Plastic Transistors Reach Maturity for Mass Applications in Microelectronics**

Frank Würthner*

During the last decade of the twentieth century we witnessed a tremendous development in the field of organic materials for electronic devices. These practical applications were already initiated in 1977 by the revolutionary discovery of electrical conductivity in a polymer, polyacetylene, by Alan J. Heeger, Alan G. MacDiarmid, and Hideki Shirakawa who were awarded the Nobel prize for Chemistry in 2000.[1] However, the first technical applications of (semi)conducting organic materials were not realized as synthetic metals but as photoconductors in copiers and laser printers,[2] as light-emitting diodes (LEDs),[3] and as antistatic coatings.

For these applications it was of considerable importance that apart from optimized molecular properties (redox potentials, stability of radical cations, luminescence) amorphous solid-state materials could be derived which allow a hopping transport of the charges from one interface to the other without being hindered by grain boundaries such as occurs in polycrystalline materials. On the other hand, as a result of the high structural and energetic disorder only low charge-carrier mobilities are possible in these amorphous solid-state materials, which accordingly can not compete with inorganic semiconductors in terms of the switching frequencies demanded in semiconductor electronics.

An increase in the charge-carrier mobility by several orders of magnitude is feasible in more ordered organic materials if the π systems exhibit sufficient π overlap with adjacent molecules in the crystal lattice and if macroscopic ordering on a suitable substrate leads to a desired orientation and large domain sizes. Another important aspect for a successful implementation of organic semiconductors in microelectronic switching and memory devices is the availability of p-type (= hole-carrying) as well as n-type (= electron-carrying) semiconducting materials to enable important logic elements such as pn junction diodes, bipolar transistors, and complementary circuits to be prepared. After a short overview of the progress achieved in the development of transistors based on p-type semiconducting organic materials during the 1990s the recent breakthrough in n-semiconducting organic materials will be highlighted in this article.

Figure 1 shows the basic scheme of a field-effect transistor (FET) which contains a thin active layer of a semiconductive organic material. The latter may be prepared by vacuum deposition or, at lower costs, by liquid phase processing techniques. When a voltage is applied between the source and gate electrode charge carriers are injected into the semiconductor (positive charge carriers in p- and negative charge carriers in n-semiconductors) which leads to the formation of a conductive channel. It is important for the performance of the transistor that upon application of the gate bias a substantial increase in the conductivity from an initially nonconductive state into a highly conductive state takes place (on/off current ratio $>10^5$). After generation of the charge carriers at the insulator/semiconductor interface a current may flow from the source to the drain electrode, with the magnitude of the current being now mainly dependent on the source-drain voltage as well as the charge-carrier mobility.

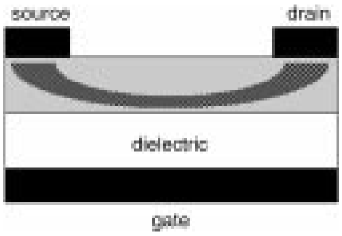


Figure 1. Schematic representation of an organic thin-film transistor (TFT) consisting of metallic contacts (black), a semiconducting organic layer (gray), and an insulating dielectric (white). After a voltage is applied at the gate electrode charges are injected into the semiconductor and a conductive channel (hatched in black) is generated between the source and drain electrodes. The charge carriers in these organic semiconductors are radical anions (n-type semiconductors) or radical cations (p-type semiconductors).

The only difference between these organic FETs and similarly constructed, commercially available TFT transistors[4] is the active layer, which contains an organic semiconductor instead of amorphous silicon. However, all-plastic chips based entirely on organic materials have already been

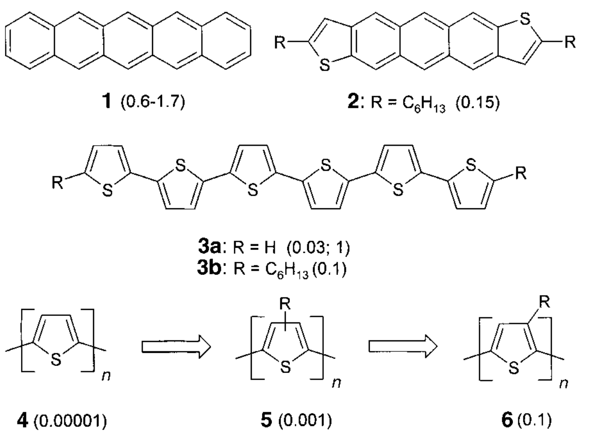
---

[*] Dr. F. Würthner
Abteilung Organische Chemie II
Universität Ulm
Albert-Einstein-Allee 11, 89081 Ulm (Germany)
Fax: (+49) 731-5022840
E-mail: frank.wuerthner@chemie.uni-ulm.de

[**] I wish to thank the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft for a Liebig and a Habilitanden fellowship, and Prof. Peter Bäuerle for numerous helpful discussions especially about the topic reviewed in this article.

demonstrated whose mechanical flexibility offers totally new perspectives to the rapidly growing market of identification and product tagging as well as for pixel drivers for flexible displays.[5, 6]

Currently, the most developed organic FETs are based on pentacene **1**[7] and oligo- or polythiophene **3**–**6** p-type semiconductors (Scheme 1).[8, 9] The highest charge-carrier mobilities (up to 1–2 $cm^2V^{-1}s^{-1}$) and the highest on/off ratios (more than 10^6) are realized by vacuum deposition of the low molar mass derivatives. Although these values are not in the range demanded for high-performance applications such as computer chips, they match the requirements for numerous other application such as pixel drivers for liquid crystal displays or basic switching and memory chips. It is known from X-ray diffraction data that these materials exhibit a crystalline ordering (in contrast to the above-mentioned amorphous semiconductors in xerography and in LEDs[2, 3]) which is essential for the high conductivity in the channel between the source and drain electrode.[8]



Scheme 1. Examples of p-type organic semiconductors with high field-effect mobilities (numbers in parentheses are in $cm^2V^{-1}s^{-1}$ for thin-film transistor devices; only the second value for **3a** was measured from a single crystal).

Interestingly also, (undoped)[10] polymeric materials with continuously increasing mobility have been prepared during the last few years despite the fact that they are more disordered and deposition from solution has to be carried out under less stringent conditions. In the case of polythiophenes an increase in the mobility from 10^{-5} (in 1986) up to 0.1 $cm^2V^{-1}s^{-1}$ (in 1998)[9] could be achieved by first improving the solubility (and the related processability) of the polymer by means of β-alkyl substituents (**5**) and finally increasing the supramolecular order by a regioregular attachment of these substituents at the polythiophene backbone (**6**).[8, 9] As a result of the regioregularity of these β-alkyl substituents highly ordered microcrystalline domains are formed which lead to a favorable merger of polymer-type properties (such as processability) with structural ordering, as is typically observed in liquid crystalline (microphase segregation) and crystalline materials (interdigitation of alkyl chains).[11]

In contrast to organic p-type semiconductors, n-type semiconductors remained less developed for a long time. This was partly a result of the lack of electron-poor polymers but also because of theoretical arguments which predict a reduced stability of the n-conducting radical anions under ambient conditions.[12] This situation is illustrated in Figure 2 for a number of typical electron-poor π systems which all exhibit reduction potentials below the half-wave potential of oxygen.[13] Therefore, from the thermodynamic point of view, vacuum conditions or encapsulated devices should be mandatory in the case of n-channel FETs.

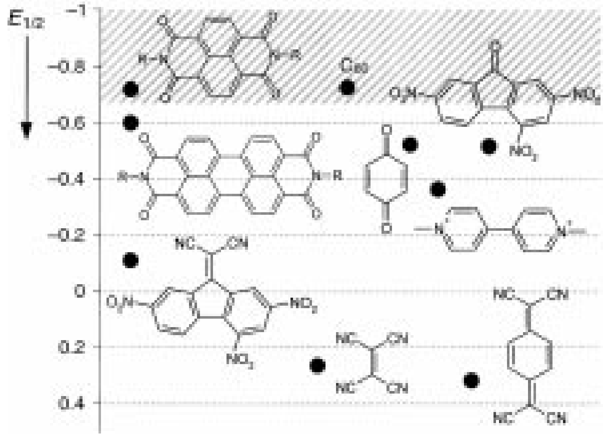
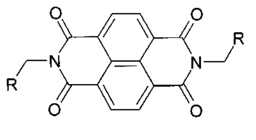


Figure 2. Reduction potentials $E_{1/2}$ in V (versus the standard calomel electrode) of potential n-type semiconductors according to cyclic voltammetric measurements made in solution. From the thermodynamic point of view none of these redox couples are sufficiently high to arrive at n-type doped materials which are stable under ambient conditions (oxygen reduction $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ at $E_{1/2} = +0.57$ V; water reduction $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ at $E_{1/2} = -0.66$ V (hatched area).[12]

Against this background the recent work of Katz and coworkers was very surprising. They reported high electron mobilities (>0.1 $cm^2V^{-1}s^{-1}$) and excellent on/off current ratios (>10^5) for the fluorine-substituted naphthalenebisimides **7a**, **b**, even in the presence of air.[14] These remarkable results can be explained by the following:[14a] 1) Naphthalenebisimide radical anions are generated by the gate bias. 2) There is a favorable macroscopic ordering of the naphthalenebisimide molecules at the semiconductor/insulator interface which allows for high lateral charge carrier mobilities (see Figure 1). 3) The remarkable stability of these transistors in air is the result of a dense packing of the fluorinated chains which prevents the penetration of oxygen and water into the n-conducting channel region. Comparative studies on *N*,*N*′-dialkyl- and -dibenzylnaphthalenebisimides **7c**, **d** did not show this quality, despite an even higher mobility of **7c** under ultra-high vacuum conditions (up to 0.16 $cm^2V^{-1}s^{-1}$).



7a: R = $(CF_2)_6CF_3$
7b: R = p-$CF_3C_6H_4$
7c: R = $(CH_2)_6CH_3$
7d: R = p-$CH_3C_6H_4$

In the meantime two more papers appeared on the electrochemical and crystallographic studies of these compounds and confirmed these initial statements. All the naphthalenebisimides studied exhibit reversible reduction waves in their cyclic voltammograms, with the highest value being for **7a** with a potential of about -0.6 V (versus SCE).[14b] The solid-state single-crystal X-ray crystallographic study on all the investigated compounds (**7a–c**)[14c] revealed layer structures which seem suited for charge transport within two dimensions (herringbone packing motif, similar to oligothiophenes[8]). These layers, especially in the case of **7a**, are separated by densely packed fluorinated chains that provide a barrier against the diffusion of oxygen into the n-type channel. Additional conductivity measurements as a function of temperature carried out on single crystals of **7c**, **d** suggest that a bandlike charge-transport mechanism occurs at temperatures <300 K.[14c]

In addition to these naphthalenebisimides, experiments performed on perfluorinated copper phthalocyanines,[15] perylenebisimides,[16] and α,α'-diperfluorohexyl-substituted sexithiophene[17] recently revealed impressive n-type mobilities. These results show there is now a higher variety of n- than p-type low molar mass materials. Moreover Schön et al. succeeded in the preparation of ambipolar FETs based on single crystals of pentacene (**1**)[18a] and sexithiophene (**3a**)[18b] which showed p- as well as n-type semiconductivity depending on the gate bias. After this encouraging progress it seems to be only a question of time until n-type semiconducting polymers and mass-produced chips are available which make use of the cost and processing advantages of organic compared to inorganic materials.

---

[1] H. Shirakawa, E. J. Louis, A. G. MacDiarmid, C. K. Chiang, A. J. Heeger, *J. Chem. Soc. Chem. Commun.* **1977**, 578–580.

[2] a) R. O. Loufty, A.-M. Hor, C.-K. Hsiao, G. Baranyi, P. Kazmaier, *Pure Appl. Chem.* **1988**, *60*, 1047–1054; b) H. Bässler, *Adv. Mater.* **1993**, *5*, 662–665.

[3] a) U. Mitschke, P. Bäuerle, *J. Mater. Chem.* **2000**, *10*, 1471–1507; b) A. Kraft, A. C. Grimsdale, A. B. Holmes, *Angew. Chem.* **1998**, *110*, 416–443; *Angew. Chem. Int. Ed.* **1998**, *37*, 402–428.

[4] TFTs (= Thin-Film Transistors) contain amorphous silicon as the semiconductive material (charge-carrier mobility about $0.5\ \mathrm{cm^2\,V^{-1}\,s^{-1}}$) whereas higher performance MOSFETs (= Metal Oxide Semiconductor FETs) use crystalline silicon to accomplish the high mobilities demanded for high switching frequencies.

[5] a) F. Garnier, R. Hajlaoui, A. Yassar, P. Srivastava, *Science* **1994**, *265*, 1684–1686; b) Z. Bao, Y. Feng, A. Dodabalapur, V. R. Raju, A. J. Lovinger, *Chem. Mater.* **1997**, *9*, 1299–1301.

[6] The Dutch electronic company Philips has already presented all-plastic display prototypes. In these devices not only is a flexible polymeric LED display used but in addition each pixel is driven individually by a thin-film transistor based on a polymeric semiconductor, see D. de Leeuw, *Physics World* **1999**, *12*(3) 31–34 and at www.research.philips.com.

[7] a) S. F. Nelson, Y.-Y. Lin, D. J. Gundlach, T. N. Jackson, *Appl. Phys. Lett.* **1998**, *72*, 1854–1856; b) J. H. Schön, S. Berg, C. Kloc, B. Batlogg, *Science* **2000**, *287*, 1022–1023; c) H. Klauk, D. Gundlach, J. A. Nichols, C. D. Sheraw, M. Bonse, T. N. Jackson, *Solid State Technol.* **2000**, *43*, 63–67.

[8] a) F. Garnier in *Electronic Materials: The Oligomer Approach* (Eds.: K. Müllen, G. Wegner), Wiley-VCH, Weinheim, **1998**, pp. 559–583; b) H. E. Katz, A. Dodabalapur, Z. Bao in *Handbook of Oligo- and Polythiophenes* (Ed.: D. Fichou), Wiley-VCH, Weinheim, **1999**, pp. 459–489; c) G. Horowitz, *J. Mater. Chem.* **1999**, *9*, 2021–2026.

[9] a) Z. Bao, A. Dodabalapur, A. J. Lovinger, *Appl. Phys. Lett.* **1996**, *69*, 4108–4110; b) H. Sirringhaus, N. Tessler, R. H. Friend, *Science* **1998**, *280*, 1741–1744.

[10] "Doping" (= oxidation or reduction) of uncharged polymers into the more conductive (that is, metallic) state leads to source-to-drain conduction, even in the absence of a gate voltage, thus causing low on/off current ratios.

[11] a) H. Sirringhaus, P. J. Brown, R. H. Friend, M. M. Nielsen, K. Bechgaard, B. M. W. Langeveld-Voss, A. J. H. Spiering, R. A. J. Janssen, E. W. Meijer, P. Herwig, D. M. de Leeuw, *Nature* **1999**, *401*, 685–588; b) The structure of two-dimensional layers of regioregular poly-(3-alkylthiophenes) were recently characterized by scanning tunneling microscopy, see E. Mena-Osteritz, A. Meyer, B. M. W. Langeveld-Voss, R. A. J. Janssen, E. W. Meijer, P. Bäuerle, *Angew. Chem.* **2000**, *112*, 2792–2796; *Angew. Chem. Int. Ed.* **2000**, *39*, 2680–2684.

[12] D. M. Leeuw, M. M. J. Simenon, A. R. Brown, R. E. F. Einerhand, *Synth. Met.* **1997**, *87*, 53–59.

[13] It has to be emphasized that redox potentials based on solution-phase cyclic voltammetry give only a crude estimate of the energy of the orbitals in the solid state because the influence of the electronic coupling to neighboring molecules and interfacial effects are neglected.

[14] a) H. E. Katz, A. J. Lovinger, C. Kloc, T. Siegrist, Y.-Y. Lin, A. Dodabalapur, *Nature* **2000**, *404*, 478–480; b) H. E. Katz, J. Johnson, A. J. Lovinger, W. Li, *J. Am. Chem. Soc.* **2000**, *122*, 7787–7792; c) H. E. Katz, T. Siegrist, J. H. Schön, C. Kloc, B. Batlogg, A. J. Lovinger, J. Johnson, *ChemPhysChem* **2001**, 167–172.

[15] Z. Bao, A. J. Lovinger, J. Brown, *J. Am. Chem. Soc.* **1998**, *120*, 207–208.

[16] a) C. W. Stuijk, A. B. Sieval, J. E. J. Dakhorst, M. van Dijk, P. Kimkes, R. B. M. Koehorst, H. Donker, T. J. Schaafsma, S. J. Picken, A. M. van de Craats, J. M. Warman, H. Zuilhof, E. J. R. Sudhölter, *J. Am. Chem. Soc.* **2000**, *122*, 11057–11066; b) F. Würthner, C. Thalacker, S. Diele, C. Tschierske, *Chem. Eur. J.*, in press.

[17] a) A. Facchetti, A. Wang, T. J. Marks, H. Sirringhaus, Y. Deng, R. J. Friend, *Polym. Mater. Sci. Eng.* **2000**, *83*, 290–291; b) A. Facchetti, Y. Deng, A. Wang, Y. Koide, H. Sirringhaus, T. J. Marks, R. Friend, *Angew. Chem.* **2000**, *112*, 4721–4725; *Angew. Chem. Int. Ed.* **2000**, *39*, 4547–4551.

[18] a) J. H. Schön, S. Berg, C. Kloc, B. Batlogg, *Science* **2000**, *287*, 1022–1023; b) J. H. Schön, A. Dodabalapur, C. Kloc, B. Batlogg, *Science* **2000**, *290*, 963–965.