film after exposure to air is also shown; (d) Fourier transform infrared (FTIR) absorption spectra in the C – N stretching region for neat IDTBT and neat TCNQ as well as IDTBT with 5 wt.% of TCNQ before and after exposure to air for 72h.

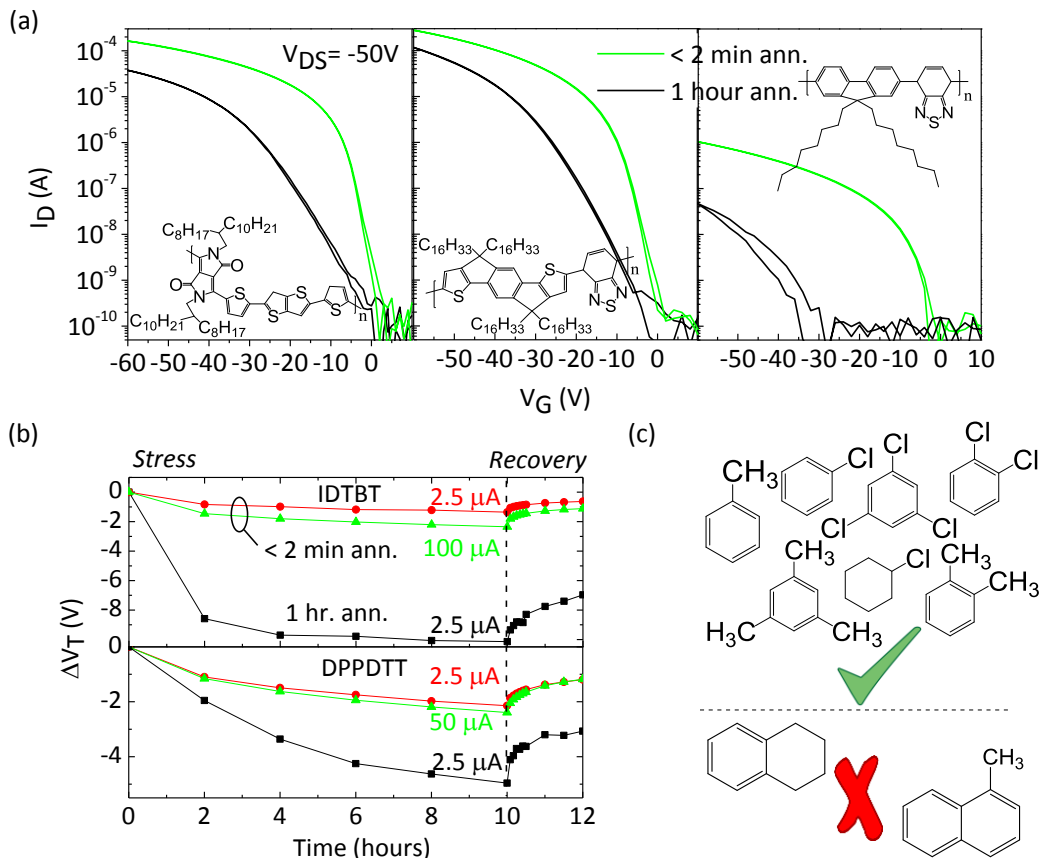


Figure 3 Effect of residual solvents on polymer FET performance and stability (a) Improvement of the transfer characteristics for DPP-D-TT (left), IDTBT (centre) and F8BT (right) FETs by leaving residual solvent (DCB) in the polymer film as an additive. Films were annealed for < 2 min at 100°C leaving residual solvent in the film or for 1 hour to remove residual solvent; (b) Comparison of current-stress stability of IDTBT (top) and DPPDTT FETs with and without residual solvent in the polymer films; (c) List of solvents that lead to performance and stability improvement if left in films of IDTBT (top) as well as solvents that do not show a beneficial effect on device stability and performance (bottom).

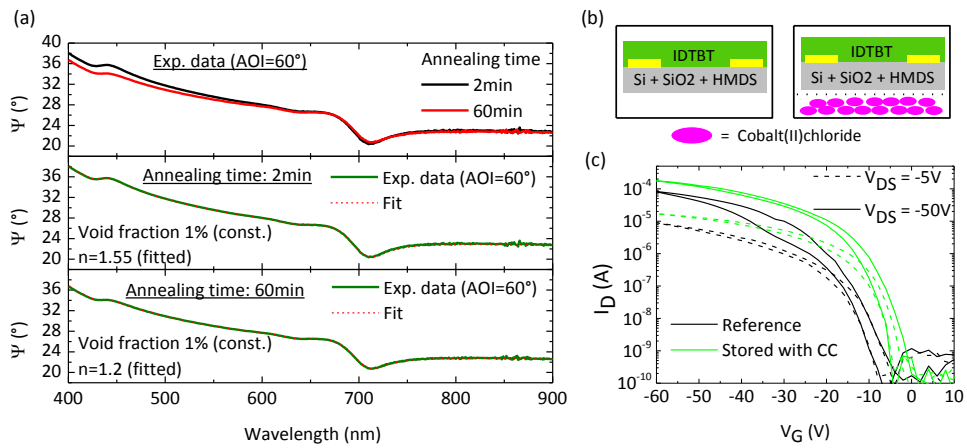


Figure 4 Interaction of water with polymer semiconductors (a) Experimental VASE data for an IDTBT film after 2 and 60 minutes of annealing (top). Experimental data after 2min (middle) and 60min (bottom) of annealing fitted with an effective medium approximation (EMA) model fitting the refractive index of voids in the polymer assuming a void fraction of 1% consistent with QCM measurements. (b) Schematic diagram of the experiment used for strictly removing water from an IDTBT transistor with cobalt(II) chloride powder (c) IDTBT bottom-gate OFET treated with Cobalt(II) Chloride powder as compared to a reference device.

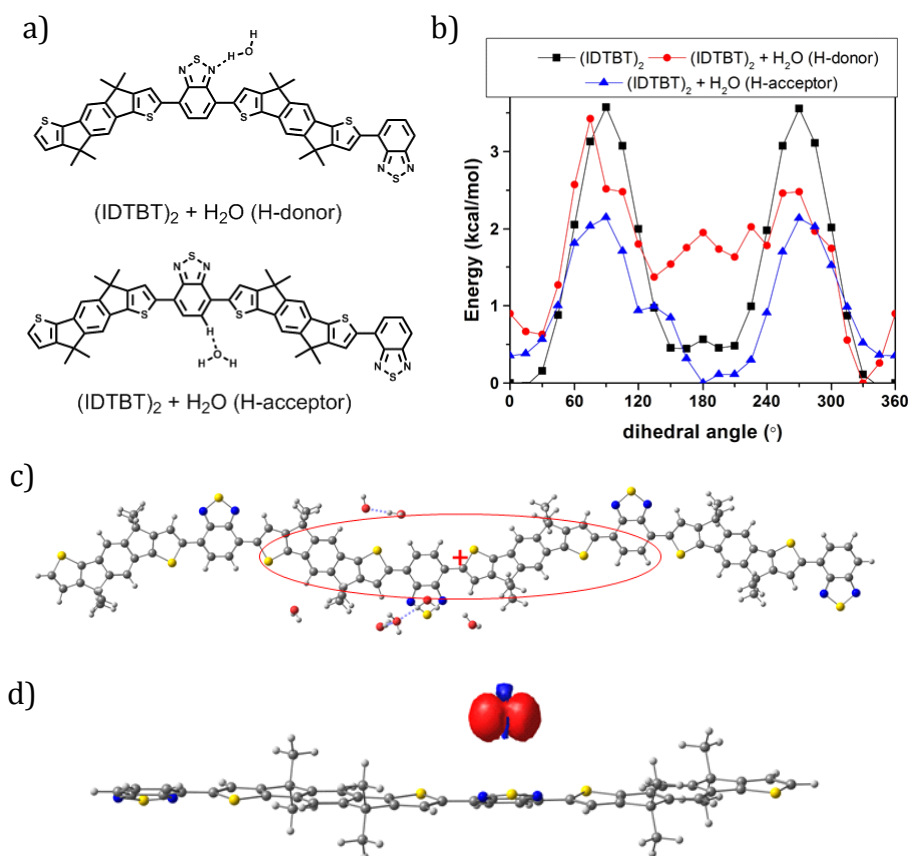


Figure 5 Computational evaluation of the interaction between a water molecule and the polymer backbone (a) Chemical structures of $(\text{IDTBT})_2\text{-H}_2\text{O}$ complexes with water acting as H-donor or H-acceptor; (b) torsional potential of the bond bridging the central IDT and BT units in the absence and presence of water; (c) illustration of the interaction between a positive polaron and water molecules (the calculated average interaction energy per water molecule is given in the SI); (d) illustration of the electron transfer between an hydroxyl anion and a positive polaron, which leads to an hydroxyl radical (whose spin density is represented) and the loss of the polaron (see SI for full details). All calculations incorporate the effect of the surrounding medium (IEF-PCM model with $\epsilon=3.5$) and were performed at the tuned $\omega\text{B97X-D}$ level of theory.