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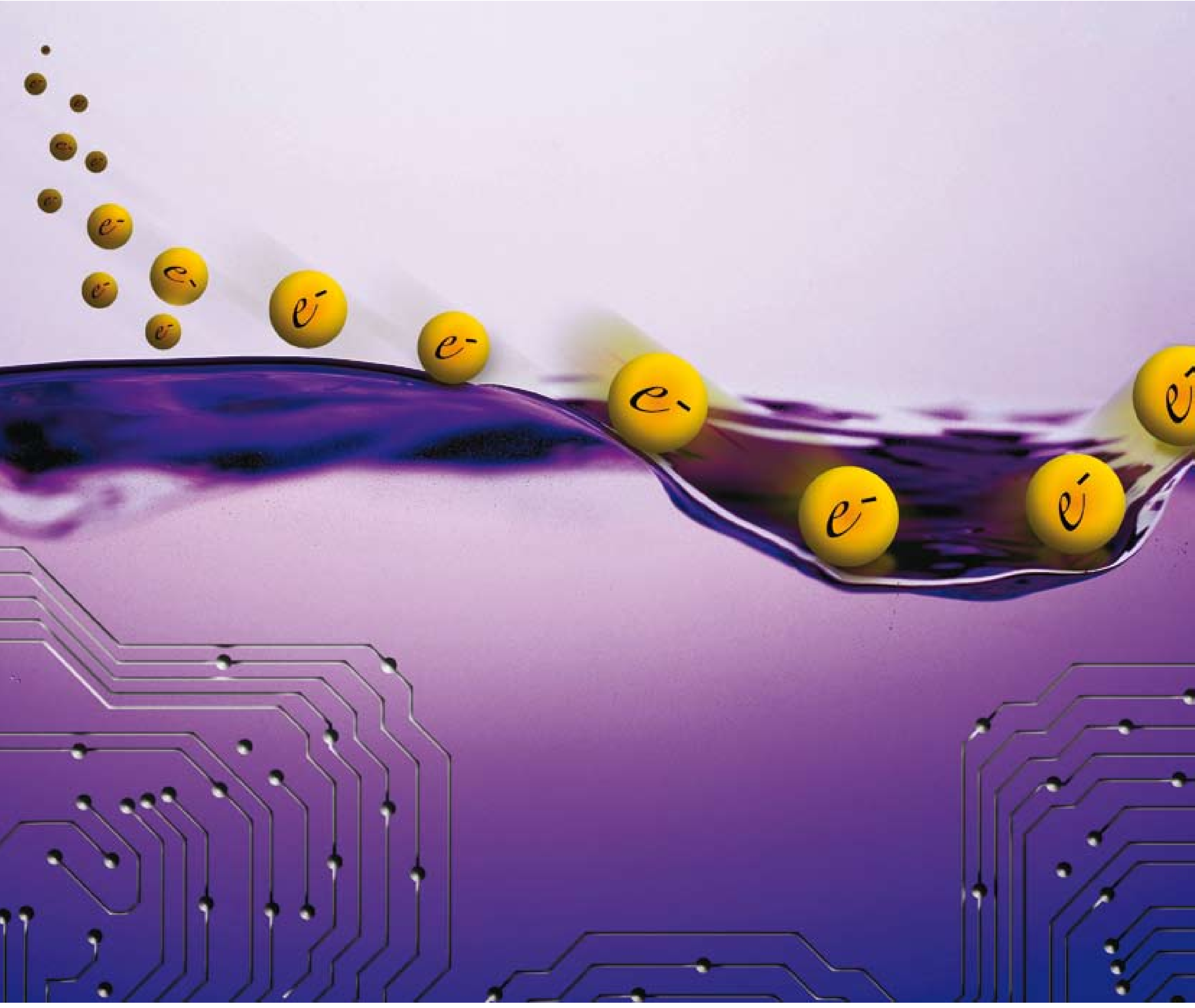

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CRITICAL REVIEW
Marta Mas-Torrent
and Concepció Rovira
Novel small molecules for organic field-effect transistors: towards processability and high performance

TUTORIAL REVIEW
Rein V. Ulijn and Andrew M. Smith
Designing peptide based nanomaterials

RSC Publishing

Novel small molecules for organic field-effect transistors: towards processability and high performance

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The processing characteristics of organic semiconductors make them potentially useful for electronic applications where low-cost, large area coverage and structural flexibility are required. This *critical review* gives a general introduction about the current standing in the area of OFETs focusing on the new processable small molecules that have been recently reported for their use as organic semiconductors. A general description of the OFETs device operation and the transport mechanisms that dominate organic semiconductors is provided, followed by an overview of the strategies and materials employed to fabricate p-type, n-type and ambipolar OFETs. Some new tendencies and applications that are currently being developed employing OFETs are also described, such as the preparation of electronic paper, sensors or light emitting transistors (85 references).

1. Introduction

Our daily life involves the continuous use of electronic devices (*e.g.* TV, bank cards, computer screens, *etc.*). Since the invention of the first transistor in 1947 by John Bardeen, William Shockley and Walter Brattain, the vast majority of these devices have mainly been based on inorganic semiconductors and, in particular, on silicon. However, due to technological limitations associated with the use of silicon, substantial efforts are currently devoted to developing organic electronics. The processing characteristics of organic semiconductors make them potentially useful for electronic applications where low-cost, large area coverage and structural flexibility are required. Contrary to amorphous silicon, which is widely used in solar cells and flat screen displays, organic materials offer the benefits that they can be deposited on plastic substrates at low temperature by employing solution-based printing techniques,[1] which would result in a dramatic reduction of the manufacturing costs. Organic-based electronics will thus not replace high density and high speed silicon circuits, but might play an important role in applications such as identification tags, electronic bar codes or active matrix elements for displays, and might also emerge in a large variety of new uses and applications.

Field-effect transistors are the main logic units in electronic circuits, where they usually function as either a switch or an amplifier. Organic field-effect transistors (OFETs) have been mainly based on two types of semiconductors: conjugated polymers and small conjugated molecules. The first OFET was reported in 1986 and was based on a film of electrochemically grown polythiophene.[2] Four years later, the first OFET employing a small conjugated molecule (sexithiophene) was fabricated.[3] The performance of OFETs in the last 20 years has improved enormously.[4] Nowadays, charge carrier mobilities of the same order as amorphous silicon (0.1–1 $cm^2 V^{-1} s^{-1}$) are achieved in the best OFETs. Thiophene and, especially, acene derivatives are considered to be the benchmark in OFETs and most of the best mobilities have been found in these two families of compounds. However, devices prepared with these molecules are typically prepared by evaporation of the organic materials due to their low solubility in common organic solvents. In order to reduce manufacturing costs, solution-based techniques such as spin-

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coating or printing techniques are required. Polymers in OFETs are deposited from solution fulfilling the requirements for low cost electronics. However, the higher molecular disorder in polymers limits the charge transport resulting typically in lower mobilities compared to the devices based on small molecules. Hence, although not interesting for practical applications, the fundamental material characteristics of organic semiconductors are most clearly measured in single-crystals, where the highest mobilities have been observed due to their higher molecular order and to the fact that they do not present grain boundaries (a mobility of up to 18 $\text{cm}^2\ \text{V}^{-1}\ \text{s}^{-1}$ has been reported for a rubrene single crystal).[5] To promote, therefore, the development and utility of organic semiconductors, there is a clear need to find materials that can be solution-processed and, simultaneously, achieve a high OFET mobility.

The main goal of this review is to give a general overview about the current standing in the area of OFETs focusing on the new processable small molecules that have been recently reported for their use as organic semiconductors. The present paper will be divided into four sections. We will start with a general description of the OFETs device operation followed by the transport mechanisms that dominate organic semiconductors. Next, we will concentrate on the novel OFET materials recently reported considering the type of semiconductor: p type, n type and materials with ambipolar properties (p and n). We will finish by describing briefly new tendencies and applications that are currently being developed employing OFETs, such as the preparation of electronic paper, sensors or light emitting transistors. For a more detailed description of the OFET devices physics, we encourage the readers to consult other published reviews.[6]

2. Device operation

A field-effect transistor can be described as a three terminal device in which the current through the semiconductor connected to two terminals (namely source and drain) is controlled at the third terminal (the gate) by a voltage that creates an electric field through the dielectric on which the semiconductor is deposited. As shown in Fig. 1, there are two common device configurations used in OFETs: *top contact*, when the source and drain electrodes are evaporated on the top of the organic material, and *bottom contact*, when they are evaporated on the dielectric before depositing the organic semiconductor. The voltage applied to the gate (V_G) induces an electric field through the dielectric and causes the formation of an accumulation layer of charges at the interface of the semiconductor deposited above. Then, by applying a source–drain voltage (V_{SD}) it is possible to measure current between the source and the drain (I_{SD}).

The typical electrical characteristics obtained in an OFET are shown in Fig. 2. There are two regimes, the linear regime, where the current is described by a parabola, and the saturation regime where the source–drain current is independent of the source–drain voltage. The nature and quality of the organic semiconductor is crucial for achieving high OFET performance, which is mainly determined by the charge carrier mobility (μ) that is a measure of the charge carrier drift velocity per unit of electric field. Other important parameters are the On/Off ratio, which is the ratio of current in the accumulation mode over the current in the depletion mode, and the threshold voltage (V_T), that is, the gate voltage from which the conduction channel starts to form.

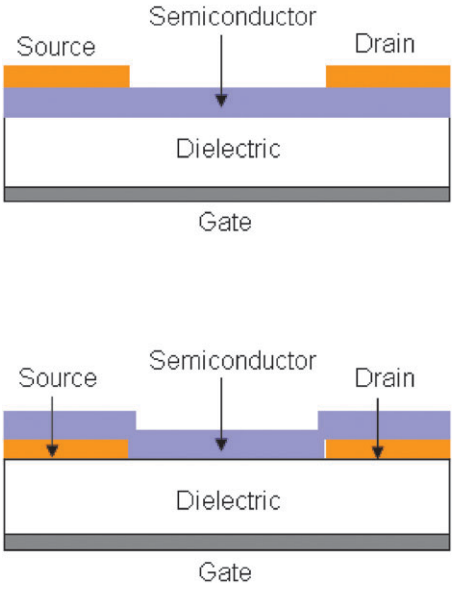


Fig. 1 Possible OFET configurations: (a) Top contact. (b) Bottom contact.

The two transport regimes are described according to the following equations:

Linear regime:

$$I_{SD} = \frac{W}{L}\mu C V_{SD}\left(V_G - V_T - \frac{1}{2}V_{SD}\right)$$

Saturation regime:

$$I_{SD} = \frac{W}{2L}\mu C (V_G - V_T)^2$$

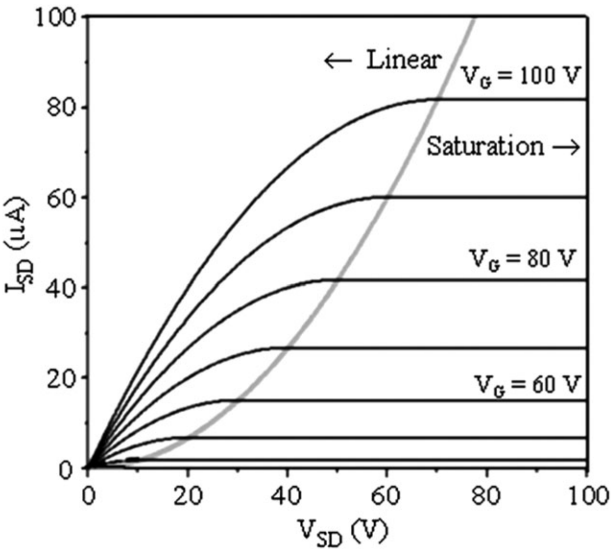


Fig. 2 Typical electrical characteristics obtained in a field-effect transistor. The boundary between linear and saturation regime is indicated by a grey curve.

Here L is the length of the transistor from source to drain in the direction that the current flows, W is the width of the transistor and C is the capacitance per unit area of the insulating layer.

We can understand the basic principles that govern the field-effect operation in terms of energy level diagrams.[7] We should bear in mind that the organic semiconductors used in OFETs, if they are not doped, are not intrinsically charged and, thus, are not conducting at zero gate bias. However, a voltage applied to the gate will shift the energy levels electrostatically and can thereby modulate the conductivity of the channel. If a negative gate voltage is applied, the HOMO (highest occupied molecular orbital) and the LUMO (lowest unoccupied molecular orbital) orbitals of the organic material will shift up with respect to the Fermi level (E_F) of the metal. If the HOMO becomes resonant with E_F, it will be possible to have flow of hole mobile charges between the HOMO and the metal. In this case, the material will behave as a p-type semiconductor. Otherwise, if a positive gate voltage is applied, the HOMO and LUMO orbitals will shift down, and if the LUMO becomes resonant with E_F, electrons will flow from the metal to the LUMO. This material will behave then as an n-type semiconductor. Materials able to conduct electrons and holes are known to behave as ambipolar semiconductors.

The design of the device configuration will influence on the measured electronic properties. For instance, the choice of metal electrodes will affect the contact resistance. It is important to choose the electrode metal according to the nature of the organic semiconductor to have efficient charge injection. That is, for an n-type material it will be more suitable to have a metal with low work function (*i.e.* the minimum energy required to remove an electron from the Fermi level to the vacuum level), whereas for a p-type material a metal with high work function would be desired. The dielectric material is also fundamental in the final device operation since it will influence the electric field created along it, the current leakage through the gate insulator and the quality of the interface between the organic semiconductor and the dielectric. The most widely used dielectric in OFETs has been SiO_2 grown on doped Si gates following the same technologies as the ones established for inorganic microelectronics. The characteristics of the dielectric can also be modified with surface treatments. For example, growing a self-assembled monolayer of an organic molecule on silica will change the hydrophilic nature of the oxide to hydrophobic. It has been demonstrated that these treatments often have strong effects on the film structure and on the resulting electrical characteristics.[8] In the last few years, there has been a lot of work on studying the influence on the OFET performance of different types of inorganic dielectrics as well as organic dielectrics compatible with solution processability, flexible substrates and low temperature processes. Since this topic is beyond the scope of this review, we refer the reader to other published literature.[9]

The organic semiconductor can be deposited on the device employing solution-based techniques such as drop-casting or spin-coating. The use of such techniques is the most promising route to produce low manufacturing costs and to fabricate devices of large-area coverage. In addition, by combining them with stamping or printing techniques,[4c,10] it is possible to pattern organic semiconductors eliminating the use of lithography. However, since organic semiconductors are often not very soluble, an alternative deposition method is by sublimation of the organic material in a variety of vacuum depositions systems. Parameters such as pressure and substrate temperature determine the morphology and quality of the resulting films.

3. Charge transport mechanisms

In inorganic semiconductors like Si or Ge, atoms are held together by strong covalent bonds permitting charge transport to take place *via* delocalized states following a band transport regime. The transport is limited by the lattice vibrations and, thus, at lower temperatures the conductivity in these materials increases. However, since the intermolecular forces in organic semiconductors are weak van der Waals interactions, completely different transport mechanisms occur.[11] Although time-of-flight experiments in very pure crystals of naphthalene have shown that when lowering temperature the mobility increases similarly to inorganic semiconductors,[12] it is generally agreed that, at least at room temperature, the charge mobility of semiconducting organic materials is determined by a hopping transport process. This transport mechanism is phonon assisted and thus is thermally activated. Hopping transport can be depicted as an electron or hole transfer reaction in which an electron or hole is transferred from one molecule to the neighboring one. The charges localise on a molecule for a time long enough so the nuclei can relax to their optimum geometry. It is also generally granted that the localization of the charge induces a lattice deformation around forming a polaron. Two major parameters determine self-exchange rates and, thus, the charge mobility:[13] (i) the electronic coupling between adjacent molecules, which needs to be maximized, and (ii) the reorganization energy (λ_{reorg}), which needs to be small for efficient charge transport. The reorganization energy of self-exchange in a hole-hopping material is defined as the sum of the geometrical relaxation energies of one molecule upon going from the neutral-state geometry to the charged-state geometry and the neighboring molecule upon going through the inverse process [$A(0) + A'(+) \rightarrow A(+) + A'(0)$]. These two portions of λ_{reorg} are typically nearly identical.[14] Some theoretical works have attempted to explain the high mobility of pentacene OFETs in terms of its low λ_{reorg}.[13b–15] However, high mobilities have been found in materials with high λ_{reorg} and, importantly, it has been shown that local intermolecular interactions can have a strong influence on λ_{reorg} values and, thus, on hopping mobilities.[16]

Despite all the intense work devoted to OFETs, charge transport mechanisms on organic semiconductors are still uncertain. Indeed, studies of the dependence of mobility with temperature elucidate that simply the hopping mechanism is not enough to explain the transport processes. In some cases, temperature independent mobility has been observed, in others, mobility initially increased with decreasing temperature until a maximum was reached, after which the mobility decreased.[17] Trapping phenomena or contacts effects could be important factors to consider. Also very recently, Bromley *et al.* reported that the reorganization energy in organic molecular crystals is strongly dependent on carrier localization and it was suggested that the relevant carriers are neither band-forming nor fully-localised but the carriers are delocalized over a few molecules.[18] Similar sentiments as to the intermediate character of charge carriers in OFETs have also been expressed in other studies.[19] Further work should be performed in order to understand the transport mechanisms in OFETs, which will be helpful for designing new organic semiconductors.

4. Organic semiconductors

As mentioned before, polymers and small conjugated molecules are the two families of organic semiconductors that have been studied. Typically, solution processed polymers form complex microstructures, where microcrystalline domains are embedded in an amorphous matrix. The disordered matrix limits the charge transport resulting in low field-effect mobilities. The most studied polymer for OFETs is poly(3-hexylthiophene) (P3HT), which has reported to have an OFET mobility of 0.1 cm^2 V^{-1} s^{-1}.[20] This high mobility is related to structural order in the polymer film induced by the regioregular head-to-tail coupling of the hexyl side chains.[21] Also, very recently McCulloch *et al.* reported on OFETs based on the liquid crystalline poly(2,5-bis(3-alkylthiophen-2yl)-thieno[3,2-*b*]thiophene) that exhibited a mobility of up to 0.7 cm^2 V^{-1} s^{-1} in the well-organised mesophase.[22] From now on though, we will focus on small conjugated molecules semiconductors, which tend to provide devices with higher mobilities. In this section we will describe these materials classified regarding the nature of the charge carriers and paying particular attention to the recent works on novel soluble small molecules employed for OFETs.

4.1 p-Type semiconductors

p-Type semiconductors are materials in which the majority of carriers are holes. As stated before, the most studied materials for OFETs have been acene and thiophene derivatives. Field-effect hole mobilities of 1.1 and 3 cm^2 V^{-1} s^{-1} have been reported for thin films of alkyl-substituted oligothiophene[23] and pentacene,[24] respectively. Also, promising organic semiconductors based on π-extended heteroarenes have resulted in high mobilities between 2.1 and 2.9 cm^2 V^{-1} s^{-1}.[25] In the last few years, tetrathiafulvalene derivatives have also shown to be very interesting for preparing p-type OFETs, mainly as thin film.[26,27] All these devices were prepared by evaporation of the organic material. Typically, the use of vapor phases allows for the obtaining of higher purity materials which tends to give rise to higher OFET mobilities. However, there is a great interest in developing molecules and processing methods to achieve improved processability and higher mobilities for low cost electronics.

One of the routes followed to impart solubility to organic semiconductors is the preparation of a precursor compound which can be converted thermally or by irradiation into the parent semiconductor (Fig. 3). Pentacene adducts that undergo a retro Diels–Alder reaction to give pentacene have been synthesised. Müllen and coworkers showed that compound **1** and **2** can be converted to pentacene after heating. Films of **1** and **2** prepared by spin coating a solution in methylene chloride resulted in mobilities of the order of 0.1–0.2 cm^2 V^{-1} s^{-1} after annealing at 200 °C.[28] More recently, Philips Research Laboratories have used these derivatives to fabricate active matrix displays formed by large integrated circuits of 1888 transistors.[29] A similar strategy was employed by Afzali *et al.*[30] Compound **3** was obtained on a one-step Diels–Alder reaction between pentacene and *N*-sulfinylamide as a dienophile giving a pentacene adduct soluble in chlorinated solvents and ethers. Spin coated films of **3** were prepared from a solution in chloroform. After annealing the films at 200 °C the OFET properties were measured giving a mobility of 0.89 cm^2 V^{-1} s^{-1}. Analogous materials such as compound **4** were prepared that could be converted by UV light to pentacene, permitting also to photopattern the channel material in the devices. The highest mobility obtained for **4** was 0.25 cm^2 V^{-1} s^{-1}.[31] Additionally, thiophene precursors have also been recently reported bearing solubilising groups that render solubility to the oligomer and can be thermally removed. The diester functionalised sexithiophene **5** contains secondary esters at the α- and ω-positions which are known to undergo thermolysis between 150 and 300 °C leaving pendant alkene groups on the oligomer. Mobilities of up to 0.07 cm^2 V^{-1} s^{-1} were reported for this semiconductor.[32] Phthalocyanines and porphyrins have been also demonstrated as promising semiconductors. Following the precursor approach, the soluble compound CP was synthesised and converted after annealing to 1,4:8,11:15,18:22,25-tetraethano-29*H*,31*H*-tetrabenzo[*b*,*g*,*l*,*q*]porphine giving a maximum OFET mobility of 0.017 cm^2 V^{-1} s^{-1}.[33]

The preparation of soluble precursor molecules has thus yielded OFETs with very high mobilities. Nevertheless, these methods require an annealing step typically reaching temperatures of around 200 °C. An alternative strategy is to prepare structurally modified organic semiconductors to impart solubility and achieve higher stability. Some works have focused on the functionalisation of acene derivatives in order to obtain soluble materials and to increase π–π interactions.[34] Payne *et al.* prepared films of bis(triethylsilylethynyl) anthradithiophene (TES-ADT) and bis(triisopropylsilylethynyl) pentacene (TIPS-PEN) by spreading a solution in toluene of these compounds across the device using a plastic blade and heating at 90 °C, giving mobilities of 1.0 and 0.17 cm^2 V^{-1} s^{-1}, respectively.[35] Contrary to pentacene that crystallises following a herringbone pattern dominated by edge-to-face interactions, these two materials form a 2D "bricklayer" arrangement in the solid state with significant π–π overlapping. In addition, in films of TES-ADT it was demonstrated that the device performance can be improved by solvent vapor annealing.[36] Recently, higher mobilities of 1.42 cm^2 V^{-1} s^{-1} were reported in devices using single-crystalline microribbons of TIPS-PEN.[37] The microribbons were prepared by the specific-solvent exchange method, which consisted in the injection of a concentrated solution of TIPS-PEN in toluene into acetonitrile, a solvent in which the molecule is not soluble. OFETs with a maximum mobility of 0.27 cm^2 V^{-1} s^{-1} for single crystals of hexathiapentacene (HTP) have also recently been prepared by drop casting a suspension of HTP nanowires on the prefabricated electrodes.[38] This work demonstrates that even materials with low solubility can be solution-processed by preparing suspensions of them.

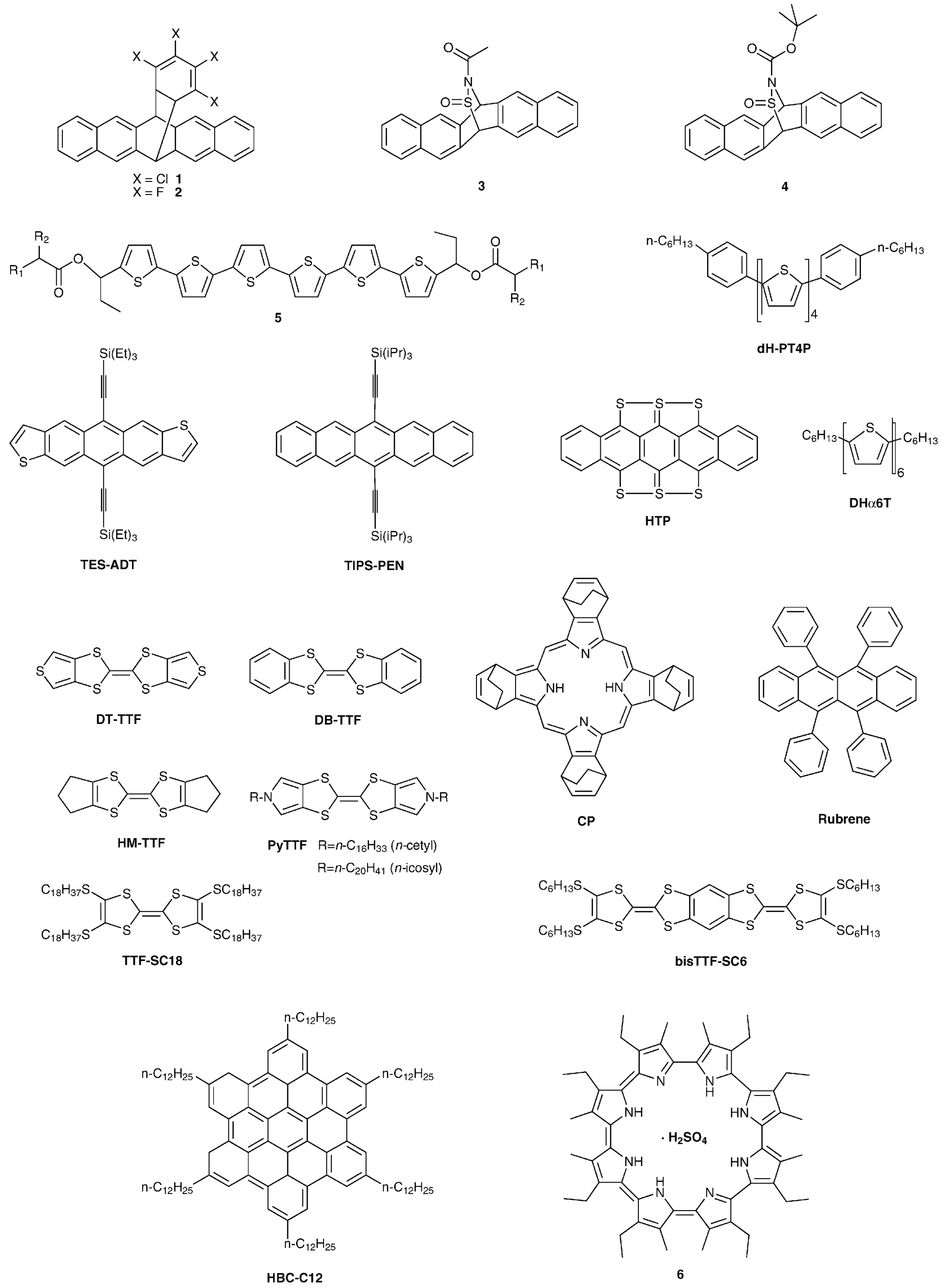


Fig. 3 Organic p-type semiconductors employed for solution processable OFETs.

Alkyl and alkylphenyl substituted thiophene derivatives have also been synthesised in order to achieve higher solubility. In these devices, the alkyl length and the solid state morphology have a strong effect on the device performance and it is important, therefore, that the functionalisation of the molecules does not hamper the intermolecular interactions. Mobilities of the order of 0.01–0.05 $cm^2\ V^{-1}\ s^{-1}$ have been found for this family of materials.[39]

Tetrathiafulvalene or TTF derivatives have promised to be good candidate molecules for the preparation of OFETs since they are generally soluble in various solvents, are easily chemically modified, and are good electron donors. TTFs have been successfully used as building blocks for charge transfer salts, giving rise to a multitude of organic conductors and superconductors, as well as for the preparation of a wide range of molecular materials.[40] However, it has not been until these last few years that the application of TTFs in OFETs has been initiated.[26] The early obtained results already point out the high potential of these materials, which can be easily processed and tailor synthesised. With the aim of establishing a correlation between crystal structure and charge carrier mobility, OFETs based on neutral TTF crystals grown from solution were prepared by drop casting a solution of the TTF derivative onto the SiO_2 gate insulator and the prefabricated source and drain gold electrodes.[17d,41] The solution was allowed to evaporate slowly at room temperature which

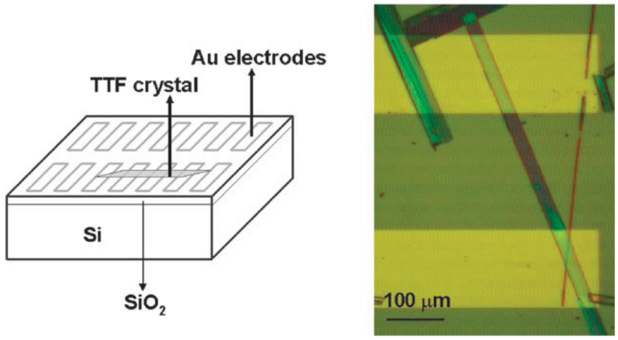


Fig. 4 Left: Device configuration used. Right: Optical microscope image of a DT-TTF single crystal lying on the gold electrodes. Reprinted with permission from ref. 41*a*. Copyright 2004 American Chemical Society.

resulted in the formation of crystals, some of which connected two of the microfabricated electrodes (Fig. 4). All the crystals revealed a p-type behaviour as the conductivity increased as a more negative gate voltage was applied. Fig. 5 shows the electrical measurements performed on a dithiophenetetrathiafulvalene (DT-TTF) crystal. A clear correlation between crystal structure and device performance was observed. The derivatives that crystallise forming uniform stacks of almost planar molecules along the *b* axis with a very short interplanar distances between molecules of one stack of 3.56–3.66 Å showed the best device performance. The highest mobility found was as high as 3.6 $cm^2\ V^{-1}\ s^{-1}$ for a DT-TTF crystal with a high ON/OFF ratio exceeding 10^6.[41c] Calculations of the transfer integral and the reorganization energy of these materials taking into account their crystal packing were in agreement with the experimental results; that is, the materials showing higher mobility, have lower reorganisation energy and larger transfer integral.[16,41b] This result has proved to be of great importance for the future design of new promising materials.[17d] Very recently, in solution-grown crystals of hexamethylenetetrathiafulvalene (HM-TTF) mobilities of 0.02 $cm^2\ V^{-1}\ s^{-1}$ were measured when using gold electrodes, but values of up to 10.4 $cm^2\ V^{-1}\ s^{-1}$ were achieved by employing TTF-TCNQ organic metal electrodes, which was attributed to the matching of the energy levels resulting in efficient hole injection.[42]

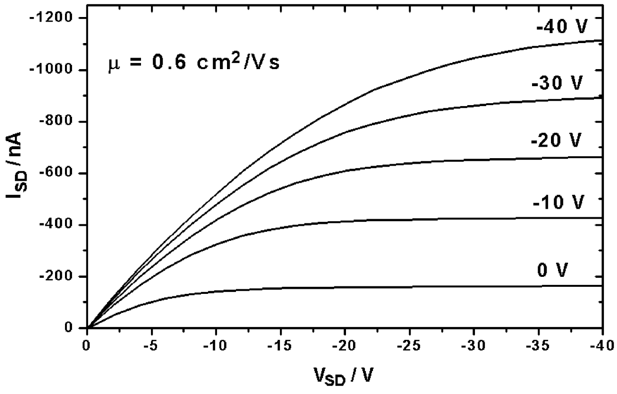


Fig. 5 Source–drain current *versus* source–drain voltage at different gate voltages for a DT-TTF single crystal OFET. Reprinted with permission from ref. 41*b*. Copyright 2004 American Chemical Society.

Thin films of DT-TTF and the amphiphilic TTF derivative tetrakis-(octadecylthio)-tetrathiafulvalene (TTF-4SC18), which incorporates alky chains that ensure solubility and facilitate intermolecular π–π overlapping due to the extremely closely packed nature of the long alkyl chains, have also been prepared by zone-casting.[43] Highly oriented films of these compounds covering large areas revealed a remarkably high performance, with a maximum charge carrier mobility close to 0.1 $cm^2\ V^{-1}\ s^{-1}$ for TTF-SC18 and 0.17 $cm^2\ V^{-1}\ s^{-1}$ for DT-TTF, which makes these materials very interesting for future applications. The zone-casting technique has also been applied for preparing aligned films of discotic liquid-crystalline hexa-*peri*-hexabenzocoronene bearing alky chains (HBC-C12) giving an OFET mobility of 0.01 $cm^2\ V^{-1}\ s^{-1}$.[44] Thin films prepared by spin coating of a new linear benzene-fused bisTTF (bisTTF-SC6), which has a more extended π conjugation, and *N*-alkyl substituted bispyrroloTTFs (PyTTF) have also been reported to give a mobility of 0.02 and 0.01 $cm^2\ V^{-1}\ s^{-1}$, respectively.[45,46] Although the mobility in these devices is about one order of magnitude lower than the one found for TTF-4SC18 and DT-TTF, it is worth mentioning that the spin coating technique might be more promising for industrial applications since it can be more easily scaled up and is a very fast technique.

Langmuir–Blodgett (LB) films represent another solution-based route to obtain ordered films. LB films are constructed by transferring monolayers of organic amphiphilic molecules on water surface to a solid substrate. Thin films of cyclo[8]-pyrrole **6** prepared by the LB method exhibited a maximum mobility of 0.68 $cm^2\ V^{-1}\ s^{-1}$ and by X-ray characterisation the ordering in the films was confirmed.[47]

A novel and simple procedure has also recently been reported for controlling the generation of organic thin films of high crystalline quality.[48] This method consists in preparing an homogenous mixture of an organic semiconductor (in this case, rubrene), a vitrifying diluent (1,2-diphenylanthracene), that hampers crystallisation on casting from solution, and a high-molecular-weight polymer (atactic polystyrene), that provides good-film forming characteristics. When annealing a hypereutectic mixture of the semiconductor and the glass-inducing specie at a temperature above the T_{eutectic}, crystallisation of the semiconductor takes place. A very high OFET performance with a mobility of 0.7 $cm^2\ V^{-1}\ s^{-1}$ has been obtained with this method, which could be extended for other organic semiconductors.

Table 1 summarises the mobilities obtained for the above-mentioned soluble p-type semiconductors. Overall, by employing a variety of solution-based techniques with these materials, high performance OFET characteristics have already been achieved, reaching hole mobilities of the order of amorphous silicon.

4.2 n-Type semiconductors

In n-type semiconductors the majority of carriers are electrons. The development in devices using these semiconductors is still far from the performance achieved with p-type materials due to the fact that the transport in n-channel conductors is

Table 1 Preparation method and performance of p-type semiconductors employed in OFETs using solution-based techniques

Compound	Deposition method	$\mu_{\max}$/cm^2 V^{-1} s^{-1}	ON/OFF ratio[a]	Ref.
1–2	Spin-coating in CH_2Cl_2 and annealing at 200 °C	0.2	$>10^6$	28
3	Spin-coating in $CHCl_3$ and annealing at 200 °C	0.89	2×10^7	30
4	Spin-coating in $CHCl_3$, UV light and heating at 130 °C	0.25	8×10^4	31
5	Spin-coating in $CHCl_3$ and annealing at 180–200 °C	0.07	$>10^5$	32
CP	Spin-coating in $CHCl_3$ and annealing at 210 °C	0.017	10^5	33
TES-ADT	Solution in toluene spread across the device and heating at 90 °C	1.0	10^7	35
TIPS-PEN	Solution in toluene spread across the device and heating at 90 °C	0.17	10^5	35
	Specific solvent exchange method (drop of toluene solution in CH_3CN)	1.42	10^5	37
HTP	Drop casting nanowires suspension in $CHCl_3$	0.27	$>10^3$	38
dH-PT4P	Solution cast in xylene at a substrate temperature of 115 °C	0.028	10^3	39*a*
DHα6T	Solution cast in 1,2,4-tricholorobenzene at a substrate temperature of 70 °C	0.05	10^5	39*c*
DT-TTF	Drop casting from a toluene solution	3.6	10^6	41*c*
DB-TTF	Drop casting from a chlorobenzene solution	1.0	10^6	17*d*
HM-TTF	Recrystallisation from chlorobenzene and crystals placed on the device	0.02(Au) 10.4(TTF-TCNQ)	n.r.	42
TTF-4SC18	Zone casting at 75 °C in toluene and annealing at 65 °C	0.08	10^4	43
bisTTF-SC6	Spin-coating in $CHCl_3$	0.02	10^2	45
PyTTF	Spin-coating in toluene or chlorobenzene	0.013	10^4	46
HBC-C12	Zone casting at 51 °C in THF	0.01	10^4	44
6	Langmuir–Blodgett (air–water interface)	0.68	8×10^4	47
Rubrene + glass diluent	Casting from toluene, drying at 90 °C and crystallization at 235–245 °C	0.7	$\geq 10^6$	48

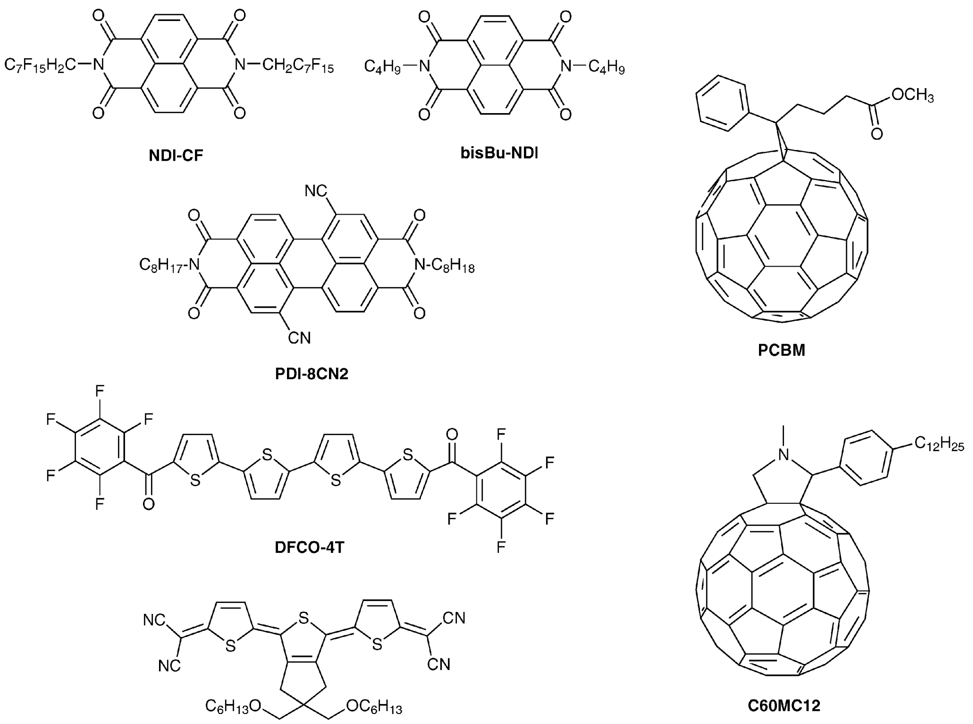
[a] n.r. stands for not reported.

degraded easily by air, which acts as electron traps together with the dielectric surface trapping sites, and that most of the known organic materials tend to conduct holes better than electrons. An added difficulty in progressing on the fabrication of electron conducting OFETs is finding suitable metals for contacts. Typically, the metal used in OFETs is gold, which has a work function of 5.1 eV close to the ionization potential of most p-type organic semiconductors. Thus, gold is a very suitable metal for injecting holes into the HOMO of most organic materials that behave as p-semiconductors. However, to inject electrons to the LUMO of n-type organic semiconductors it is more appropriate to employ metals with low work functions, such as Al, Ca or Mg. The drawback is that these metals tend to oxidize easily.

Currently, there is a growing interest in developing n-type materials in order to fabricate complementary circuits.[49] It is thus imperative to achieve device performances with n semiconductors of the same order as the ones already achieved with p semiconductors. The challenge lies not only in finding new materials with high electron mobility but also that these materials should exhibit a low deterioration of the electronic properties over time.

N-type materials should have high enough electron affinity to allow efficient injection of the electrons into the LUMO of the molecules (*i.e.* at least 3 eV). One strategy consists in attaching electron withdrawing groups to oligothiophenes, acenes, tetrathiafulvalenes or metallophthalocyanines in order to increase their electronic affinity.[50] A mobility of up to 0.6 cm^2 V^{-1} s^{-1} has recently been reported for vacuum deposited films of carbonyl-functionalised quarterthiophenes.[50*a*] Interestingly, thiazole oligomers bearing trifluoromethylphenyl groups have recently revealed electron mobilities as high as 1.83 cm^2 V^{-1} s^{-1}.[51] The most extensive work on n-channel organic materials has involved compounds formed by adding dianhydride or diimide electron acceptor groups to naphthalene and perylene cores. Thermally evaporated films of *N*,*N*′-ditridecyl-3,4,9,10-perylenetetracarboxylic diimide annealed at 140 °C have resulted in mobilities of 2.1 cm^2 V^{-1} s^{-1}.[52] Fullerene and its derivatives, which are good electron acceptor molecules, have also been widely studied as n-type semiconductors. The highest mobility (μ = 6 cm^2 V^{-1} s^{-1}) has been found on hot wall epitaxy-grown fullerene thin films on polymeric dielectrics.[53]

Despite all these recent outstanding results obtained with vacuum deposited thin films, solution processable n-type conductors are scarce (Fig. 6). The first soluble and air-stable organic semiconductor revealing high electron mobility exceeding 0.01 cm^2 V^{-1} s^{-1} was found for a naphthalenetetracarboxylic diimide bearing fluorinated alkyl chains (NDI-CF).[54] This n-channel OFET was successfully integrated with solution-deposited p-channel OFET producing a complementary inverter circuit whose active layers were deposited entirely from the liquid phase. Mobilities of the same order of magnitude measured under argon have also been found for *N*,*N*′-bis-butyl-1,4,5,8-naphthalene diimide (bisBu-NDI) when using polyvinyl alcohol (PVA) as a dielectric.[55] The performance of these devices, however, diminished to half of their value when they were measured under air. As mentioned before, perylene-substituted derivatives are also promising semiconductors for n-type OFETs. Devices prepared from solution with a micro-injector patterning technique using the cyano-perylene derivative PDI-8CN2 and carrying out surface treatments has resulted in electron mobilities of up to 0.024 cm^2 V^{-1} s^{-1}.[56] To our knowledge, the highest electron OFET mobility reported to date for a soluble material has been for a phenacyl–quartethiophene compound (DFCO-4T, μ = 0.21 cm^2 V^{-1} s^{-1}).[57] This molecule crystallises forming a herringbone motif with very short inter-core distances of 3.50 Å. Amorphous spin coated films of the dicyanomethylene-substituted terthienoquinoid **7** resulted in air-stable devices with OFET electron mobilities of 0.025 cm^2 V^{-1} s^{-1}.[58] However, thermal annealing of these films gave rise to


NDI-CF

bisBu-NDI

PCBM

PDI-8CN2

DFCO-4T

C60MC12

7

Fig. 6 Organic n-type semiconductors employed for solution processable OFETs.

crystalline films that exhibited an enhanced mobility of 0.16 $cm^2\ V^{-1}\ s^{-1}$. The soluble fullerene derivative [6,6]-phenyl C_{61}-butyric acid methyl ester (PCBM) has also been employed for the preparation of n-type OFETs. With this material, Lee *et al.* studied the influence of the contact electrodes on the device mobility. They found that the field-effect mobility in the transistor linearly increases as the metal workfunction decreases, indicating that the electron current is contact-limited. The maximum mobility (0.1 $cm^2\ V^{-1}\ s^{-1}$) was found using Ca electrodes.[59] In this work the first all-solution processed n-type transistor was also demonstrated by depositing the source and drain metal by a spinning metal process. Simultaneous studies on PCBM showed the influence on different polymeric gate dielectrics on the device performance reaching a mobility of 0.2 $cm^2\ V^{-1}\ s^{-1}$ with PVA.[60] This work elucidates the importance of the dielectric in the device performance, which is particularly important in n-type devices due to the trapping of the electrons at the semiconductor–dielectric interface. This has also been proved very recently by preparing long n-alkyl self-assembled monolayers on the SiO_2 dielectric, which resulted in a significant improvement of electron mobility due to the suppression of the influence of electron trap sites on the oxide.[61] With the aim of gaining solubility and higher molecular order, Chikamatsu *et al.* have fabricated devices with C_{60} derivatives bearing long alkyl chains.[62] Fused *N*-methylpyrrolidine-*meta*-C12 phenyl (C60MC12) forms well-ordered films and a mobility of up to 0.09 $cm^2\ V^{-1}\ s^{-1}$ was achieved. Table 2 summarises the device characteristics of the soluble n-type materials mentioned above.

4.3 Ambipolar semiconductors

Most of the organic transistors that have been fabricated to date show only unipolar conduction (either holes or electrons). However, the fabrication of devices exhibiting ambipolar conduction is crucial in order to design robust circuits of low power consumption and a good noise margin following CMOS technology. An ambipolar transistor exhibits hole accumulation for negative gate bias and electron accumulation for positive gate bias. Ambipolar OFETs have been prepared by using a heterostructure active layer combining an n-type semiconductor (with high electron affinity) with a p-type

Table 2 Preparation method and performance of n-type semiconductors employed for OFETs using solution-based techniques

Compound	Deposition method	$\mu_{max}/cm^2\ V^{-1}\ s^{-1}$	ON/OFF ratio[c]	Ref.
NDI-CF	Casting in α,α,α-trifluorotoluene at 100 °C	>0.01	n.r.	54
bisBu-NDI	Spin-coating in acetonitrile	0.012[a]	10^4	55
PDI-8CN2	Solution jetting in 1,2-dichlorobenzene and annealing at 110 °C	0.024[b]	10^4	56
DFCO-4T	Drop casting from xylene on a substrate kept at 120 °C	0.25[a]	10^5	57
7	Spin-coating in chloroform and thermal annealing at 150 °C	0.16	10^3	58
PCBM	Spin-coating in chlorobenzene	0.2[a]	10^3	60
C60MC12	Spin-coating in chloroform	0.09[b]	4×10^5	62

[a] Measured under argon. [b] Measured under vacuum. [c] n.r. stands for not reported.

semiconductor (with low ionization potential).[63] Following this approach, devices based on a bilayer of vacuum deposited C_{60} and pentacene have given electron and hole mobilities of 0.23 and 0.14 $cm^2 V^{-1} s^{-1}$, respectively.[64] It is important though to fabricate ambipolar devices employing a single-component molecular semiconductor to simplify the device fabrication processes. Meijer *et al.* have argued that hole and electron conduction are both generic properties of organic semiconductors, and they depend on the matching of the energy levels between the HOMO and LUMO of the molecule and the metal work function.[65] However, since the range of metal work functions is limited, in practice, most organic semiconductors will show one conduction polarity. Only a few materials with low band gap have shown to behave as ambipolar semiconductors. An evaporated film of a carbonyl-functionalised quaterthiophene resulted in hole/electron mobilities of 0.01/0.1 $cm^2 V^{-1} s^{-1}$[50a] and single crystals prepared from the vapor phase of iron–phthalocyanine gave hole/electron mobilities of 0.3/0.03 $cm^2 V^{-1} s^{-1}$.[66] Surprisingly, ambipolar transport has also been observed in wide-band-gap semiconductors, such as pentacene and rubrene, using hydroxyl-free gate dielectrics to avoid trapping of the electrons at the semiconductor–dielectric interface.[67]

The design for integrated organic circuits for complementary technology also calls for solution processability for maintaining the attractiveness of organic materials to fabricate low cost devices. Nevertheless, there are only limited examples of solution-processed ambipolar transistors. Ambipolar transport has been achieved in films of interpenetrating networks formed form soluble blends of various p-type semiconducting polymers (*i.e.* P3HT, poly-*p*-phenylene-vinylene) and the n-type small molecule PCBM.[65] With these materials the first complementary-like inverter consisting of single channel OFETs was demonstrated. Also, employing a blend of an n-type polymer (*i.e.* poly(benzobisimidazo-benzophenanthroline)) and copper phthalocyanine ambipolar operation was observed.[68] However, these devices show poor mobilities of the order of 10^{-5}–10^{-4} $cm^2 V^{-1} s^{-1}$ with typically unbalanced hole and electron charge transport. More recently, it has been shown for a spin-coated film of thieno[2,3-*b*]thiophene terthiophene polymer and PCBM that the application of appropriate surface-engineering techniques can facilitate balanced ambipolar transport. Thus, by functionalizing the SiO_2 insulator layer with a self assembled monolayer of octyltrichlorosilane hole and electron mobilities of 4×10^{-3} and 9×10^{-3} $cm^2 V^{-1} s^{-1}$, respectively, were obtained.[69]

A few examples of soluble single molecular compounds that can operate as p and n conductors are also found in the literature. A triad formed by an oligothiophene (well-known as a p-type semiconductor) attached to two [60]fullerene units (well-known as an n-type semiconductor) was synthesized and showed ambipolar conduction in vacuum with charge mobilities of the order of 10^{-5} $cm^2 V^{-1} s^{-1}$.[70] Another single component ambipolar semiconductor is the nickel complex bis(4-dimethylaminothiobenzyl)nickel which has a low band gap of 0.9 eV. Although spin-coated thin films of this material exhibited moderate mobilities of the order of 10^{-4} $cm^2 V^{-1} s^{-1}$, the devices revealed no noticeable degradation in ambient.[71] The solution processable methanofullerene derivative PCBM has also shown to operate as ambipolar transport even when a high work function metal (Au) is employed as the source and drain electrodes. The charge carrier mobilities found were in the order of 1×10^{-2} $cm^2 V^{-1} s^{-1}$ for electrons and 8×10^{-3} $cm^2 V^{-1} s^{-1}$ for holes, and the possibility of fabricating logic inverters with good operating characteristics were also demonstrated for this semiconductor.[72] Despite these encouraging results, methanofullerenes degrade rapidly upon exposure to atmospheric air. Thus, with the aim of improving stability to air and light, devices with the higher fullerene analogues [70]PCBM and [84]PCBM were fabricated.[73] Although lower mobilities were achieved, the OFETs were more stable and easier to reproduce.

The development of ambipolar semiconductors, specially the ones that can be solution-processed, is still at its infancy. Carrier mobility is the main limiting factor in the operating frequency of complementary circuits, so there is an urgent need to find materials with much higher mobilities for both holes and electrons. Characteristics such as processability and stability are also highly desirable.

5. New perspectives

Circuits based on organic transistors are being extensively investigated for a wide range of applications, in particular, those requiring large-area coverage and compatibility with flexible substrates.[74] One of the first emerging devices realized with OFETs has been active-matrix electronic paper.[75] These systems consist of an organic transistor backplane in which each transistor functions as a switch that locally controls the display of microencapsulated electrophoretic "inks" formed by charged pigments. Activating the transistors generate an electric field that causes movement of the pigment within the microcapsules, which changes the color of the pixel. The high potential of these devices is confirmed by their high stability and excellent paper-like contrast, making the commercialization of these products imminent. Fig. 7 shows a prototype of an electronic paper fabricated by Plastic Logic, who recently has announced their intention to develop A4 size flexible electronic paper displays with resolution of up to 150 ppi in its newly opened prototype manufacturing line.[76]

OFETs also offer a great deal of promise for applications in chemical and biological sensing.[74,77] The detection of analytes at low concentrations with sufficient stability, reproducibility and selectivity is essential for applications in food processing, environmental remediation and medical diagnostics. Organic semiconductors can interact with different analytes and, due to their semiconductor behavior, it is possible to transduce the chemical information to electronic information. Another advantage of OFETs sensors is that from their electrical characterization it is possible to extract many different electronic parameters offering thus a combination of variables to characterize the sensor response.

Most of the OFETs sensors reported consist in measuring the current–voltage response in the presence of certain chemical vapors in the surrounding environment. The responses of several organic semiconductors to a range of vapor analytes (including alcohols, ketones, thiols, nitriles, esters and ring compounds) in the ppm scale was carefully studied by Crone

Fig. 7 Flexible active matrix display using e-ink Imaging Film. Printed with permission from Plastic Logic.

et al. (Fig. 8).[78] The responses to the different type of analytes were distinguishable among semiconductors with different lengths of side chain and different carrier types. This work represents a step forward to realize "electronic noses", in which any semiconductor-analyte pair would provide a unique pattern of responses ("fingerprint").

In addition to the molecular structure of the semiconductor and the nature of the analyte (*e.g.* electron donating/accepting, dipole moment, *etc.*), it has been shown that in large-scale transistors the number of grain boundaries and interfaces determine largely the device sensitivity due to the fact that the analyte molecules at the grain boundaries trap the mobile charges. However, when the device channel length is reduced being close to or smaller than the average grain size, other sensor mechanisms become dominant. In nanoscale devices, the analyte molecules influence the charge injection properties of the contact giving rise to completely different sensing responses.[79]

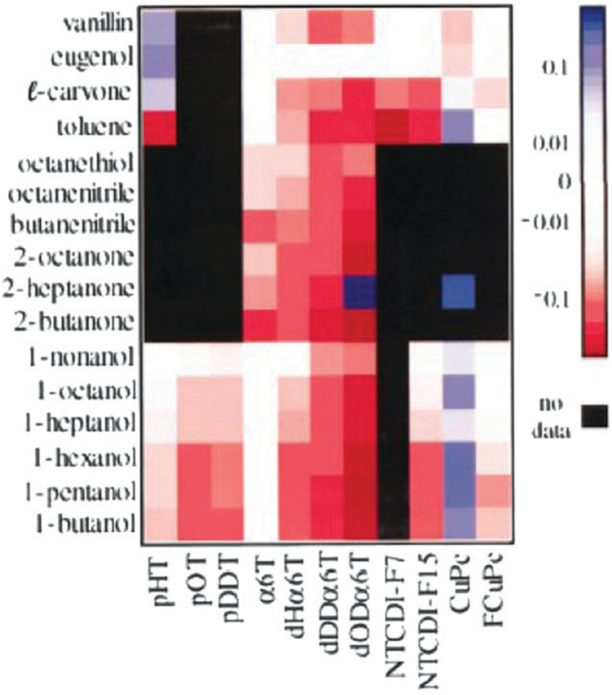


Fig. 8 Map illustrating the responses of 11 organic semiconductors to 16 vapors. Black indicates that data are not available and white negligible response. Positive changes are shown in blue shades and negative changes in shades of red. Reprinted with permission from ref. 78. Copyright 2001, American Institute of Physics.

For biological applications the analyte of interest must be in an aqueous medium rather than in the vapor phase. Devices for sensing lactic acid and glucose in water was achieved by Someya *et al.* by coating the electrodes with an hydrophobic insulator to confine the water to the active region of the transistor to avoid electrical shorts.[80]

Pressure sensors have also been demonstrated using a pentacene-based OFET on a Mylar™ substrate, which acts as gate insulator and also as mechanical support.[81] The drain current revealed a reversibly marked sensitivity to the elastic deformation induced by a mechanical stimulus applied on the device channel, making this device attractive for applications in smart textiles and robotic interfaces.

Organic semiconductors have also been employed to realize organic light-emitting transistors (OLETs).[82] These devices combine the electrical switching functionality of a field-effect transistor with the capability of a light-emitting diode (OLED) to generate light. The operation principle of these devices is based on the formation of an exciton, by recombination of holes and electrons present in the transistor channel, than can relax radiatively. The first OLET was reported on an unipolar p-type OFET based on tetracene.[83] The injected electrons were thus trapped near the gold–tetracene interface where recombination and light emission took place. However, ambipolar OFETs are in principle more suitable for OLETs since the two types of charge carrier can be transported efficiently across the transistor and, therefore, they can provide electron-hole balance and an effective pn-junction within the channel. In addition, contrary to unipolar OLETs where the light emission is restricted to a region close to the contact that injects the charge carriers of lower mobility, in ambipolar OFETs the recombination region can be adjusted between the source and drain by tuning the gate voltage. The first ambipolar OLET was described by Rost *et al.* using a bulk heterojunction of PTCDI-$C_{13}H_{27}$ and α-quinquethiophene.[84] More recently, a single component polymer-based ambipolar OLET has been fabricated using two different electrodes for the source and drain electrodes, and it was shown that the emission zone could be moved across the channel by modifying the gate bias.[85] To progress in this field towards optoelectronic applications, there is now a need to find electroluminescent materials that show remarkable OFET mobilities.

6. Conclusions

As the vast amount of papers published proves, it has been an extremely intense work on the fabrication and study of OFETs in the last 20 years. OFET performances of the same order as amorphous silicon are currently achieved. However, there are still many questions, such as understanding the charge transport mechanisms and the relation structure–mobility, that remain open and which should be addressed to further progress in the field. Finding materials for n-type and ambipolar devices will be also fundamental for the future design of complementary circuits. Finally, if low-cost, flexible and large area-coverage devices are to be realized with organic semiconductors, it is imperative to search for materials with high charge carrier mobility that can be soluble processed, as well as solution-based techniques which allow the preparation of reproducible devices. In conclusion, although there is a lot of work to be done, OFETs promise to be tremendously important for future applications in areas where electronics meets with information technology, biomedicine or optics.

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