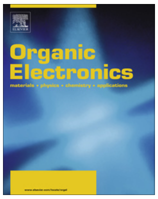
Organic Electronics 26 (2015) 340–344

Contents lists available at ScienceDirect

Organic Electronics

journal homepage: www.elsevier.com/locate/orgel



Separating the impact of oxygen and water on the long-term stability of n-channel perylene diimide thin-film transistors

Ute Zschieschang [a], Konstantin Amsharov [a,1], Martin Jansen [a], Klaus Kern [a,b], Hagen Klauk [a], R. Thomas Weitz [a,*]

[a] Max Planck Institute for Solid State Research, Heisenbergstr. 1, 70569 Stuttgart, Germany
[b] Institut de Physique de la Matière Condensée, Ecole Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland

ARTICLE INFO

Article history:
Received 7 May 2015
Received in revised form 29 July 2015
Accepted 30 July 2015

Keywords:
Organic transistor
Ambient stability
n-Channel
Perylene diimide

ABSTRACT

A detailed understanding for the mechanisms that control degradation of the electrical performance of organic thin-film transistors (TFTs) during exposure to various environments, such as oxygen and humidity, is still developing. This is particularly true for n-channel organic TFTs. Here we present an investigation of the long-term stability of n-channel TFTs based on the small-molecule organic semiconductor N,N′-bis(2,2,3,3,4,4,4-heptafluorobutyl-1,7-dicyano-perylene-(3,4:9,10)-tetracarboxylic diimide (PDI-FCN$_2$) during storage in dry nitrogen, dry air, wet nitrogen and ambient air. By monitoring the electrical characteristics of the TFTs over a period of six weeks, we are able to show that the degradation of the electrical parameters (charge-carrier mobility and the simultaneous shift of the threshold voltage) is caused by two distinct mechanisms with different time constants. Exposure to oxygen or nitrogen (in the absence of humidity) causes the carrier mobility to drop by a factor of two and the threshold voltage to shift towards more positive values within 20 days, possibly due to a slight rearrangement of the conjugated molecules within the semiconductor layer. Storing the TFTs in saturated water vapor or in ambient air causes the threshold voltage and the carrier mobility to change much more rapidly, within just one day. The observed degradation in ambient air can be explained by an electrochemical instability of the radical anion of the organic semiconductor.

The electrical performance of organic thin-film transistors (TFTs) has seen substantial improvements over the past few years. For example, the field-effect mobility of organic TFTs has been increased up to about 40 cm^2/Vs [1]. But a large carrier mobility is only one of the factors that are important for the commercial applicability of organic TFTs. The long-term stability of the carrier mobility (and that of the other electrical TFT parameters, including the on/off current ratio, the threshold voltage, and the subthreshold slope) is also a critical requirement. The mechanisms by which the carrier mobility of organic TFTs degrades during long-term storage in ambient air (or in other environments that contain oxygen and/or humidity) are still under debate, and only some aspects of this degradation are understood.

For example, if the organic molecules are susceptible to oxidation (as is the case with pentacene [2]), oxidation of the molecules may lead to the loss of π-conjugation, so that the oxidation products no longer participate in charge transport, or they may form charge traps, both of which will cause the carrier mobility to drop. But even if the conjugated molecules are stable against oxidation, the carrier mobility of organic TFTs can degrade during long-term exposure to oxygen and/or humidity, for example as a result of the intercalation of oxygen and/or water into the organic semiconductor layer or due to the oxygen- or water-induced formation of charge traps at the semiconductor/dielectric interface. Water was unambiguously identified to lead to a degradation of the carrier mobility of pentacene transistors, both in the case of polycrystalline thin films of pentacene [3,4] as well as in the case of pentacene single-crystals [5]. This water-induced mobility degradation was attributed to the generation of scattering sites by the intercalation of water either into the crystals [5] or into the grain boundaries of the polycrystalline films [3]. Furthermore, it was shown that water leads to an increase of the off-state drain current of pentacene TFTs, possibly by introducing mobile species into the semiconductor film [3,4]. Unlike the effects of water, for which there seems to be some consensus, as described above, the effects of oxygen on the electrical parameters of pentacene FETs are still controversially discussed in literature.

---

* Corresponding author at: BASF SE, 67056 Ludwigshafen, Germany.
E-mail address: thomas.weitz@basf.com (R.T. Weitz).

[1] Current address: Institute of Organic Chemistry II, University Erlangen-Nürnberg, 91054 Erlangen, Germany.

http://dx.doi.org/10.1016/j.orgel.2015.07.060
1566-1199/© 2015 Elsevier B.V. All rights reserved.

Observations range from the oxygen-induced generation of trap states deep in the bandgap that degrade either the entire current–voltage characteristics [6] or only the subthreshold behavior [7] to an oxygen-induced increase of the on-state drain current [5] that was attributed to a change of the work function of the gold source/drain contacts of the TFTs [8]. Interestingly, the opposite effect, i.e., an oxygen-induced decrease of the on-state drain current along with a positive shift of the threshold voltage have also been reported for pentacene TFTs [9].

For p-channel TFTs based on semiconducting polymers, de Leeuw and co-workers have developed a theory to explain the often-observed shift of the threshold voltage during prolonged negative gate-bias stress by an electrolytic generation of protons from water at the semiconductor/dielectric interface [10].

For n-channel organic TFTs, significantly fewer studies have been conducted so far [11]. Aguirre et al. showed the degradation of electron transport due to the redox reaction between solvated oxygen in single-walled carbon nanotube FETs [12]. Hang et al. showed for polymer FETs based on poly{[N,N′-bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-alt-5,5′-(2,2′-bisthiophene)} (P(NDI2OD-T2)) that both oxygen and water form traps in this semiconductor [13]. This observation is in agreement with previous reports by Di Pietro et al. [14] who found that the exposure of P(NDI2OD-T2) to oxygen leads to the formation of an oxygen/P(NDI2OD-T2) complex that acts as an electron trap with an energy level of 0.34 eV below the LUMO level, and that this trap state has a negative effect on the electron mobility [14]. Di Pietro et al. also found that in the presence of water (or water and oxygen), electron traps in the form of OH^- groups are created that cause a decrease of the carrier mobility and a positive shift of the threshold voltage [14,15].

Here we investigate the stability of the electrical parameters of n-channel TFTs based on the small-molecule semiconductor N,N′-bis(2,2,3,3,4,4,4-heptafluorobutyl-1,7-dicyano-perylene-(3,4:9,10)-tetracarboxylic diimide PDI-FCN_2, Fig. 1a) in four different environments: dry nitrogen, dry air, wet nitrogen and ambient (humid) air. Conjugated molecules of this type are known to be inert with respect to photo-oxidation [16], so in evaluating the degradation processes we will assume that the molecules themselves remain intact and that the observed degradation occurs only within the semiconductor film.

PDI-FCN_2 was selected for this study because of its superior combination of performance [17] and air stability [17] and was synthesized by previously reported methods [17]. TFTs were fabricated by vacuum deposition of a 30 nm thick layer of the organic semiconductor onto a doped silicon wafer covered with a 100 nm thick thermally grown SiO_2 gate dielectric passivated with a self-assembled monolayer (SAM) of octadecyltrichlorosilane (OTS). The OTS SAM was prepared from the vapor phase by placing the oxygen-plasma-activated substrate along with a small amount of OTS into a desiccator continuously purged with dry nitrogen, and heating the desiccator to a temperature of 150 °C in an oven for about 4 h. Compared with the preparation of OTS SAMs from solution, the vapor-phase method can be helpful in preventing the undesirable polymerization of OTS. The silicon wafer serves both as the substrate and as the gate electrode of the TFTs. During the vacuum deposition of the organic semiconductor, the substrate was held at a temperature of 120 °C in order to allow the molecules to form a well-ordered polycrystalline film [18]. Gold source and drain contacts were then deposited by vacuum evaporation through a shadow mask. A schematic cross-section of the devices is shown in Fig. 1b.

In order to ensure good process uniformity, all TFTs employed in this study were fabricated on the same substrate within the same deposition run. After deposition of the source/drain contacts onto the semiconductor layer, the substrate was divided into four pieces, and several TFTs on each piece were electrically characterized. Devices were then stored for 42 days in desiccators under four different environments: Dry nitrogen (relative humidity 5%), dry air (relative humidity 5%), wet nitrogen (relative humidity >97%) and ambient air (relative humidity ~50%). The desiccators were not intentionally protected from the weak yellow laboratory light. For the electrical measurements, which were performed in ambient air under yellow light, the samples were briefly removed from the desiccators. In order to make sure that the observed evolution of the carrier mobility and the threshold voltage was not affected by the operation of the transistors in the laboratory ambient [19], we monitored for the first five days also TFTs that had not been previously measured. It was found that the evolution of the carrier mobility of pristine TFTs and of TFTs that had been previously measured were identical. We can therefore safely assume that the observed degradation was not induced by the electric fields applied during the measurements, but stems from processes that occur in the absence of externally applied voltages. Also, the applied gate-source voltage was always limited to 30 V in order to minimize bias-induced shifts of the threshold voltage or changes in the hysteresis in the transfer characteristics.

Fig. 2 shows the transfer characteristics of the TFTs measured immediately after device fabrication and the transfer curves recorded after the TFTs had been stored for 42 days in dry nitrogen, dry air, wet nitrogen and ambient air (for the plots showing the square root of the drain current, please refer to the Supplementary data). During these 42 days, we periodically measured the transfer characteristics and extracted the saturation mobility and the threshold voltage (compare Fig. 3). As can be seen, the carrier mobility of all TFTs decreases and the threshold voltage

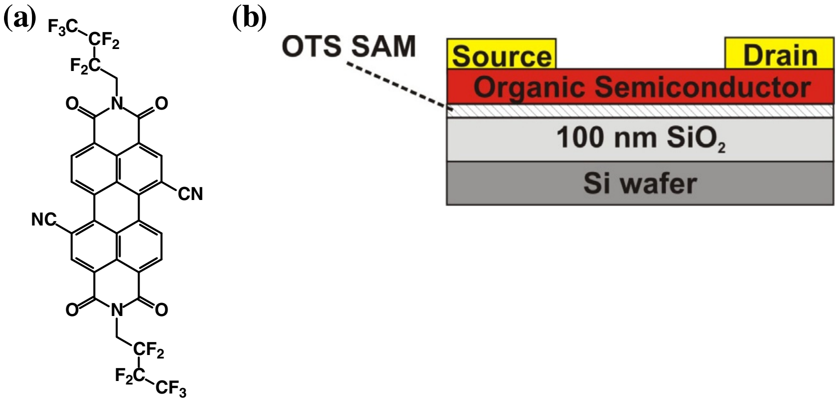


Fig. 1. (a) Chemical structure of the organic semiconductor PDI-FCN_2 (b) schematic cross-section of the thin-film transistors.

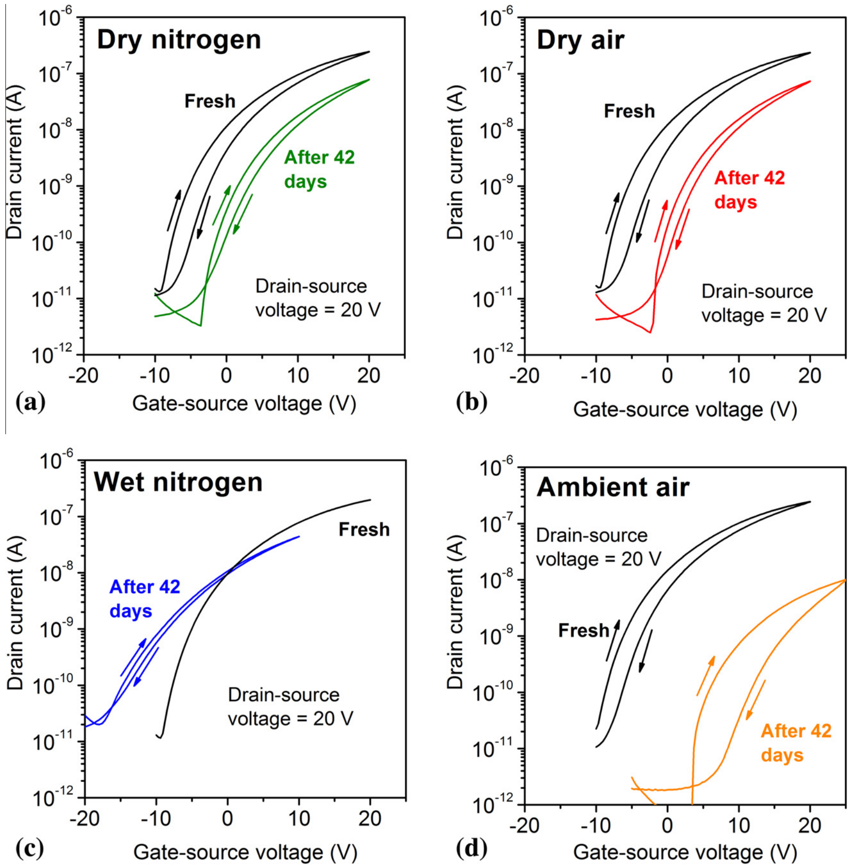


Fig. 2. Transfer characteristics of PDI-FCN$_2$ TFTs measured immediately after device fabrication and measured again after the devices had been stored for 42 days in (a) dry nitrogen (relative humidity 5%), (b) dry air (relative humidity 5%), (c) wet nitrogen (relative humidity > 97%) or (d) ambient air (relative humidity ~50%). The desiccators were not protected from the weak yellow laboratory light. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

of all TFTs shifts over time, regardless of the environment in which the devices were stored, as expected for polycrystalline thin films of PDI-FCN$_2$ [20]. However, the rate at which the parameters change as well as the direction of the threshold-voltage shift are affected significantly by the environment.

Fig. 2a shows that when the TFTs are stored for 42 days in dry nitrogen, the mobility decreases by a factor of two, and the threshold voltage shifts towards more positive values, from −4 V to +2 V. See also Table 1 for a summary of the electrical data. The observation that the TFT parameters change in dry nitrogen, i.e., under inert conditions, may initially be surprising. However, for TFTs based on other organic semiconductors, such as copper phthalocyanine (CuPc), it was previously shown that the thin-film morphology and thus the HOMO and LUMO energies of the semiconductor can change over time when exposed to nitrogen [21]. This was ascribed to a slight increase of the disorder in the molecular packing structure by the diffusion of nitrogen into the semiconductor film. In our experiments, the same mechanism may be responsible for the observed drop of the carrier mobility. Increased disorder can be expected to also degrade the subthreshold slope, which is indeed consistent with our observations (Table 1).

A comparison between Fig. 2a and b shows that the changes in the carrier mobility, the threshold voltage and the subthreshold slope of TFTs exposed to dry air are virtually identical to those of TFTs exposed to dry nitrogen, despite the fact that dry air contains oxygen. This finding is surprising, since it has been reported that in n-channel TFTs based on other organic semiconductors, for example P(NDI2OD-T2), exposure to dry oxygen leads to the formation of shallow electron traps in the semiconductor layer [14]. Apparently, this effect does not occur in the PDI-FCN$_2$ TFTs investigated here, possibly due to the fact that PDI-FCN$_2$ has a lower-lying LUMO level (4.5 eV below vacuum [22]) than P(NDI2OD-T2) (4.0 eV below vacuum [23]).

Fig. 2c and d show that water has a much stronger effect on the electrical parameters of the PDI-FCN$_2$ TFTs than dry nitrogen and dry oxygen. During 42 days of storage in a wet nitrogen environment with >97% humidity, the threshold voltage shows a large shift towards more negative values, from −4 to about −12 V, and the carrier mobility decreases by a factor of 4. The large negative shift of the threshold voltage cannot be explained by an electrochemical instability of the semiconducting molecules towards water, because the electrochemical potential at which water dissociates is much smaller than the first reduction potential of PDI-FCN$_2$ ($2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ @ −0.658 V [24], PDI-FCN$_2$ → PDI-FCN$_2^+$ + e^- @ 0.04 V [22], all values taken versus saturated calomel electrode, SCE). The large observed threshold-voltage shift is also not consistent with the introduction of a dipole layer of water molecules at the semiconductor/dielectric interface, because the dipole moment of water (1.84 D) is too small to produce such a large threshold-voltage shift (for which a dipole moment greater than 10 D would be required [25]). Our observation of a negative threshold-voltage shift induced by exposure to water is also at odds with a previous report by Di Pietro et al. who observed that the threshold voltage of n-channel polymer TFTs based on P(NDI2OD-T2) shifts in the positive (as opposed to the negative) direction upon exposure to water [14]. The negative threshold-voltage shift in our TFTs is also inconsistent with

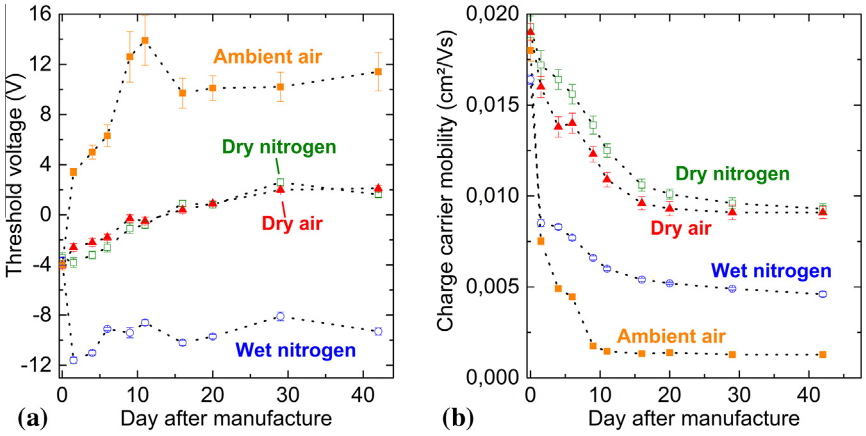


Fig. 3. Evolution of (a) the threshold voltage and (b) the carrier mobility of PDI-FCN$_2$ TFTs during storage of the devices in dry nitrogen, dry air, wet nitrogen, and ambient air. Each data point is an average of five TFTs.

Table 1
Evolution of the electrical data of PDI-FCN$_2$ TFTs during storage of the devices in dry nitrogen, dry air, wet nitrogen, and ambient air. The change in mobility Δ between day 1 and day 42 is given in percent of the initial mobility.

	Subthreshold slope (V/dec)			Hysteresis (at 10^{-9} A) (V)		
	Day1	Day 42	Δ	Day 1	Day 42	Δ
Dry N$_2$	1.4	1.5	0.1	2.5	1.7	−0.9
Wet N$_2$	1.7	3.7	2		1.1	−1.4
Dry air	1.4	1.6	0.2		1.5	−1
Ambient air	1.5	0.6	−0.9		5.6	2.9
	Mobility (cm^2/Vs)			Threshold voltage (V)		
	Day1	Day 42	Δ (%)	Day 1	Day 42	Δ
Dry N$_2$	0.0193	0.0093	48	−3.4	1.6	+5
Wet N$_2$	0.0164	0.0046	28	−3.7	−9.3	− 5.6
Dry air	0.019	0.0091	48	−4	2.1	+6.1
Ambient air	0.018	0.0013	7	−4	11.4	+15.4

the positive threshold-voltage shift which Kumaki et al. have reported for n-channel TFTs based on a benzothiadiazole (BDT) derivative during storage in ambient air and which they attributed to the water-induced deprotonation of SiOH groups on the surface of the SiO$_2$ gate dielectric (which had not been passivated with a SAM), according to the reaction SiOH + H$_2$O → SiO$^-$ + H$_3$O$^+$ [26]. In our TFTs, the density of silanol groups on the SiO$_2$ surface is greatly reduced by the hydrophobic OTS SAM, and even if the effect of the SAM was diminished by a conceivably incomplete coverage, the threshold voltage would be expected to shift towards more positive values, according to Kumaki et al., whereas a negative shift is observed in our TFTs during storage in wet nitrogen, so that a reaction of water with the SiO$_2$ surface can be ruled out in the case of our TFTs. Along with the negative threshold-voltage shift and the significant decrease of the carrier mobility in our devices, a significant degradation of the subthreshold slope can also be seen (Table 1). A possible explanation is that the water molecules induce the formation of charge traps, including a weak doping of the semiconductor with electrons; this would explain the negative threshold-voltage shift, the degradation of the subthreshold slope, and the decrease of the carrier mobility.

A comparison between Fig. 2a and c shows that the transfer characteristics of PDI-FCN$_2$ TFTs exposed to water show a slightly smaller hysteresis than the transfer curves of the devices that had been exposed to a dry environment. It seems that in our experiment the hysteresis is suppressed by water. This finding is in contrast to previous reports which have shown water to be the cause of a hysteresis in the transfer characteristics, for example in field-effect transistors based on carbon nanotubes [27].

Finally, we turn to the TFTs that were stored in ambient air, thus being exposed to both oxygen and water. These TFTs are characterized by a significant shift of the threshold voltage towards more positive values by about 16 V, and by a substantial decrease of the carrier mobility by more than one order of magnitude. Also, the transfer characteristics of these TFTs have a significantly larger hysteresis (Table 1). All of these observations can be explained by an electrochemical instability of the semiconductor anion towards oxygen and water. The redox potential at which the oxidation of the radical anion occurs is well below that at which oxygen and water dissociate, according to the reaction $O_2 + 2H_2O + 4e^- \rightarrow 4HO^-$ (at 0.571 V versus SCE) [24]. The same mechanism was previously also held responsible for the observation of a decrease of the electron conductivity of field-effect transistors based on semiconducting single-walled carbon nanotubes [12]. The fact that anions of the organic semiconductor are indeed present in the thin film is supported by the observation that the fresh TFTs have a negative threshold voltage (see Fig. 2d). Since OH$^-$ ions screen the gate field, their presence at the semiconductor/dielectric interface leads to a positive shift of the threshold voltage and an increase in the hysteresis [14]. Furthermore, such electron traps have also been shown to lead to a decrease of the carrier mobility [14]. Comparing Fig. 2c (wet nitrogen) and 2d (ambient air) it is apparent that the combined effects of oxygen and water are more severe (threshold-voltage shift by +15.4 V and increase of the hysteresis) than the effect of water alone (threshold-voltage shift by −5.6 V and reduction of the hysteresis). We believe this can be explained by the different interaction mechanisms of the different environments with the semiconductor: The simultaneous presence of oxygen and water leads to an electrochemical oxidation of the radical anion of the organic semiconductor and therefore to a strong influence on the electrical parameters (decrease of the carrier mobility, shift of the threshold voltage, increase of the hysteresis). In contrast, water alone interacts only weakly with the semiconductor, without causing an electrochemical instability, so that the changes in the electrical TFT characteristics are smaller.

Further insight into the degradation mechanism can be gained by comparing the timescale of the evolution of the threshold voltage and the carrier mobility for the TFTs stored under different environments (Fig. 3). It appears that there are two distinct, independent processes with different time constants that contribute to the degradation. Storing the TFTs in a dry environment leads to a slow increase of the threshold voltage and a slow decrease of the electron mobility on the timescale of a few days. This process is possibly related to a slow reorientation of PDI-FCN$_2$ molecules within the semiconductor film, at the grain boundaries or at the semiconductor/dielectric interface. On the other hand, storing the TFTs in a wet or humid environment (containing O_2, N_2 and H_2O) leads to a dramatic change of both the threshold voltage (negative shift in the case of H_2O, positive shift in the case of ambient air) and the carrier mobility within the first day. However, following this very fast initial degradation due to an electrochemical instability caused by humidity, the further degradation appears to proceed at a much slower rate, similar to the slow rate at which the TFTs are seen to degrade in the dry environments, and the threshold voltage begins to shift back towards more positive values. Thus, it appears that the degradation in wet or humid environment is caused by two distinct processes described above with different time constants.

In summary, we have investigated the stability of the electrical characteristics of organic n-channel TFTs based on vacuum-deposited thin films of the small-molecule semiconductor PDI-FCN_2 during long-term storage in four different environments. We have found that two independent mechanisms lead to a degradation of the electron mobility and to a shift of the threshold voltage of the devices. When the TFTs are stored in dry nitrogen or dry oxygen, the threshold voltage shifts by about 6 V towards more positive values within about 20 days, and this shift is accompanied by a decrease of the carrier mobility by a factor of two. We attribute this degradation to morphological changes in the semiconductor layer. This degradation route is also present when the TFTs are stored in wet nitrogen or in ambient (i.e., humid) air. In the latter two environments, an additional and much faster degradation route opens up, with a time constant on the order of one day. The cause of the negative threshold-voltage shift and the simultaneous decrease of the carrier mobility in the presence of humidity is not entirely clear. In ambient air (where both water and oxygen are present), the TFTs degrade due to an electrochemical instability of the semiconductor radical anion via the degradation route $O_2 + 2H_2O + 4e^- \rightarrow 4HO^-$. The OH^- ions act as charge traps, and consequently lead to a decrease in the carrier mobility, and since they also screen the gate field, a significant shift of the threshold voltage towards more positive values is observed. Our results show that for an efficient long-term operation of PDI-FCN_2 TFTs, the semiconductor layer should be protected from water, while an additional protection from oxygen is not necessary.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.orgel.2015.07.060.

References

[1] Y. Diao, B.C.K. Tee, G. Giri, J. Xu, D.H. Kim, H.A. Becerril, R.M. Stoltenberg, T.H. Lee, G. Xue, S.C.B. Mannsfeld, Z. Bao, Solution coating of large-area organic semiconductor thin films with aligned single-crystalline domains, Nat. Mater. 12 (7) (2013) 665–671.

[2] F. De Angelis, M. Gaspari, A. Procopio, G. Cuda, E. Di Fabrizio, Direct mass spectrometry investigation on pentacene thin film oxidation upon exposure to air, Chem. Phys. Lett. 468 (4–6) (2009) 193–196.

[3] D.W. Li, E.J. Borkent, R. Nortrup, H. Moon, H. Katz, Z.N. Bao, Humidity effect on electrical performance of organic thin-film transistors, Appl. Phys. Lett. 86 (2005) 4.

[4] F. De Angelis, S. Cipolloni, L. Mariucci, G. Fortunato, Aging effects in pentacene thin-film transistors: analysis of the density of states modification, Appl. Phys. Lett. 88 (2006) 19.

[5] O.D. Jurchescu, J. Baas, T.T.M. Palstra, Electronic transport properties of pentacene single crystals upon exposure to air, Appl. Phys. Lett. 87 (2005) 5.

[6] L. Tsetseris, S.T. Pantelides, Intercalation of oxygen and water molecules in pentacene crystals: first-principles calculations, Phys. Rev. B 75 (2007) 15.

[7] A. Benor, A. Hoppe, V. Wagner, D. Knipp, Electrical stability of pentacene thin film transistors, Org. Electron. 8 (6) (2007) 749–758.

[8] A. Vollmer, O.D. Jurchescu, I. Arfaoui, I. Salzmann, T.T.M. Palstra, P. Rudolf, J. Niemax, J. Pflaum, J.P. Rabe, N. Koch, The effect of oxygen exposure on pentacene electronic structure, Eur. Phys. J. E 17 (3) (2005) 339–343.

[9] S.H. Han, J.H. Kim, J. Jang, S.M. Cho, M.H. Oh, S.H. Lee, D.J. Choo, Lifetime of organic thin-film transistors with organic passivation layers, Appl. Phys. Lett. 88 (2006) 7.

[10] A. Sharma, S.G.J. Mathijssen, M. Kemerink, D.M. de Leeuw, P.A. Bobbert, Proton migration mechanism for the instability of organic field-effect transistors, Appl. Phys. Lett. 95 (2009) 25.

[11] W.H. Lee, H.H. Choi, D.H. Kim, K. Cho, 25th anniversary article: microstructure dependent bias stability of organic transistors, Adv. Mater. 26 (11) (2014) 1660–1680.

[12] C.M. Aguirre, P.L. Levesque, M. Paillet, F. Lapointe, B.C. St-Antoine, P. Desjardins, R. Martel, The role of the oxygen/water redox couple in suppressing electron conduction in field-effect transistors, Adv. Mater. 21 (30) (2009). 3087-+.

[13] D.K. Hwang, C. Fuentes-Hernandez, M. Fenoll, M. Yun, J. Park, J.W. Shim, K.A. Knauer, A. Dindar, H. Kim, Y. Kim, J. Kim, H. Cheun, M.M. Payne, S. Graham, S. Im, J.E. Anthony, B. Kippelen, Systematic reliability study of top-gate p- and n-channel organic field-effect transistors, Acs Appl. Mater. Interfaces 6 (5) (2014) 3378–3386.

[14] R. Di Pietro, D. Fazzi, T.B. Kehoe, H. Sirringhaus, Spectroscopic investigation of oxygen- and water-induced electron trapping and charge transport instabilities in n-type polymer semiconductors, J. Am. Chem. Soc. 134 (36) (2012) 14877–14889.

[15] R. Di Pietro, H. Sirringhaus, High resolution optical spectroscopy of air-induced electrical instabilities in n-type polymer semiconductors, Adv. Mater. 24 (25) (2012) 3367–3372.

[16] F. Wurthner, Perylene bisimide dyes as versatile building blocks for functional supramolecular architectures, Chem. Commun. 14 (2004) 1564–1579.

[17] B.A. Jones, M.J. Ahrens, M.H. Yoon, A. Facchetti, T.J. Marks, M.R. Wasielewski, High-mobility air-stable n-type semiconductors with processing versatility: dicyanoperylene-3,4:9,10-bis(dicarboximides), Angew. Chem. Int. Ed. 43 (46) (2004) 6363–6366.

[18] R.T. Weitz, K. Amsharov, U. Zschieschang, E.B. Villas, D.K. Goswami, M. Burghard, H. Dosch, M. Jansen, K. Kern, H. Klauk, Organic n-channel transistors based on core-cyanated perylene carboxylic diimide derivatives, J. Am. Chem. Soc. 130 (14) (2008) 4637–4645.

[19] D. Knipp, J.E. Northrup, Electric-field-induced gap states in pentacene, Adv. Mater. 21 (2009). 2511-+.

[20] R.T. Weitz, K. Amsharov, U. Zschieschang, M. Burghard, M. Jansen, M. Kelsch, B. Rhamati, P.A. van Aken, K. Kern, H. Klauk, The importance of grain boundaries for the time-dependent mobility degradation in organic thin-film transistors, Chem. Mater. 21 (20) (2009) 4949–4954.

[21] T. Sueyoshi, H. Kakuta, M. Ono, K. Sakamoto, S. Kera, N. Ueno, Band gap states of copper phthalocyanine thin films induced by nitrogen exposure, Appl. Phys. Lett. 96 (2010) 9.

[22] B.A. Jones, A. Facchetti, M.R. Wasielewski, T.J. Marks, Tuning orbital energetics in arylene diimide semiconductors. Materials design for ambient stability of n-type charge transport, J. Am. Chem. Soc. 129 (49) (2007) 15259–15278.

[23] H. Yan, Z. Chen, Y. Zheng, C. Newman, J.R. Quinn, F. Dotz, M. Kastler, A. Facchetti, A high-mobility electron-transporting polymer for printed transistors, Nature 457 (7230) (2009). 679-U1.

[24] D.M. deLeeuw, M.M.J. Simenon, A.R. Brown, R.E.F. Einerhand, Stability of n-type doped conducting polymers and consequences for polymeric microelectronic devices, Synthetic Met. 87 (1) (1997) 53–59.

[25] S.K. Possanner, K. Zojer, P. Pacher, E. Zojer, F. Schuerrer, Threshold voltage shifts in organic thin-film transistors due to self-assembled monolayers at the dielectric surface, Adv. Funct. Mater. 19 (6) (2009) 958–967.

[26] D. Kumaki, T. Umeda, S. Tokito, Influence of H(2)O and O(2) on threshold voltage shift in organic thin-film transistors: Deprotonation of SiOH on SiO(2) gate-insulator surface, Appl. Phys. Lett. 92 (2008) 9.

[27] R.T. Weitz, U. Zschieschang, F. Effenberger, H. Klauk, M. Burghard, K. Kern, High-performance carbon nanotube field effect transistors with a thin gate dielectric based on a self-assembled monolayer, Nano Lett. 7 (1) (2007) 22–27.

Supplementary material for:

Separating the Impact of Oxygen and Water on the Long-Term Stability of n-Channel Perylene Diimide Thin-Film Transistors

Ute Zschieschang[1], Konstantin Amsharov[1,#], Martin Jansen[1], Klaus Kern[1,2], Hagen Klauk[1],
R. Thomas Weitz[*1,+],

1: Max Planck Institute for Solid State Research, Heisenbergstr. 1, 70569 Stuttgart, Germany
2: Institut de Physique de la Matière Condensée, Ecole Polytechnique Fédérale de Lausanne,
1015 Lausanne, Switzerland

+ current address: BASF SE, 67056 Ludwigshafen, Germany
# current address: Institute of Organic Chemistry II, University Erlangen-Nürnberg, 91054 Erlangen, Germany
* Corresponding author: thomas.weitz@basf.com

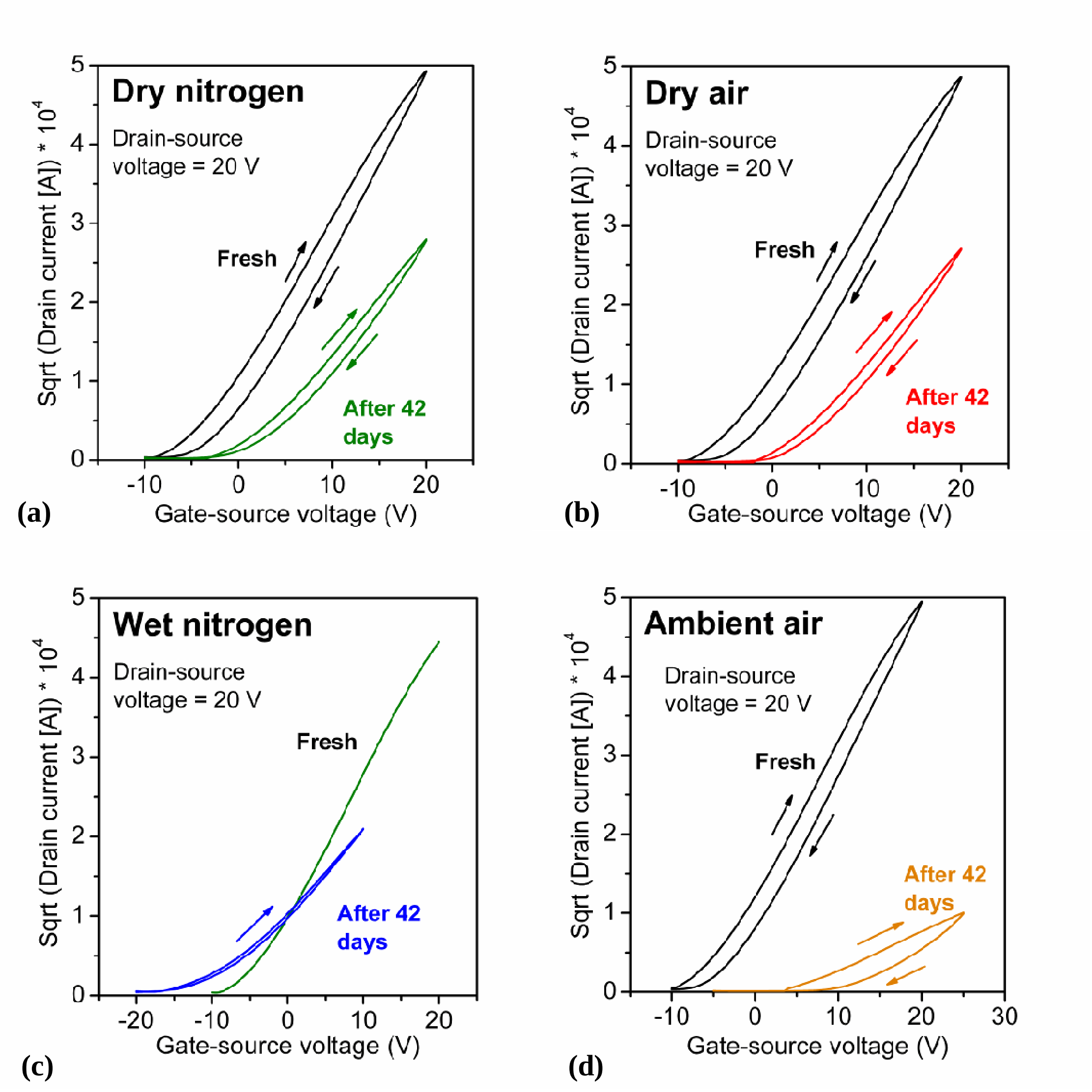


Figure S1. Square root of the drain current as a function of the gate-source voltage of PDI-FCN_2 TFTs measured immediately after device fabrication and measured again after the devices had been stored for 42 days in **(a)** dry nitrogen (relative humidity 5%), **(b)** dry air (relative humidity 5%), **(c)** wet nitrogen (relative humidity >97%) or **(d)** ambient air (relative humidity ~50%). The desiccators were not protected from the weak yellow laboratory light. The data are the same as those shown in Figure 2.