Performance Improvements in Conjugated Polymer Devices by Removal of Water Induced Traps

Mark Nikolka[*]*, Guillaume Schweicher, John Armitage, Cameron Jellett, Zhijie Guo, Michael Hurhangee, Aditya Sadhanala, Iain McCulloch, Christian B. Nielsen and Henning Sirringhaus*[*]

Dr. M. Nikolka, Dr Guillaume Schweicher, John Armitage, Dr. A. Sadhanala, Prof. H. Sirringhaus
Optoelectronics Group, Cavendish Laboratory, JJ Thomson Avenue, Cambridge CB3 0HE, United Kingdom.
E-mail: mn390@cam.ac.uk, hs220@cam.ac.uk
Dr. M Hurhangee, Cameron Jellett
Department of Chemistry and Centre for Plastic Electronics Imperial College London, Exhibition Road, SW7 2AZ, United Kingdom
Prof. I. McCulloch
King Abdullah University of Science and Technology (KAUST), Kaust Solar Center (KSC), Thuwal 23955-6900, Saudi Arabia and Department of Chemistry and Centre for Plastic Electronics Imperial College London, Exhibition Road, SW7 2AZ, United Kingdom
Dr. Christian B. Nielsen, Zhijie Guo
Materials Research Institute and School of Biological and Chemical Sciences, Queen Mary University of London, Mile End Road, London E1 4NS, UK

The exploration of a wide range of molecular structures has led to the development of high-performance conjugated polymer semiconductors for flexible electronic applications including displays, sensor and logic circuits. Nevertheless, many conjugated polymer field-effect transistors (OFETs) exhibit non-ideal device characteristics and device instabilities rendering them unfit for industrial applications. These often do not originate in the material's intrinsic molecular structure, but rather in external trap states caused by chemical impurities or environmental species such as water. Here we demonstrate a highly efficient mechanism for the removal of water induced traps that are omnipresent in conjugated polymer devices even when processed in inert environments; we show the underlying mechanism by which small molecular

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additives with water binding nitrile groups or alternatively water-solvent azeotropes are capable of removing water-induced traps leading to a significant improvement in OFETs performance. We also show how certain polymer structures containing strong hydrogen accepting groups will suffer from poor performances due to their high susceptibility to interact with water molecules; this allows us to set forth design guidelines for a next generation of stable, high performing conjugated polymers.

Recently, donor-acceptor co-polymers with high field-effect mobilities > $1 cm^2/Vs$ have been reported with some materials showing exceptionally low disorder and performances exceeding that of amorphous silicon[1],[2],[3]. Due to their low cost and easy processing, these materials are promising candidates for applications in flexible displays or low-demanding organic electronic circuitry. As a result a lot of research effort has been put into further improving the performance of conjugated polymers by understanding their detailed structure-property relations[4],[5]. Often however, seemingly rational and carefully argued molecular design guidelines, such as the use of fluorine substitution and hydrogen-bonding interactions to improve the planarity of the backbone, fail to result in the desired performance improvements[6],[7]. Even carefully designed and synthesized polymers deployed in optimized device structures frequently exhibit significant non-idealities in their characteristics, such as high turn-on and threshold voltages, strongly gate voltage dependent charge carrier mobilities or environmental degradation. Often such disappointing performance of new materials is attributed to factors such as kinks along the polymer backbone[8], the purity of the synthesis, remnant impurities acting as trap sites[9], or low molecular weight[10]. What is often overlooked or understated is however, the role that environmental species may play in influencing the performance of organic electronic devices and how effects due to extrinsic environmental species can mask more intrinsic molecular structure – electronic property relationships. Water and oxygen for instance have been well known to severely degrade charge transport characteristics in n-type polymers[11],[12]. Also in p-type OFETs water has been shown to be causing long-term bias stress effects[13] but its influence on the device characteristics is often ignored[14]. Given however, our current limited understanding of how species such as water behave when confined to a molecular superstructure such as the free volume of a polymer[15], this may be questionable. The complexity of the interactions between water and polymers is exemplified by studies demonstrating how organic molecules are capable of imposing highly organized local structures on water molecules[16],

fundamentally changing their characteristics. Here, we demonstrate how trap states caused by water molecules are one of the main origins for non-ideal transfer characteristics in p-type polymer FETs and in some cases, even the reason for underperformance of novel molecular designs.

The work reported here builds on our recent discovery of a surprising improvement in the uniformity, operational and environmental stability of polymer FETs when molecular additives, such as certain small molecules or even residual solvents are incorporated into the polymer films[17]. We could show that the underlying mechanism is related to voids present in the microstructure of these amorphous and semi-crystalline donor-acceptor copolymers (Fig 1a); water molecules present in the polymer powder, the solvents (even if anhydrous), the substrate, the dielectric or the environment get incorporated into these voids during processing (even if done under inert conditions) and act as traps to charge transport (Fig 1a); once a molecular additive is introduced to the polymer film, the voids are "filled" by the additive and device performance is significantly improved. Nevertheless, up to this point the precise interaction between the additive and individual water molecules has remained somewhat unclear and it has been difficult to establish if the additive is binding, displacing or removing water molecules. In the present work we are aiming to answer these questions by analyzing the interaction between trap-passivating solvent additives and water. We show that additives that form water-solvent azeotropes or hydrogen bonds to nitrile-groups or fluorine atoms are particularly effective in improving device performance and stability.

We fabricated OFETs from the well-studied polymer indacenodithiophene-co-benzothiadiazole (IDT-BT)[18],[2],[1] with the polymer film spun from various solvents and subsequently the films were annealed for only 2 minutes to remove the majority of the solvent yet to retain ~1 wt.% of residual solvent in the films (Fig 1b)[17]. We have now investigated an even wider range of solvents than in Ref. 17. Such an experiment is possible because IDT-BT is highly soluble in a wide range of non-polar and even some moderately polar solvents. For a wide range of solvents, the devices annealed for 2 minutes perform significantly better than reference devices annealed for 60 minutes (Fig. 1c). For some solvents such as 1-methylnaphthalene[17] or 1,4-butanedithiol, the performance however, is not improved over the reference devices, i.e. the on-current is low and device turn-on is sluggish. We have aimed to establish what characteristics of the solvent lead to device improvement and were surprised to find a perfect empirical correlation between those solvents that improve device

performance and those that form azeotropes with water (Tab. 1). Azeotropes are known to form when two or more distinct liquid compounds form a mixture that has the same, constant boiling point and boils congruently. The boiling point of the azeotrope can either be lower than that of any of the constituents (referred to as a positive azeotrope) or, less commonly, greater than the boiling point of any of the constituents (negative azeotrope). Often such as in the case of the ethanol-water azeotrope the relevant interactions are due to hydrogen bonding. There is however, no clear rule as to if two compounds form an azeotrope or are zeotropic (i.e. do not from azeotropes). Apart from tetralin, all the investigated azeotropes are positive, i.e., they have a reduced boiling point in comparison to water; interestingly tetralin which forms a negative azeotrope is also the solvent that leads to the least improvement in device characteristics and on-currents among the azeotrope solvents. Since the formation of a negative azeotrope implies a strong interaction between the compounds it is likely that water traps get passivated (i.e. water molecules interact more strongly with the solvent than they do with the polymer) while most of the water molecules still remains in the film; we expect this mechanism to be very similar to the case observed for small molecular additives before[17]. For the positive azeotropes on the other hand, the strong suppression in boiling point will make it easier to remove water molecules entirely resulting in the overall better performance observed. Between the various positive azeotropes we hence attribute the observed variations in on-current to both the differences in boiling point as well as azeotrope composition indicating how much water can efficiently be removed at a suppressed boiling point.

We tested our hypothesis further by dipping the IDT-BT films into orthogonal solvents such as methanol, isopropanol (IPA), acetonitrile, n-butyl acetate or ethanol prior to a 1h, 100°C anneal and the deposition of the dielectric layer (process schematically shown in Fig. 1b). We again find that all orthogonal solvents that are known to form azeotropes with water, significantly improve device performance (Fig. 1d, Tab 1). Acetonitrile, which forms the azeotrope with the lowest boiling point as well as the highest strength (i.e. the highest fraction of water in the composition), results in the biggest improvement in device performance. Furthermore, all devices that have been exposed to an azeotrope solvent show ideal, textbook-like device characteristics including ideal output characteristics (Supplementary Section 1), a reduction of the threshold voltage and a significantly reduced gate voltage dependence of the charge carrier mobility with gate-voltage independent mobilities of 3 cm^2/Vs being obtained for devices treated with acetonitrile (Fig. 2a). These are the highest mobilities and best performance reported for IDT-BT devices to date.

Furthermore, we observe a significant improvement in the output characteristics which turn from a highly non-ideal S-shape for the pristine device (Fig. 2b) into a perfectly linear shape after treatment with an azeotrope solvent (Fig. 2c). Methanol, on the other hand, which is zeotropic (non-azeotrope)[19] does not lead to improved devices over the reference. It is noteworthy, that this proposed mechanism could also help to explain why azeotrope forming and amine containing solvents have previously been shown to remove traps in e.g. P3HT films[20]. The clear correlation between device performance and the ability of the solvent to form an azeotrope with water strongly suggests that unbound water molecules trapped in the polymer's microstructure are indeed responsible for device degradation as was argued already in Ref. 17. Their removal and/or passivation when the films are dipped into an azeotrope solvent leads to significantly improved device performance. Incidentally, it is interesting to note that this observation could also explain why polymer FETs with certain polymer dielectrics tend to show superior device performance. Commonly used dielectric polymers such as PMMA are frequently dissolved in azeotrope solvents like acetonitrile or n-butyl acetate.

Although significantly improved device performance can be obtained either by spinning directly from an azeotrope solvent or alternatively by orthogonal treatment, the device performance usually degrades again if the films are annealed after being in contact with the azeotrope solvent. However, the durability of the improved device characteristics against annealing varies with the solvent used. Devices spun from DCB and then annealed for 60 minutes are degraded and the beneficial effect of residual DCB solvent that can be observed in films annealed for only 2 minutes has clearly worn-off, most likely due to all solvent having evaporated. Further annealing degrades these devices even more significantly (Supplementary Fig S4a). Devices treated with an orthogonal azeotrope solvent, such as acetonitrile, are significantly more robust and only degrade slightly during extended annealing (Supplementary Fig S4b). They show, for example, only very minor reduction in on-current after annealing for one hour at 80°C. This is surprising given the comparatively lower boiling point of acetonitrile (82°C) compared to DCB (180°C). Although it is difficult to establish by how deeply the short (2 minutes) orthogonal solvent treatment swells the polymer film and penetrates into the bulk, the higher thermal stability suggests that the orthogonal solvent treatment can bind and/or remove water more efficiently than the solubilizing solvents. We attribute this to the more polar nature of the orthogonal solvents allowing them to interact with water molecules more strongly. For the solubilizing solvents on the other hand, a higher

amount of solvent is needed; once this is lost, degradation starts to set in as evident by the lower thermal stability.

For some applications such as OLED backplanes a good encapsulation is provided which might make it possible to retain residual solvents within the films over the lifetime of the device. However, for most applications such encapsulation cannot be relied on and better long-term thermal stability than what can be achieved with the solvent additives discussed so far is needed. It is therefore of interest to introduce an additive that remains in the film permanently, yet is capable of binding water just like solvent-water azeotropes do. We have previously observed, that small molecules, that are in the solid state at room temperature, such as tetrafluoro-tetracyanoquinodimethane (F4-TCNQ), tetracyanoquinodimethane (TCNQ) or 4-aminobenzonitrile (ABN) are able to provide similarly ideal transistors as obtained in the case of a water-solvent azeotrope[17]. Azeotropes form due to enthalpic interactions such as hydrogen bonding between solvents and water molecules; this makes it likely that the mechanism by which solid small molecules improve device performance, rely on a similar hydrogen bonding mechanism. Nitrile groups and fluorine atoms are some of the strongest hydrogen-bond acceptors known and are present in all molecular additives that we have so far observed to show a beneficial effect on device performance. Interestingly, owing to their strong electron withdrawing nature, these groups are also present in most organic dopants and might even contribute to device improvements seen in some doped polymer films. To investigate the specific effect of the hydrogen bond acceptor on device performance more systematically, we synthesized three new anthracene based additives AQ, DCAQ and TCAQ (Fig 3a, Supplementary Section 3) and blended them at 5wt. % into IDT-BT films processed from DCB; the ability of the additives to bind water should hence solely depend on the different electron withdrawing and hydrogen acceptor's strength between the quinone and nitrile groups. Interestingly we find that only the addition of 5 wt.% of DCAQ leads to a significant improvement in device performance whereas those devices with AQ and TCAQ perform similarly to the reference device without an additive (Fig. 3b, left panel); the absence of a change in off-current furthermore suggests that the new additives do not lead to a charge transfer to the polymer and stability improvements are hence, unrelated to doping. On first sight our finding seems surprising, as we would have expected TCAQ with four nitrile groups to be able to bind water more efficiently. Nevertheless, looking at the solubility of all 3 molecules, we find that only AQ and DCAQ are able to dissolve sufficiently well in DCB, whereas the solubility of TCAQ is too low to yield a high enough additive loading of our

polymer film (Supplementary Section 4). Motivated by these results, we attached a tert-butyl side chain to the additives TCAQ and AQ to overcome the observed solubility issues. Indeed, we find that after the addition of a tert-butyl side chain, the TCAQ derivative (t-Bu-TCAQ) is showing the most pronounced improvement in device performance (Fig. 3b, right panel). The AQ derivative (t-Bu-AQ) on the other hand, still only yields marginal improvements of the liner transfer characteristics, whereas the saturation characteristics are still unchanged from the reference device. These results indicate that an effective additive has to possess a strong hydrogen accepting group as well as show good solubility and hence dispersion in the polymer film; this may also be the reason, why devices with azeotrope solvents have so far shown the most ideal performance as phase separation and agglomeration are not issues in this case. We should note that for the t-Bu-TCAQ additive as well as for some of the orthogonal solvents, we observe a slight increase in the off-current; we attribute this to an interaction between the solvent or additive, water and oxygen with the polymer as the additive or solvent alone should not be able to dope the polymer. We also tried to extend our additive design motif and attached four 2-ethylhexyl side chains to poorly soluble TCAQ. Unfortunately, this route resulted in additives that were too bulky to fill free space in the polymer leading to significant deteriorated on-currents. This suggests that as soon as the additive is becoming too bulky to fill voids in the polymer, it will inevitably distort the polymer's microstructure (Supplementary Figure S8).

Our results clearly demonstrate that additives with hydrogen accepting groups like nitrile or quinones are capable of binding residual water molecules in the film and passivating any water associated trap states. Interestingly, this suggests that polymers which themselves comprise strong hydrogen-bond acceptors, such as fluorine groups, in their molecular structure may offer water specific strong binding sites that could lead to device degradation. In such polymers it may not be possible for the molecular additives / residual solvent molecules to compete as effectively with water binding sites on the polymer backbone as in polymers like IDT-BT that contain no such strong hydrogen bonding sites. To test this hypothesis we have synthesized derivatives of the polymer IDT-BT with fluorine atoms placed on the benzothiadiazole (BT) unit. Our original motivation for the synthesis of these fluorinated polymers was, in fact, to planarize the polymer backbone through sulphur-fluorine interactions as done previously in the literature[21]. However, to our initial surprise we found that the backbone fluorination did not lead to a performance increase but instead, to a significant loss of performance with charge carrier mobilities dropping from 1.5 cm^2/Vs for

IDT-BT over 1cm^2/Vs for IDT-FBT to 0.5 cm^2/Vs for IDT-DFBT (Fig 4a). We observed this performance drop consistently even though we used a solvent additive (DCB) to maintain nearly ideal device characteristic, i.e. a sharp turn-on of the transfer characteristics maintaining similar onset voltages and output characteristics showing similarly ideal shapes without any current suppression at low source-drain voltages (Supplementary Fig S11,12); the observed drop in current is therefore unlikely to be caused by contact resistance. Furthermore we did not observe significant changes in the polymer's energetic disorder or morphology (Supplementary Fig. S12, 13). A powerful measure of energetic disorder is the Urbach energy extracted from photothermal deflection spectroscopy (PDS). All three polymers have very similar and low values of energetic disorder of 24-25 meV (Fig 4b). IDT-BT and IDT-FBT have near identical energy gaps, the band gap of IDT-2FBT is only slightly higher. Given this close similarity in the electronic structure and microstructure of the three polymers and the beneficial effect that we expected the fluorine substitution to have on backbone planarity the relative electrical performance of these polymers were a surprise to us.

Although it is very difficult to exclude that there are not in fact subtle differences in microstructure that could provide an explanation for the observed, low performance of the fluorinated polymers, we would like to offer here a tentative, alternative explanation within the framework of water-induced traps. Owing to the strong electronegativity of the fluorine atom, the fluorine-hydrogen bond is among the strongest hydrogen bonds known; some water molecules will hence, inevitably not form an azeotrope with the solvent (keeping in mind that this mechanism relies on hydrogen bonding as well) and instead prefer to bind to the fluorine sites on the polymer backbone. The presence of highly polar water molecules close to the polymer backbone will consequently lead to a localization of charges and result in a drop in performance for the two fluorinated polymers relative to IDT-BT. Alternatively, the bonding of the fluorine groups to water molecules might prevent the planarization of the backbone, though this should manifest itself potentially in a higher Urbach energy.

It is hard to prove this mechanism through direct experimentation as the trap concentrations involved are very small and beyond the detection limit of most analytical techniques. However, supporting evidence stems from similar observations in other polymer systems. We also synthesized fluorinated versions of the polymer TIF-BT, a related high mobility, low disorder conjugated polymer with, however, a much deeper HOMO level than IDT-BT. Indeed, here we also see a drop in performance once fluorine atoms are attached to

the BT unit (Fig 4c); yet, as compared to IDT-BT, the loss of performance is more drastic most likely owing to the deeper HOMO level of TIF-BT (5.8 eV for TIF-BT instead of 5.3 eV for IDT-BT) yielding a stronger driving force for trapping of holes on the polymer in water-induced traps along the backbone[17]. Furthermore, we have compared published literature data for conjugated polymers containing fluorine substitutions; in agreement with our observations we find that in all cases (with the exception of crystalline P3HT, which has got a high energetic disorder, low lying HOMO level and furthermore, fluorination leads to a significant change in morphology), the fluorination of the polymer backbone consistently leads to a drop in device performance (Supplementary Fig. S14)[7],[22],[23],[24].

Our observations allow us to set forth new design guidelines for conjugated polymers with high performance and operational stability. To minimize the sensitivity of the polymer to water induced traps we suggest that for novel polymer designs, the amount of strong electron withdrawing groups on the polymer backbone should be considered carefully. Clearly, in some systems, such as lactam-containing polymers based on diketopyrrolopyrole (DPP) or isoindigo or imide containing polymers based on naphthalene dimide, excellent transport properties can be achieved. This may potentially be a reflection of the electronic structure of the conjugated backbone of these donor acceptor-polymers that might modify the electron with-drawing nature of these functional group. It could also be that close to points where the hydrophobic, solubilizing side chains are attached on the polymer backbone, water molecules might not be able to get close enough to these election withdrawing groups. However, our results suggest that for novel amorphous and semi-crystalline polymer designs, strong electron withdrawing groups for planarization and short-contacts should be used with care and only incorporated at positions close to the attachment of the polymer side chain; this will minimize the risk of void formation close to the strongly electronegative component and reduce the probability of lone water molecules attaching.

In summary, the results presented here provide further strong evidence that molecular water is one of the predominant sources of degradation in polymer OFETs, which comprise high mobility conjugated polymers with a near amorphous microstructure. Hydrogen bonding between water and strong electron withdrawing groups such as the nitrile group or alternatively the formation of water-solvent azeotropes can effectively bind these water molecules, passivate/eliminate the associated water-induced traps and significantly improve device performance. The beneficial effect of using water-solvent azeotropes is unfortunately

not permanent and water traps will re-form when the solvents evaporate from the film and water molecules diffuse back into the films. Hence, for permanent stability, solid, small molecular additives with strong electron withdrawing groups are needed that are capable of binding and passivating water molecules in the film. Yet, for such solid, molecular additives their solubility within the polymer needs to be sufficiently high to ensure that all water-induced traps can be efficiently passivated; a careful selection of highly soluble molecules with strong hydrogen bond accepting groups is therefore, required. However, another consideration is the design of the polymer backbone. We have shown circumstantially, that in a wide range of systems substitution of the backbone by fluorine atoms can have a detrimental impact on charge transport because the fluorine atoms induce water binding in close proximity to the charge transporting polymer backbone leading to reduction in carrier mobility. Our results provide clear strategies for further improving the performance and operation stability of polymer FETs through the use of molecular additives and refined design guidelines for novel polymer structures.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

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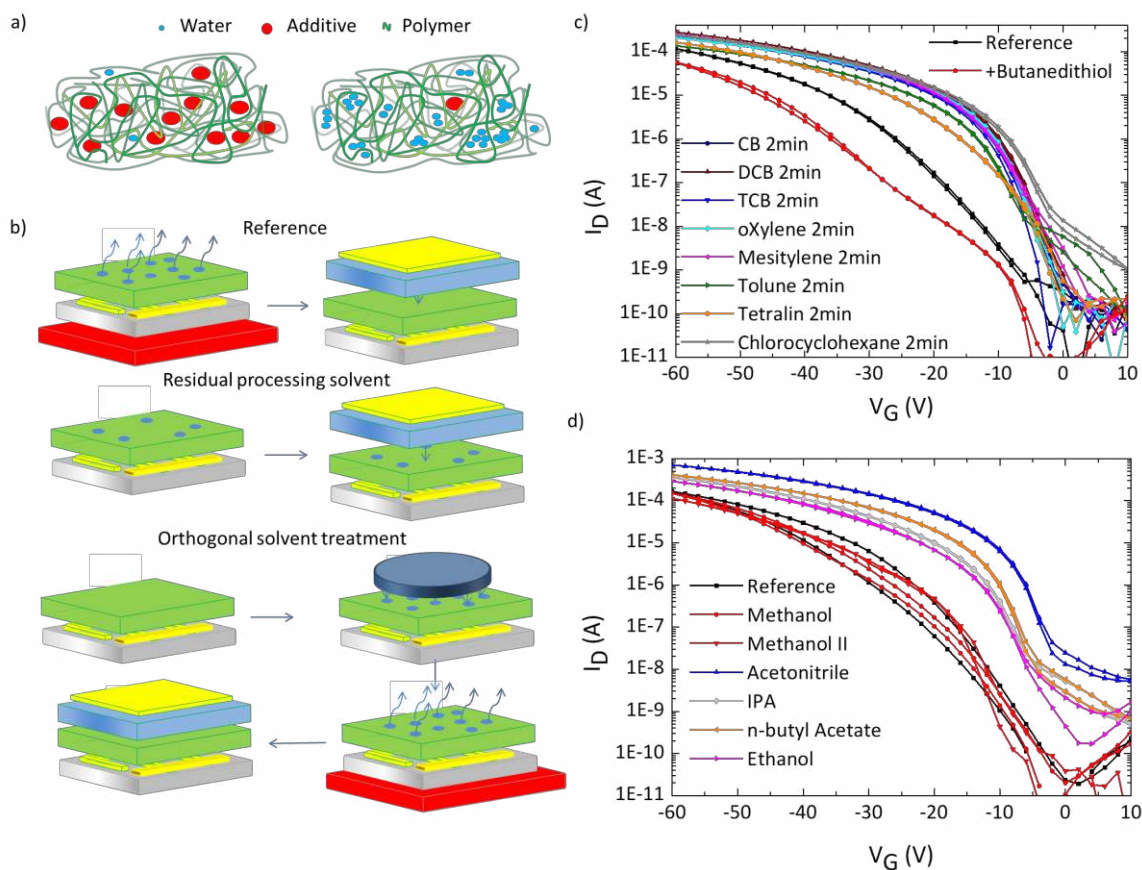
Figure 1 Effect of water removal through azeotrope solvents on the performance of OFETs (a, left panel) Passivation of water induced traps in the polymer's microstructure (green) through the use of additives (red); (a, right panel) Removal of additives allows water molecules (blue) to interact with polarons on the polymer backbone and disturb charge transport (b) Method of water removal in IDT-BT OFETs (L = 20um, W = 1mm); (i) Reference top gate device with the polymer film (green) initially containing residual solvent (blue) after spin-coating. Annealing at 100 C on a hotplate (red) for 1h removes the residual solvent. This is followed by the deposition of the dielectric (blue) and gate (yellow); (ii) Device prepared with residual solvent being deliberately left in the polymer film. Only a short anneal for 2 minutes is used which removes most of the solvent, but leaves residual solvent filling voids in the film; (iii) Devices prepared under conditions in which the annealed polymer film is soaked in an orthogonal solvent and subsequently annealed at 100°C for 1h; c) Saturation (V_{DS} = -50V) transfer characteristics of an annealed reference device (black) and devices with residual azeotrope and zeotrope solvents processed according to (ii); (d) Saturation transfer characteristics of devices treated with orthogonal solvents according to (iii). Devices treated with methanol (zeotrope) were reproduced several times with 2 devices from different batches shown.

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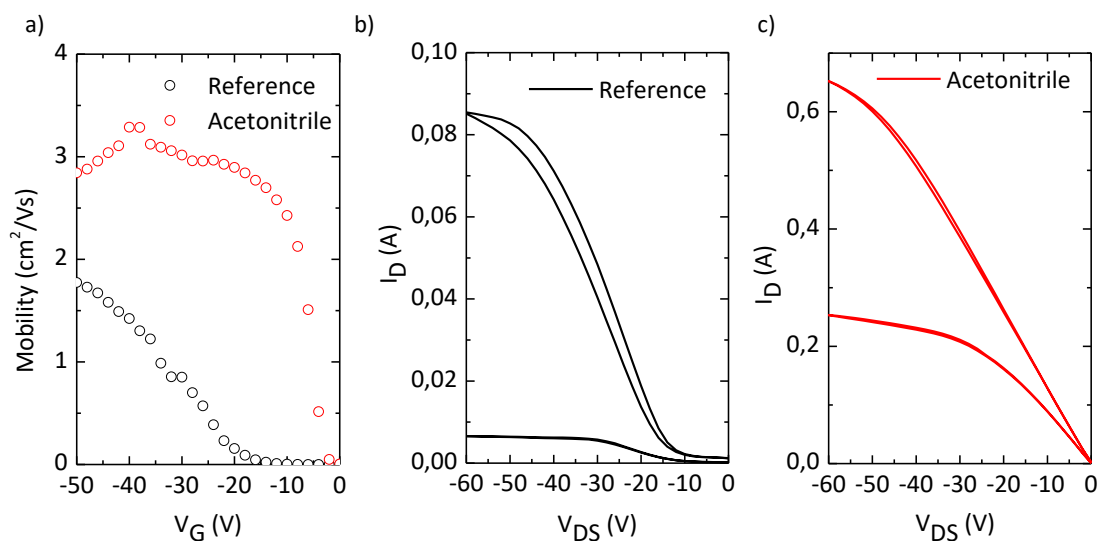
Figure 2 Azeotrope treatment yielding improved device performance (a) Gate-voltage dependence of extracted charge carrier mobility for a reference IDT-BT OFET (L = 20um, W = 1mm) and a device treated with orthogonal acetonitrile; (b) corresponding output characteristics (shown for V_G = -60 and -40 V) for a reference device; (c) output characteristics for a device after acetonitrile exposure.

Solvent	Processing	BP. Of solvent (C)	Bp of compound (C)	% by weight	Improvement
Acetonitrile	Orthogonal	82	76.0	86	Yes
N-butyl Acetate	Orthogonal	126	90.0	73	Yes
IPA	Orthogonal	82.6	82.5	88	Yes
Ethanol	Orthogonal	78.3	78.4	96	Yes
Methanol	Orthogonal	64.7	Zeotrope	-	No
Toluene	Solvating	110.6	84.1	80	Yes
Xylene	Solvating	144.0	94.5	60	Yes
Cyclohexane	Solvating	80.7	69.8	91	Yes
Chlorobenzene	Solvating	131.0	90.2	n.a.	Yes
Tetralin	Solvating	208.0	108.2	n.a.	Yes
Butanedithiol	Solvating	106	Zeotrope	-	No
Benzene	Solvating	80.1	80.2	91	Yes
(Methyl)naphtalene	Solvating	240	Zeotrope	-	No

Table 1 List of Azeotropes of various solvents with water. Azeotropes of various solvents with water introduced to the film by blending or orthogonal processing. Data taken from Ref[[25], [19], [26]]. For some solvents, the literature data for azeotrope composition by weight was not available (marked as n.a.).
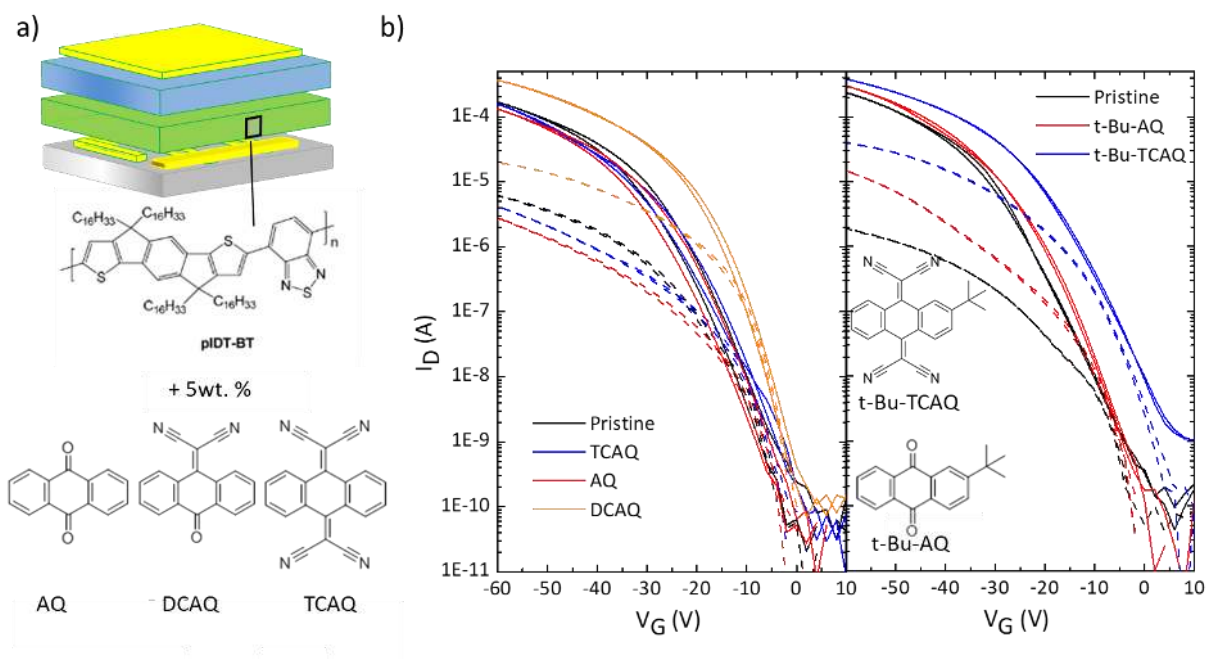
Figure 3 improving the performance of polymer OFETs with molecular additives. (a) Structure of an IDT-BT OFET (L = 20um, W = 1mm) as well as the molecular structure of the polymer IDT-BT and the additives AQ, DCAQ and TCAQ; b) Linear (dashed lines, V_D = -5V) and saturation (Solid lines, V_D = -50V) transfer characteristics of IDTBT OFETs with 5% of the molecular additives AQ, DCAQ and TCAQ (left panel) and t-Bu-AQ and t-Bu-TCAQ (right panel) blended into the polymer film. The performance is compared to a reference device (black) without any additive in the film.
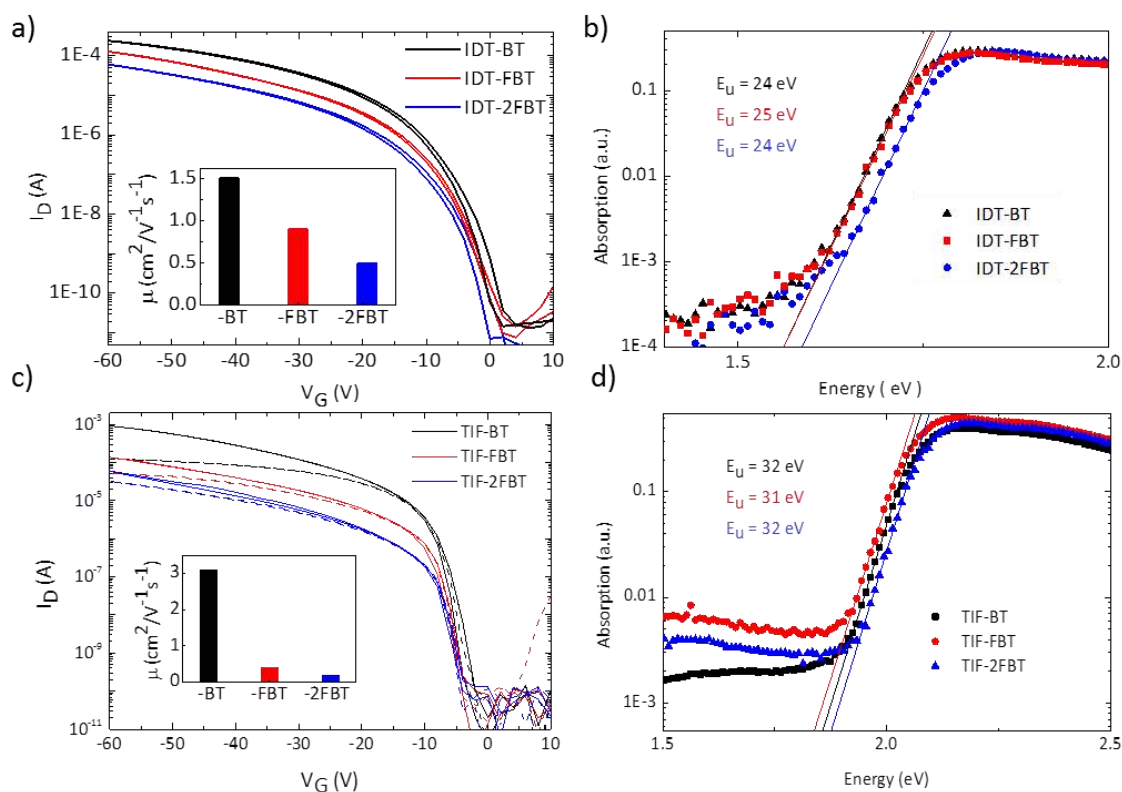
Figure 4 Effect of fluorination on charge transport. (a) Saturation (V_{DS} = -50V) transfer characteristics of OFETs made with IDT-BT, IDT-FBT and IDT-2FBT; extracted charge carrier mobilities are shown as an inset; b) Energetic disorder measured by Photothermal Deflection Spectroscopy (PDS) with all polymers exhibiting Urbach Energies (E_U) of 24-25 meV; (c) Saturation (V_{DS} = -50V) transfer characteristics of OFETs made with TIF-BT, TIF-FBT and TIF-2FBT; extracted charge carrier mobilities are shown as an inset; b) Energetic disorder measured by Photothermal Deflection Spectroscopy (PDS) of the polymers in (c). All three polymers exhibit very similar Urbach energies (E_U) of 31-32 meV.

Here we demonstrate a highly efficient mechanism for the removal of water induced traps that are omnipresent in conjugated polymer devices even when processed in inert environments; we show the underlying mechanism by which small molecular additives with water binding nitrile groups or alternatively water-solvent azeotropes are capable of completely removing water-induced traps leading to a significant improvement in OFETs performance.

Keywords: Organic Electronics, Field-Effect Transistors, Charge Transport, Stability

Mark Nikolka[*], Guillaume Schweicher, John Armitage, Cameron Jellett, Zhijie Guo, Michael Hurhange, Aditya Sadhanala, Iain McCulloch, Christian B. Nielsen and Henning Sirringhaus[*]

Removal of water induced traps for drastic performance improvements in conjugated polymer devices
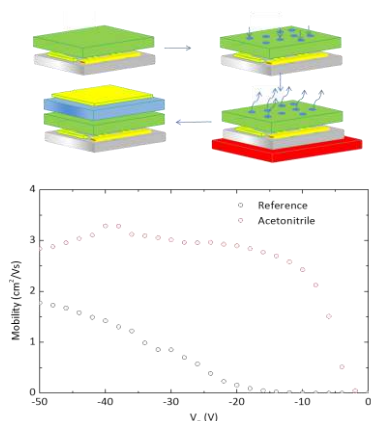
Supporting Information

Performance Improvements in Conjugated Polymer Devices by Removal of Water Induced Traps

Mark Nikolka[*], Guillaume Schweicher, John Armitage, Cameron Jellett, Zhijie Guo, Michael Hurhange, Aditya Sadhanala, Iain McCulloch, Christian B. Nielsen and Henning Sirringhaus[*]

Section 1 – Device fabrication and output characteristics of IDTBT OFETs

The devices used for this study were top-gate bottom contact field-effect transistors (L = 20um, W = 1mm) fabricated on glass substrates with photo-lithographically defined electrodes of Ti/Au (10 nm/ 30 nm). Since we are presenting a study on the effect of water molecules on charge transport, all fabrication and measurement steps described herein were carefully conducted in a N_2 glove box with controlled ppm levels of water and oxygen present. The investigation of the effects of solvent additives was done by processing the polymer films in three different ways: (i) IDTBT polymer powder was spun from 1-2-Dichlorobenzene (DCB) (10g/l) and reference devices were subsequently annealed for 1 hour at 100°C to remove most of the residual solvents from voids in the film; (ii) IDTBT polymer powder was dissolved in solvents that are known to form either azeotropes or zeotropes with water; these films were annealed for only 2 minutes at 100°C to leave residual solvent in the film; (iii) IDTBT polymer films were spun from dichlorobenzene solution and after annealing at 100°C to remove bulk solvent, films were treated for 2 minutes with an orthogonal azeotrope/zeotrope solvent; this was followed by a further 60 minute anneal at 100°C. For the investigation of small molecular solid additives, we mixed custom-synthesized additives (dissolved at 2g/l in DCB) at given weight percentages of 5wt. % into the polymer solution (10g/l in DCB) and consecutively annealed these films at 100°C for 1 hour. For all devices presented in this study, a fluorinated polymer dielectric (Cytop, annealed at 80°C for 15 minutes) was used. The last step of the sample fabrication was the evaporation of a 20nm thick gold top gate through a shadow mask. To avoid heating and thus, further annealing of the polymer, gates were evaporated at low base pressures of 5 10^{-6} mBar, in an evaporator with a water cooled sample stage and a large source-sample distance.
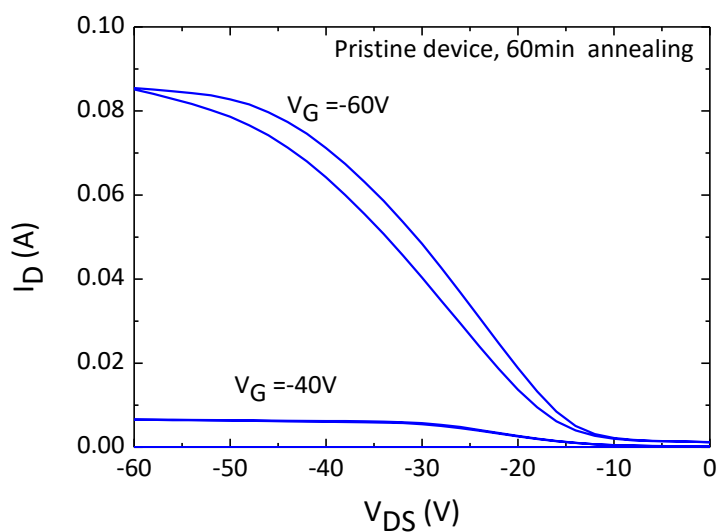
Fig. S1 Output characteristics of a pristine IDTBT OTFT (L=20um, W=1mm) processed from DCB and annealed for 60 minutes.
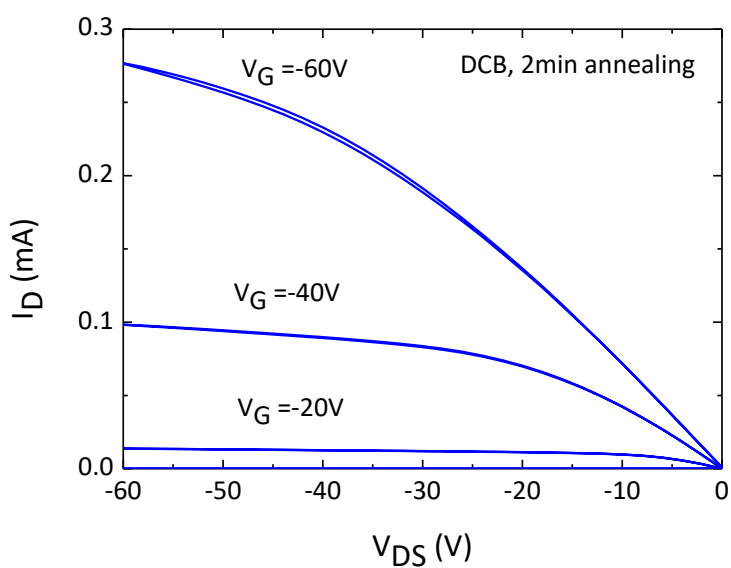

Fig. S2 Output characteristics of an IDTBT OTFT (L=20um, W=1mm) processed from DCB and annealed for 2 minutes only leaving residual solvent in the film that can hydrogen bond to water molecules in the film and form an azeotrope.
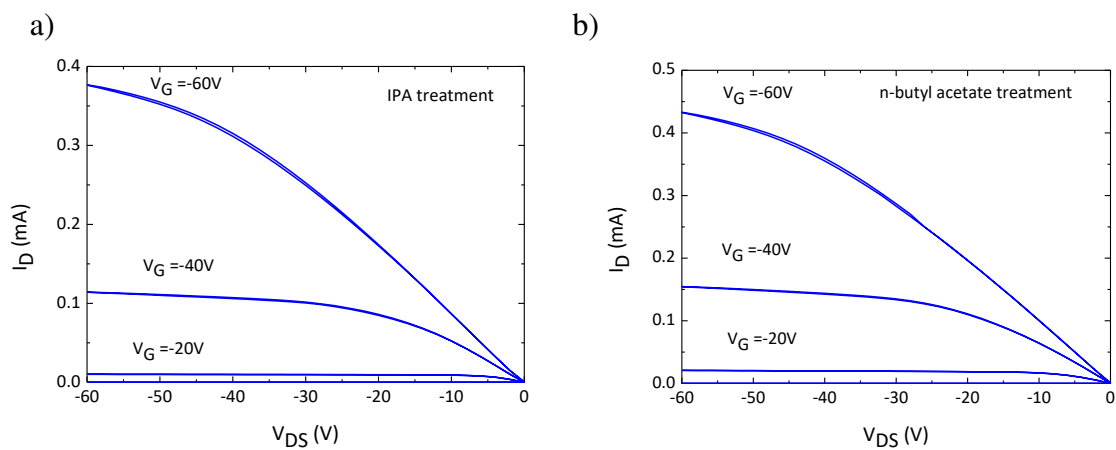
a)

b)

Fig. S3 Output characteristics of an IDTBT OTFT (L=20um, W=1mm) treated with a) IPA and b) n-butyl acetate.

Section 2 – Heat stability of solvent treated devices

We noticed that the orthogonal solvent treatment leads to significantly improved heat stability. All devices that have been treated with an orthogonal solvent, degrade significantly slower during a storage test at 80-90°C over extended time periods. These results suggest, that the reference devices are only stable as long as water forms an azeotrope with residual solvent in the film; once residual 1,2-Dichlorobenzene (DCB) solvent evaporates during extended annealing, water is released and forms charge traps. The orthogonal solvent on the contrary is capable of removing the water entirely and only slow back-diffusion of water degrades the device performance.
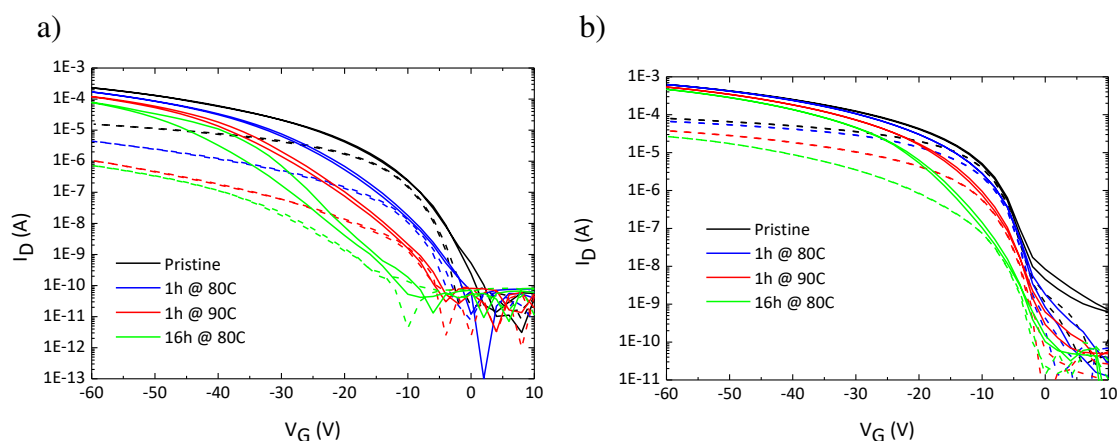
Fig. S4 Heat stability of solvent treated IDTBT OTFTs (L=20um, W=1mm); Solid lines represent saturation transfer characteristics (V_D = -50V) and dashed lines represent linear characteristics (V_D = -5V); Devices were annealed in nitrogen for (i) 1h at 80°C, (ii) 1h at 90°C and subsequently (iii) 16h at 80°C; a) Reference IDTBT OTFT spun from DCB; b) IDTBT OTFT treated with acetonitrile before depositing the dielectric.

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Section 3 – Synthesis of DCAQ, TCAQ and t-Bu-TCAQ


AQ   **DCAQ**   **TCAQ**
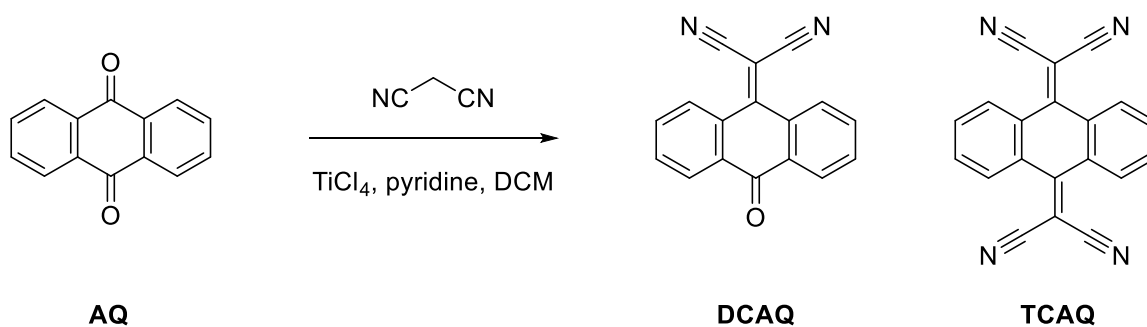
Procedure adapted from literature[27]. To an ice-cooled solution of anthraquinone (4.16 g, 20.0 mmol) and malononitrile (3.50 g, 53.0 mmol) in dichloromethane (125 ml) was added dropwise titanium tetrachloride (11.5 ml, 105 mmol) and subsequently pyridine (35 ml, 433 mmol). The reaction mixture was allowed to warm to room temperature over five hours, concentrated and subsequently quenched with aqueous hydrochloric acid and then extracted with dichloromethane. The combined organic extracts were dried over anhydrous magnesium sulphate and concentrated. Purification by column chromatography (dichloromethane/hexane, silica) afforded AQ (pale yellow solid, 0.78 g, 19% recovery of starting material), DCAQ (yellow solid, 0.25 g, 0.98 mmol, 5% yield) and TCAQ (yellow solid, 1.54 g, 5.06 mmol, 25% yield).

AQ: ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.32 (dd, J = 5.7, 3.3 Hz, 1H), 7.81 (dd, J = 5.7, 3.3 Hz, 1H).
DCAQ: ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.34 – 8.27 (m, 1H), 7.81 – 7.74 (m, 1H).
TCAQ : ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.26 (dd, J = 5.9, 3.3 Hz, 1H), 7.75 (dd, J = 5.9, 3.3 Hz, 1H).

t-Bu-AQ   **t-Bu-TCAQ**
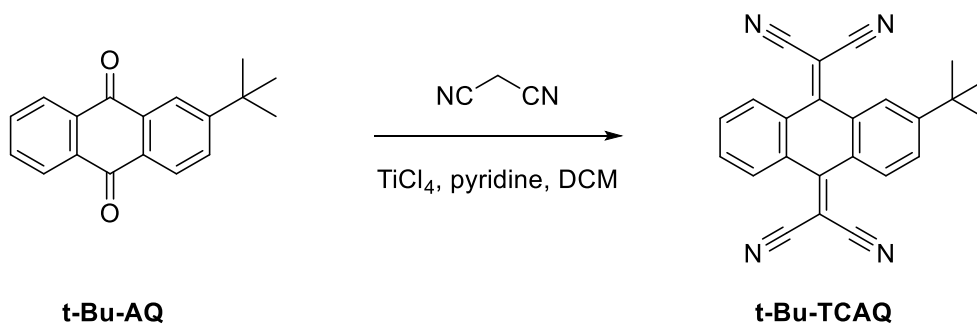
To an ice-cooled solution of 2-*tert*-butylanthraquinone (5.29 g, 20.0 mmol) and malononitrile (3.63 g, 55.0 mmol) in dichloromethane (125 ml) was added dropwise titanium tetrachloride (11.5 ml, 105 mmol) and subsequently pyridine (35 ml, 433 mmol). The reaction mixture was allowed to warm to room temperature over five hours, concentrated and subsequently quenched with aqueous hydrochloric acid. The solid product was filtered and washed several times with water and dried. Purification by column chromatography (ethyl acetate/hexane 1:4, silica) and subsequent recrystallisation from acetic acid afforded t-Bu-TCAQ as yellow crystals (4.30 g, 11.9 mmol, 60% yield).

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.28 (d, J = 1.7 Hz, 1H), 8.27 – 8.24 (m, 2H), 8.22 – 8.19 (m, 1H), 7.76 – 7.71 (m, 3H), 1.41 (s, 9H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 161.05, 160.16, 157.02, 132.47, 132.43, 130.55, 130.45, 130.19, 129.66, 127.69, 127.31, 125.40, 113.49, 113.47, 113.39, 113.30, 82.97, 82.39, 35.98, 30.86.

Section 4 – Solubility of additives

We investigated the solubility of the molecular additives AQ, DCAQ and TCAQ in 1,2-Dichlorobenzene by using UV-vis absorption spectroscopy. The molecules were dissolved in DCB at the concentrations 0.100, 0.050, 0.025, 0.001 mg/mL and their respective absorption spectra were measured (blue symbols). For normal processing, additives were added from a 2mg/ml solution. These solutions were diluted by 90 and 95% and their absorption spectra were recorded (Red symbols). Using the Beer-Lambert Law, we determined the solubility of the additive in the used solution.

a) b)
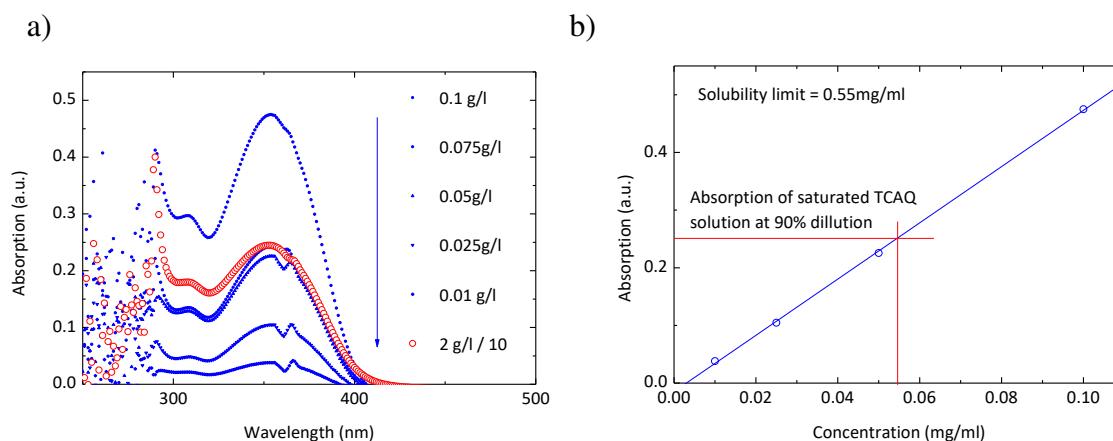
Fig. S5 a) Absorption of TCAQ solutions in 1,2-Dichlorobenzene (DCB) diluted to 0.100, 0.075, 0.050, 0.025, 0.001 mg/mL (blue) as well as the reference solution diluted by 90%; b) Beer-Lambert Law plotted for the diluted TCAQ solutions giving a solubility limit of 0.55 mg/ml

a) b)
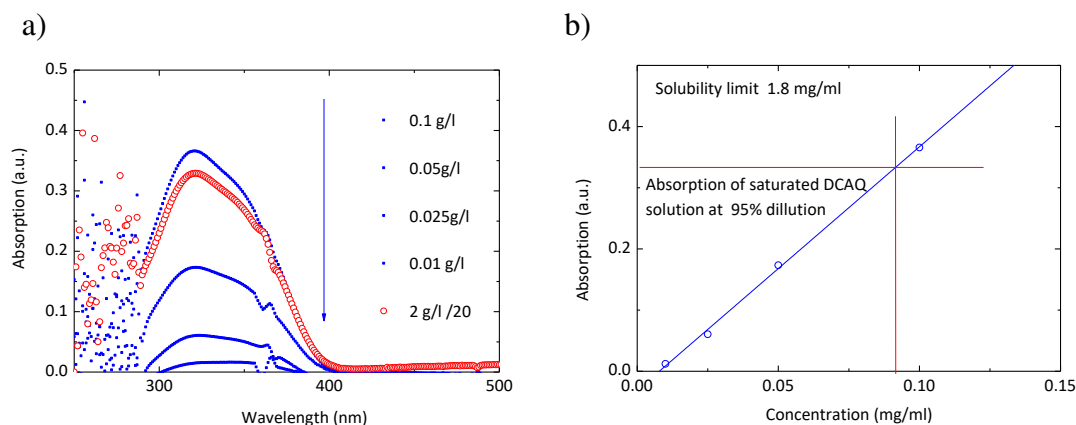
Fig. S6 Absorption of DCAQ solutions in 1,2-Dichlorobenzene (DCB) diluted to 0.100, 0.050, 0.025, 0.001 mg/mL (blue) as well as the reference solution diluted by 95%; b) Beer-Lambert Law plotted for the diluted DCAQ solutions giving a solubility limit of 1.8 mg/ml (i.e. almost all DCAQ is dissolved
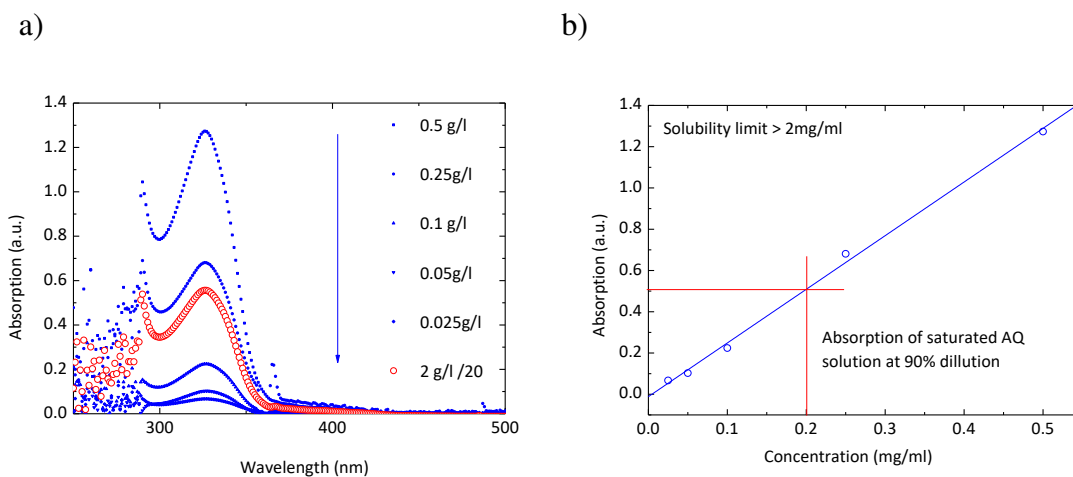
a)

b)

Fig. S7 Absorption of AQ solutions in 1,2-Dichlorobenzene (DCB) diluted to 0.500, 0.250, 0.100, 0.050, 0.025 mg/mL (blue) as well as the reference solution diluted by 95%; b) Beer-Lambert Law plotted for the diluted AQ solutions giving a solubility limit above 2 mg/ml (i.e. all AQ is dissolved)

Section 5 – Highly soluble additives

We have synthesized the highly soluble derivatives of the molecule TCAQ with four C_2C_6 alkyl side chains attached to the molecule (EH-TCAQ).
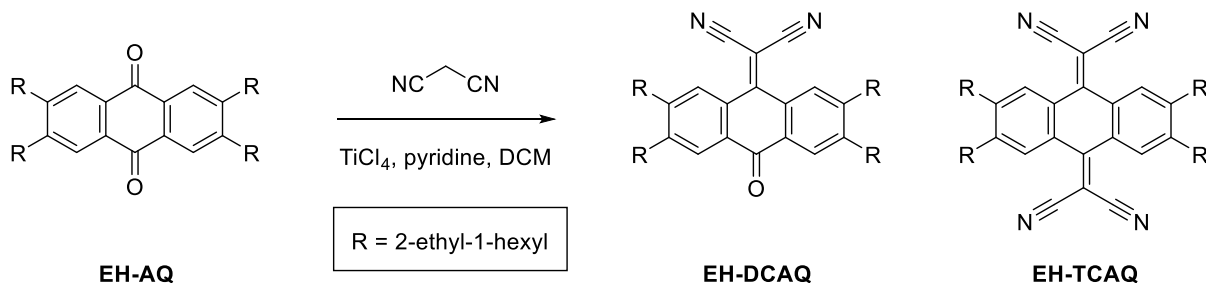
To an ice-cooled solution of 2,3,6,7-tetrakis(2-ethylhexyl)anthraquinone[28] (300 mg, 0.457 mmol) and malononitrile (106 mg, 1.6 mmol) in dichloromethane (10 ml) was added dropwise titanium tetrachloride (0.35 ml, 3.2 mmol) and subsequently pyridine (1.0 ml, 13 mmol). The reaction mixture was allowed to warm to room temperature over five hours, concentrated and subsequently quenched with aqueous hydrochloric acid and then extracted with dichloromethane. The combined organic extracts were dried over anhydrous magnesium sulphate and concentrated. Purification by column chromatography (dichloromethane/hexane, silica) afforded EH-DCAQ (yellow oil, 177 mg, 0.25 mmol, 55% yield) and EH-TCAQ (yellow oil, 87 mg, 0.12 mmol, 25% yield).

EH-AQ: ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.02 (s, 1H), 2.76 – 2.61 (m, 2H), 1.66 (dd, J = 12.1, 6.0 Hz, 1H), 1.40 – 1.15 (m, 8H), 0.88 (dt, J = 8.9, 7.2 Hz, 6H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 183.94, 147.63, 131.40, 128.67, 40.68, 37.64, 32.67, 29.02, 25.82, 23.17, 14.24, 11.05.
EH-DCAQ: ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.05 (s, 1H), 8.02 (s, 1H), 2.75 – 2.60 (m, 2H), 1.77 – 1.58 (m, 1H), 1.45 – 1.16 (m, 8H), 0.96 – 0.78 (m, 6H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 182.69, 161.41, 146.98, 146.94, 131.05, 129.65, 129.05, 128.73, 114.78, 81.03, 40.78, 40.61, 37.75, 37.51, 32.80, 32.64, 29.07, 28.97, 25.85, 25.78, 23.14, 23.13, 14.21, 14.20, 10.99, 10.98.
EH-TCAQ: ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.97 (s, 1H), 2.74 – 2.55 (m, 2H), 1.68 (dd, J = 11.9, 6.0 Hz, 1H), 1.45 – 1.22 (m, 8H), 0.95 – 0.80 (m, 6H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 160.56, 146.32, 129.20, 127.69, 113.92, 80.97, 40.72, 37.72, 32.78, 29.07, 25.77, 23.12, 14.22, 10.86.

Unfortunately, we observe a drop in transistor on-current for increasing additive loading in the polymer film. Already for a 5 wt. % additive loading with the molecule C_2C_6-TCAQ leads to a drop in transistor on-current by a factor of 3.5; this is in stark contrast to what we observe in the case of TCAQ and tert-but TCAQ (Fig. 4). Increasing the additive loading even further to 20 wt.% results in a more significant drop in the on-current by more than one order of magnitude as compared to the reference device. We hence, associate this loss of performance to the steric hindrance induced by the bulky C_2C_6 branched alkyl side chains.
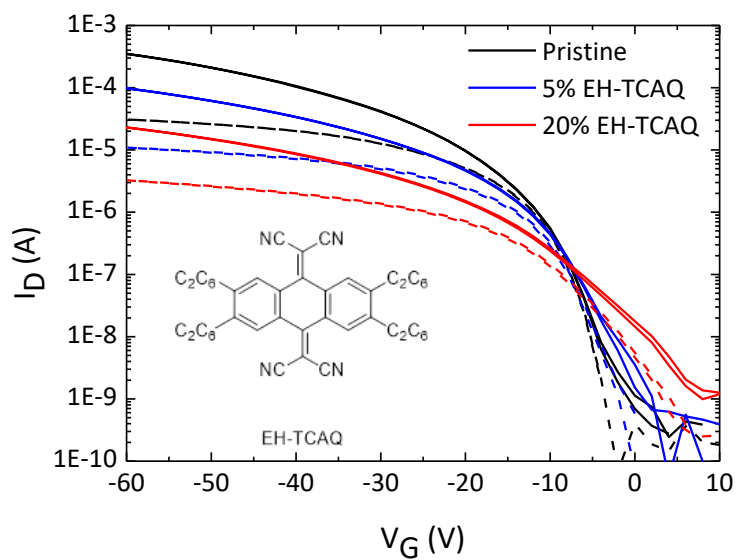
Fig. S8 Linear (dashed lines) and Saturation (solid lines) transfer characteristics of the highly soluble TCAQ derivative C2C6-TCAQ (molecular structure shown).

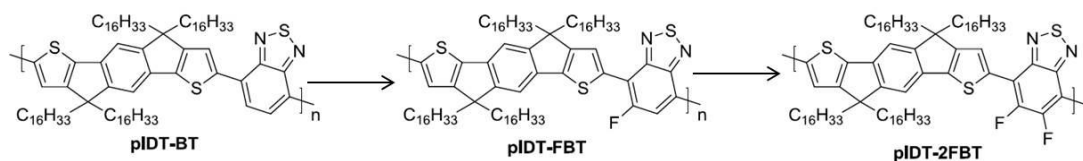**Section 6 – Backbone fluorinated polymers**

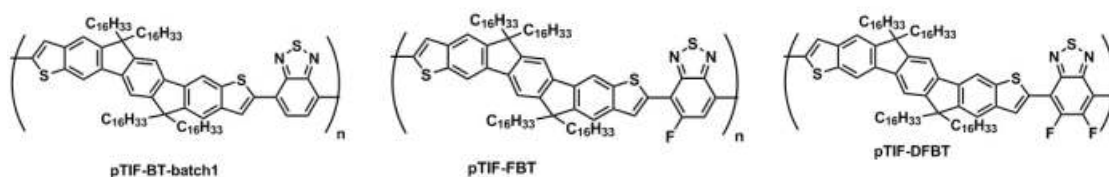Fig. S9 Molecular structures (from left to right) of the polymers IDT-BT, IDT-FBT, IDT-DFBT

Fig. S10 Molecular structures (from left to right) of the polymers TIF-BT, TIF-FBT, TIF-DFBT; information on the polymer synthesis can be found in Ref [[29]]

To exclude that the observed drop in current after adding fluorine atoms to the polymer BT unit is not caused by contact resistance, we have compared the output characteristics for the polymers IDT-BT, IDT-FBT and IDT-DFBT. We clearly find that even at low voltages, the output characteristics maintain a linear shape and no pinching or S-shape is observed, as would be the case in the absence of an additive (See Fig. S1). The solvent-azeotrope is hence, still forming. However some water molecules will inevitably hydrogen bond to the Fluorine atom(s) on the BT unit. Since this interaction is most likely stronger than the solvent-water interaction, this will lead to a drop in current.
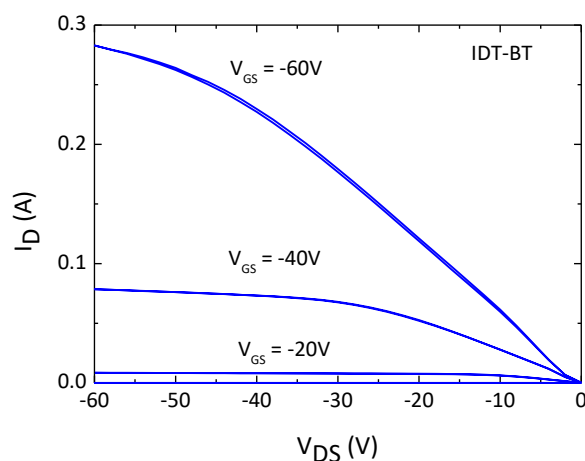

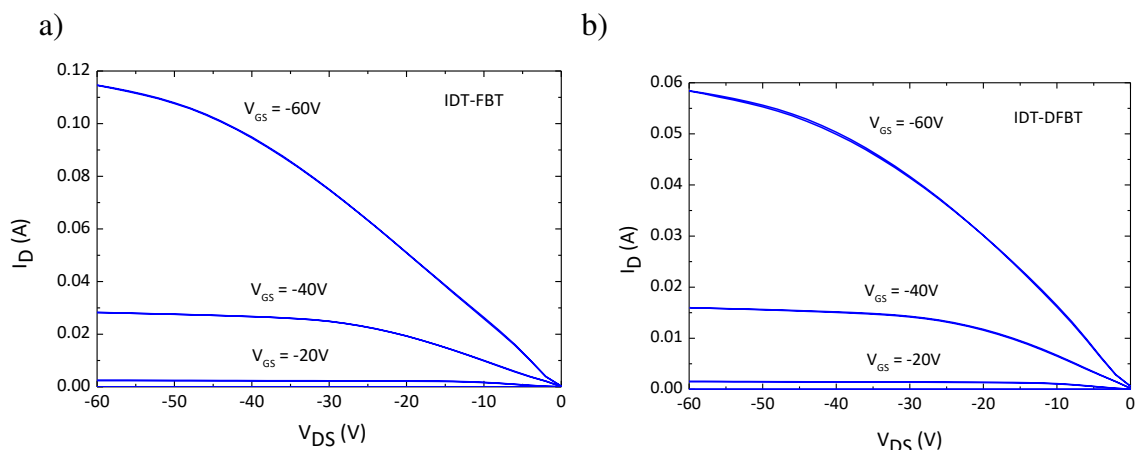Fig. S11 Output characteristics of the polymers IDT-BT

a)

b)

Fig. S12 Output characteristics of the polymers IDT-FBT and IDT-DFBT

We also confirmed that the polymer microstructure is not significantly impacted by adding fluorine atoms to the polymer backbone. Here we show representative data for the polymers from the TIF-series showing similar crystallinities and surface roughness.
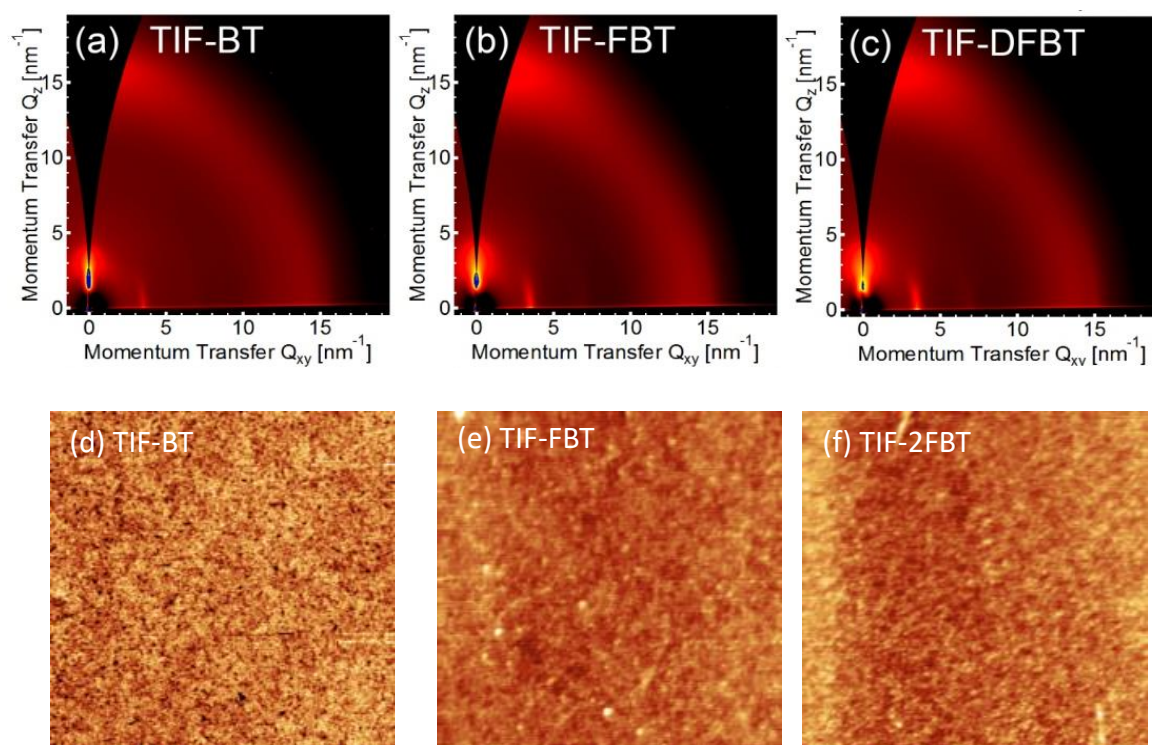

Fig. S13 GIWAXs (a-c) and Atomic-force microscopy (d-f, data scale: 0-5 nm) images of the polymers TIF-BT, TIF-FBT and TIF-DF-BT. Images adapted from Ref [29]
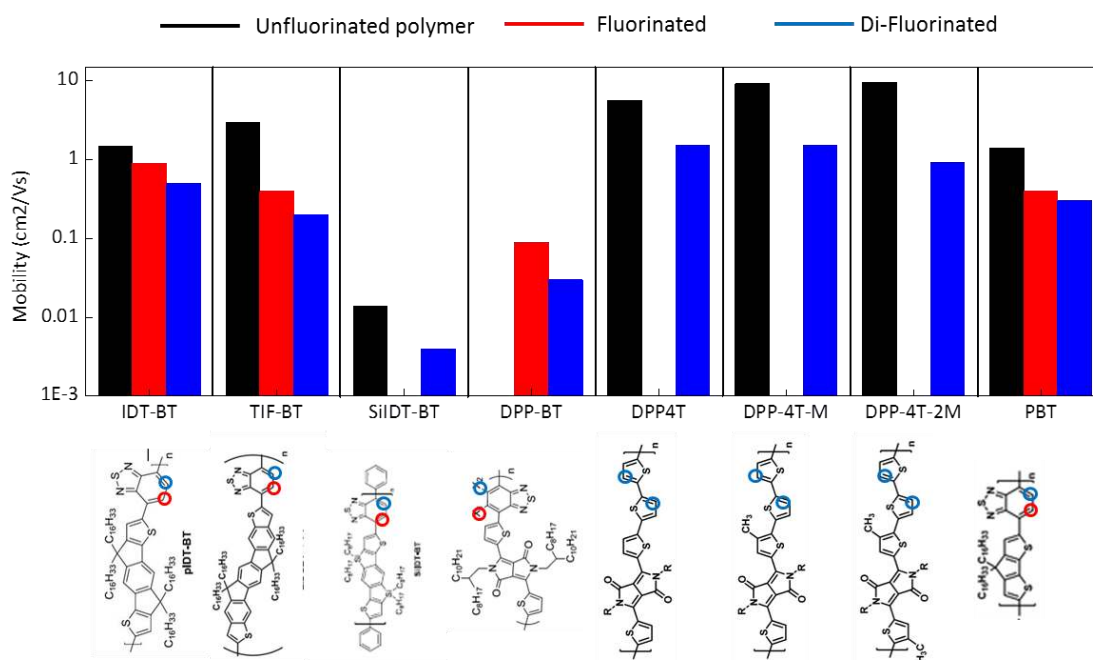
Fig. S14 Field-effect mobilities extracted for various polymers with and without fluorine attached to the backbone; black bars represent polymers without fluorine, red bars are polymers with 1 fluorine per monomer and blue bars are polymers with 2 fluorine atoms per monomer. All data shown were taken from literature[23],[24],[6] or shown explicitly in this work (IDT-BT, TIF-BT)