

# Air-stable, high-performance organic n-channel transistors

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Organic thin-film transistors (TFTs) are of interest for flexible, large-area electronics applications, such as rollable or foldable information displays, conformable sensor arrays, and plastic circuits [1]. The vast majority of the organic TFTs that have been developed to date are p-channel TFTs, meaning that the electric currents in these transistors are due to the flow of positive charge carriers. Even if only p-channel TFTs were available, all types of electronic systems could in principle be realized, which would suggest that there is no fundamental reason to also develop organic n-channel TFTs (in which the currents are due to negative charge carriers). However, many of the applications envisioned for organic TFTs are mobile devices for which a low power consumption is one of the most critical requirements. From a circuit-design perspective, the most effective approach to minimize the power consumption of electronic systems is to combine p-channel and n-channel transistors in a complementary design. In complementary circuits, the current path between the supply-voltage rail and the ground rail is always blocked either by one of the p-channel transistors or by one of the n-channel transistors (except for a brief period during switching). In contrast, the power consumption of unipolar circuits (which use only one transistor type) is dominated by the existence of significant leakage paths not only during switching, but also whenever the circuit is in one of the two static states.

The fact that the realization of air-stable, high-performance organic n-channel TFTs is more difficult than that of organic p-channel TFTs has to do with the orbital energies of organic semiconductors. In organic p-channel TFTs, the energy of the positive charge carriers that contribute to the electric current is close to the energy of the highest occupied molecular orbital (HOMO) of the semiconductor, which for most of the conjugated hydrocarbons considered for organic electronics is about 4.5 to 5.5 eV below the vacuum level. This energy is sufficiently deep below the vacuum level so that oxygen or moisture has little or no effect on the charge-carrier transport in these semiconductors. In addition, the Fermi level of noble (i.e., non-oxidizing) metals, such as gold, happens to fall into this energy range, so that the energy barrier that impedes the exchange of charges between the metallic source and drain contacts and the organic semiconductor can be vanishingly small. As a result, organic p-channel TFTs with excellent air stability, negligible contact resistance, and encouraging static and dynamic performance have already been demonstrated [2,3].

In contrast, in organic n-channel TFTs, the charge-transport level is close to the energy of the lowest unoccupied molecular orbital (LUMO), which in many hydrocarbons is typically about 2.5 to 3.5 eV below the vacuum level. Thus, unless the organic semiconductor layer is carefully protected from ambient air, the charge transport will be significantly affected by oxygen or moisture. In addition, the energy barrier between the Fermi level of noble metals (about 5 eV in the case gold) and the LUMO level of typical hydrocarbon-based organic semiconductors may be as large as 1.5 to 2.5 eV and will therefore substantially impede the charge exchange between the source/drain contacts and the semiconductor. Replacing gold with a low-workfunction (i.e., rapidly oxidizing) metal, such as aluminum, magnesium or calcium, could in theory provide a smaller energy barrier, but at the expense of the spontaneous formation of an insulating native oxide layer at the metal/semiconductor interface, which would be just as detrimental as a large energy barrier.

A key strategy in the quest for air-stable, high-performance organic n-channel TFTs is therefore the synthesis of conjugated organic semiconductors that have a LUMO energy in the range of 4.0 to 4.5 eV. This can be accomplished by incorporating strongly electronegative moieties, such as imide groups, cyano groups, or halogens, into the conjugated core of the molecule. In addition, fluoroalkyl substituents attached to the ends of the molecule have been found to be effective in providing additional stability against oxygen and moisture.

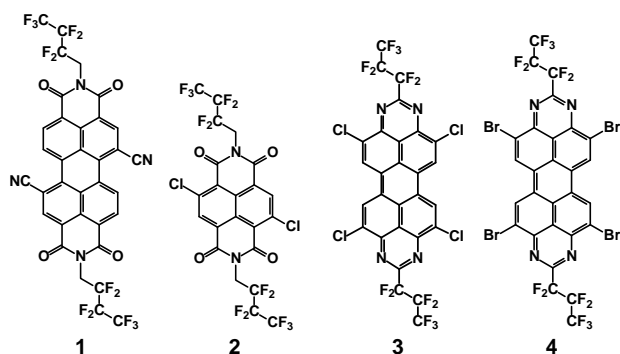


Figure 1: Chemical structures of compounds **1-4**, all of which have shown great potential for air-stable, high-performance organic n-channel thin-film transistors.

Figure 1 shows the molecular structures of four organic semiconductors that have been successfully synthesized by various groups over the past few years and which have demonstrated excellent air stability and promising static and dynamic performance in organic n-channel TFTs. Compound **1**, bisheptafluorobutyl-dicyano-perylene tetracarboxylic diimide (PTCDI-(CN)<sub>2</sub>-(CH<sub>2</sub>C<sub>3</sub>F<sub>7</sub>)<sub>2</sub>), was developed in 2004 in the group of Antonio Facchetti and is now commercially available from Polyera Corp. as ActivInk<sup>TM</sup> N1100. Compound **2**, bisheptafluorobutyl-dichloro-naphthalene tetracarboxylic diimide (NTCDI-Cl<sub>2</sub>-(CH<sub>2</sub>C<sub>3</sub>F<sub>7</sub>)<sub>2</sub>), was developed in the group of Frank Würthner at the University of Würzburg and is now commercialized by BASF. Compound **3**, bisperfluoropropyl-tetrachloro-tetraazaperopyrene (TAPP-Cl<sub>4</sub>-(C<sub>3</sub>F<sub>7</sub>)<sub>2</sub>) [4], and compound **4**, bisperfluoropropyl-tetrabromo-tetraazaperopyrene (TAPP-Br<sub>4</sub>-(C<sub>3</sub>F<sub>7</sub>)<sub>2</sub>), were developed in the group of Lutz Gade at the University of Heidelberg. Owing to the strategic incorporation of various strongly electronegative substituents and fluoroalkyl chains, the LUMO energies of compounds **1-4** are between 4.0 and 4.5 eV.

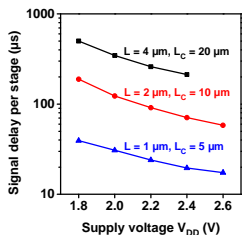
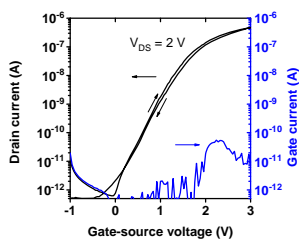


Figure 2:

(a) Current-voltage characteristics of an n-channel TFT based on compound **2** fabricated on a plastic substrate and operated in ambient air without any encapsulation.  
 (b) Signal propagation delay per stage as a function of supply voltage of a flexible 11-stage organic complementary ring oscillator using n-channel TFTs based on compound **2** and p-channel TFTs based on DNNT.

Out of the more than 100 compounds which we have investigated since 2009 in the BMBF-funded multi-partner project *Polytos*, compounds **1-4** have shown the most promising characteristics in view of air-stable organic n-channel TFTs and organic complementary circuits. Figure 2a shows the static current-voltage characteristics of an n-channel TFT based on compound **2** fabricated on a plastic substrate (125- $\mu$ m-thick polyethylene naphthalate) with gold source and drain contacts and operated in ambient air without any encapsulation. Figure 2b shows the signal propagation delay per stage as a function of supply voltage of an 11-stage complementary ring oscillator, also fabricated on flexible PEN using n-channel TFTs based on compound **2** and p-channel TFTs based on dinaphtho[2,3-b:2',3'-f]thieno[3,2-b]thiophene (DNNT) [3], both with gold source and drain contacts and also operated in air without encapsulation. At a supply voltage of 2 V, the signal propagation delay is 20  $\mu$ sec per stage, making these the fastest organic complementary circuits reported to date at supply voltages below 10 V.

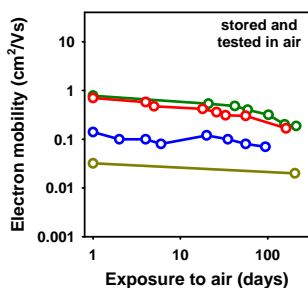


Figure 3: Evolution of the field-effect mobility of n-channel TFTs based on compounds **1-4**, demonstrating the excellent air stability of these four organic semiconductors.

The excellent air stability of organic n-channel TFTs based on compounds **1-4** is further illustrated in Figure 3. As can be seen, the electron mobility of all four TFTs shows only very little degradation over a period of several months in ambient air without encapsulation.

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