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π-Conjugated Molecules with Fused Rings for Organic Field-effect Transistors:

Design, Synthesis and Applications

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Abstract:

π-Conjugated molecular materials with fused rings are the focus of considerable interest in the emerging area of organic electronics, since the combination of excellent charge carrier mobility and high stability may lead to their practical applications. This *tutorial review* discusses the synthesis, properties and applications of π-conjugated organic semiconducting materials especially those with fused rings. The achievements to date, the remaining problems and challenges, and the key research that needs to be done in the near future are all discussed.
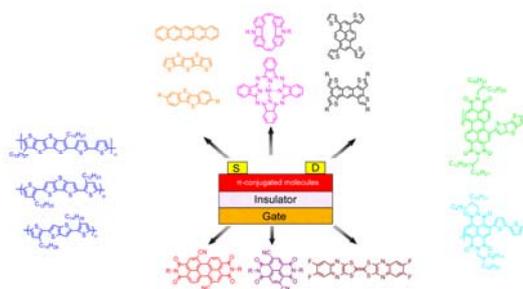
Snappy text: The synthesis, properties and applications of π-conjugated organic semiconductors especially those with fused rings are discussed in this *tutorial review*.

Content

1. Introduction

Over the past decade, the development of organic semiconductors has focused on organic π-conjugated molecules for application in electronic and photonic devices by virtue of their ability to afford high operating speeds, large device densities, low cost, and large area flexible circuits.[1] The key step in developing a suitable candidate for an electronic system such as an organic field-effect transistor (OFET) involves the design of a molecule with optimal charge carrier ability.[2] The reason for the intense research interest in the field of "plastic electronics" is the great opportunity to produce low cost devices on plastic substrates with large areas, which will open up an entire new market segment.[3]

A field-effect transistor (FET) is the type of transistor commonly used for weak-signal amplification. The device can amplify analog or digital signals and act as a switch or an oscillator. In an OFET, the current flows along the organic semiconductor path called the *channel*. At one end of the channel there is an electrode called the *source*. At the other end of the channel, there is an electrode called the *drain*. The physical diameter of the channel is fixed, but its effective electrical diameter can be varied by the application of a voltage to a control electrode called the *gate*. The conductivity of the OFET depends, at any given instant in time, on the effective electrical diameter of the channel. A small change in gate voltage can cause a large variation in the current flowing from the source to the drain. This is how the OFET amplifies signals. Charge carrier accumulation is highly localized at the interface between the organic semiconductor and the gate dielectric, and the bulk of the material is hardly, or not at all, affected by the gate-induced field. OFETs can have either a top gate or bottom gate architecture, depending on the sequence of deposition of the semiconductor and the gate dielectric. The two basic types of OFET with bottom gate architecture, bottom-contact and top-contact, are illustrated in Figure 1a and 1b, respectively. The typical output

characteristics of an OFET working in accumulation mode are depicted in Figure 1c. The output

characteristic of the transistor shows two distinct regimes: linear and saturation.
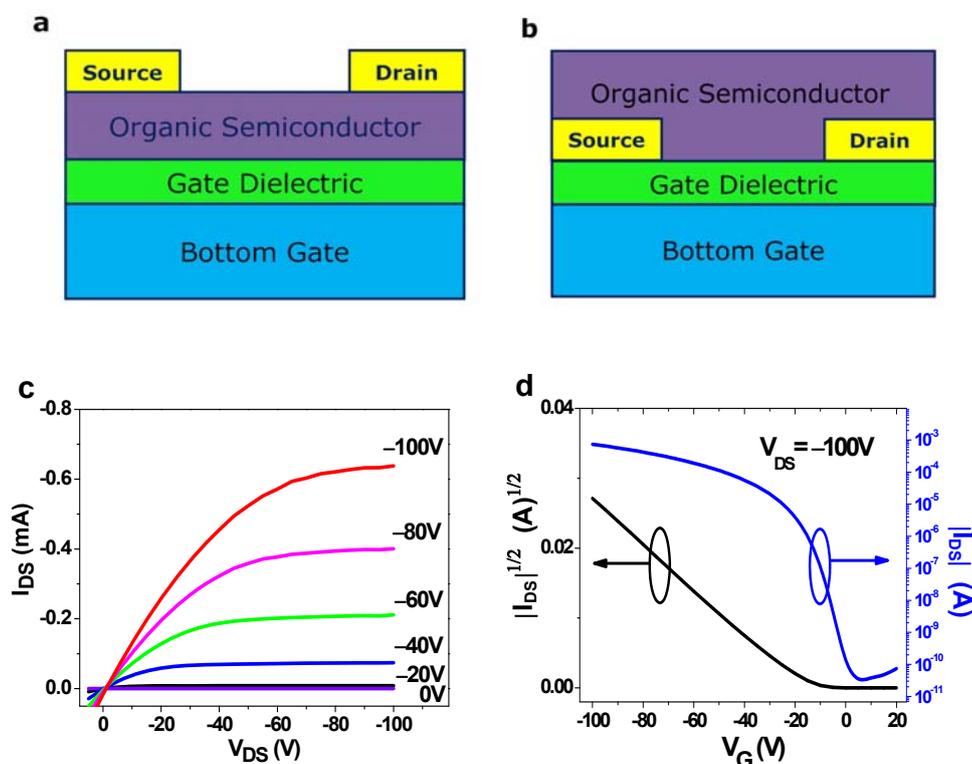
Fig. 1 Schematic illustration of bottom-gated (a) top-contact, (b) top-contact OFET configuration. (c) Output characteristics and (d) transfer characteristics of a pentacene-based top-contact p-channel OFET, whose gate dielectric is made up of 470 nm SiO_2.

The charge transport mobility of the semiconductor is one of the most important parameters that

determine device performance. The charge transport mobility, which can be extracted from the

transfer characteristics (Figure 1d), provides a measure of how easily electrons or holes drift

through a semiconductor in response to an electric field. Previous research efforts on OFETs have

concentrated on improving the mobility and stability of π-conjugated organic semiconductors,

which are the two major obstacles to practical applications of OFETs. A tremendous amount of

knowledge has been gained from research on the structure–property relationships of the molecules used for synthesis of high mobility oligomers.[4] Detailed investigations of the electronic properties of such conjugated oligomers have also been used to model the electronic properties of the polydisperse polymers employed in practical applications. The mobility determines the possible bit speed of the organic integrated circuits, mobility in the magnitude of 1 cm^2/V s is essential for high speed commercial applications in organic digital circuits. For other possible applications such as chemical sensors, mobility of 0.01~0.1 cm^2/V s would be enough. In addition to a large carrier mobility, a large on/off current ratio is required for OFET's practical applications in high speed, low power, high reliable circuits. The on/off ratio could be improved by increasing the on current (by chemical doping, by enhancing the charge injection at the electrodes, by using high-k dielectrics), reducing the off current (by controlling the doping level to minimize the conductivity of active layer, by optimizing materials purity as well as by post processing such as annealing).

OFETs are particularly attractive in that the fabrication processes involved are more cost effective and much less complex when compared with conventional silicon technology. In general, one should be careful when comparing carrier mobilities reported for the same material by various authors as they have usually been measured on samples with different morphologies and purities under different experimental conditions. These newly synthesized organic π-conjugated molecules often consist of one or two aromatic backbones (thiophenes or acenes) similar to those classical molecules (such as tetracene, pentacene, and rubrene) that are known to have large field-effect mobility. Rigid highly π-conjugated molecules are generally insoluble or poorly soluble in most common solvents due to their strong intermolecular π-interactions and/or the lack of flexible chains. Thus, the use of vacuum sublimation is usually required to fabricate OFET devices containing such materials. In the case of vapor-deposited films, the deposition temperature has been shown to exert

an important influence. For less rigid species, in general, low-temperature deposition and solution processing is effective, in contrast to the high-temperature and high-vacuum deposition and sophisticated photolithographic patterning involved in conventional silicon technology. The synthetic flexibility, the potential ease of processing—especially after attaching solubilizing chains—and the possibility of an exact tailoring of the electronic and mechanical properties to accomplish a desired function, makes organic semiconducting oligomers and polymers attractive candidates for future applications in electronic devices on flexible substrates for lightweight and foldable products.

Attractive techniques based on a controlled solvent evaporation leading towards cheap, simple, and large area electronics include drop-casting, spin-coating, zone casting or inkjet printing. Drop casting consists of letting a small volume of solution of compound fall onto the substrate surface and leaving it to dry either in air or in an atmosphere of the solvent to ensure slower evaporation. The molecular self-assembly at the surface is highly influenced by the dewetting phenomena (or rupture of the thin solvent liquid film on the substrate), which depends on the solvent, the solution concentration and the substrate nature. Spin coating is a deposition technique which offers an easy and inexpensive process for mono and multilayer formation. In spin coating, the solution of functional molecules is applied on the substrate which is then rotated on a spinning wheel at high speed so the centrifugal forces push the excess solution over the edge of the substrate and a residue on the substrate remains thanks to surface tensions. This method has several technical advantages when compared with drop casting. In these techniques, the molecular units are allowed to diffuse around the substrate according to the chain and functional groups present. Drop casting and spin coating do not allow the preparation of films with complete anisotropy over large areas. An appealing one-step method for the preparation of large area anisotropic films from a

solution-processable material is zone casting.

A key factor that influences the charge mobility of an organic semiconductor as well its overall performance in organic electronic devices is the intermolecular ordering of the molecules in the solid state. It is generally believed that face-to-face contact between the molecules is preferred for organic electronics as there is the possibility of increased $\pi\cdots\pi$ overlap between the faces of adjacent molecules which facilitates the carrier pathway in the solid. However, the majority of polycyclic aromatic hydrocarbons (PAHs) tend to assemble in an edge-to-face fashion in the crystalline state. Designing an aromatic system that will stack in a face-to-face fashion requires that one overcome these favorable edge-to-face interactions. One way commonly used to accomplish this is to build aromatic systems with a sufficiently large ratio of π-surface-to-circumference such that a perfect herringbone packing—with all intermolecular contacts being edge-to-face interactions—is impossible due to space filling requirements. In addition to adding side chains to increase solubility, substituents can also be incorporated in order to force face-to-face interactions by creating steric effects that do not allow for efficient edge-to-face interactions.

Although many kinds of organic devices utilize such π-conjugated molecules with fused rings, the emphasis of this review is on OFETs since, in this case, the control of molecular orientation is particularly critical for charge transport. After a survey of some recent one-dimensional (1-D) systems, which can be viewed as a first "chemical" attempt to control molecular orientation, the remainder of the article will discuss examples of two-dimensional (2-D) conjugated systems that have emerged in recent years. Due to space limitations, the paper will mostly focus on materials with fused rings that have actually been used for fabrication of devices. This review will also try to identify possible directions for future research in this area.

2. π-Conjugated *p*-type organic semiconductors

OFETs can be *n*-type (negative charge or electrons as the majority carrier), *p*-type (positive charge or holes as the majority carrier), or ambipolar (both electrons and holes are involved as charge carriers). If the Fermi level of the source/drain metal is close to the highest occupied molecular orbital (HOMO) level of the organic semiconductor, then positive charges can be extracted by the electrodes by applying a voltage, V_{DS}, between drain and source. Organic semiconductors with the ability to conduct only positive charge carriers are said to be *p*-type semiconductors. Recent years have seen significant improvements in charge carrier mobilities of *p*-type organic semiconductor materials for use in OFETs.

2.1 Molecular design of *p*-type organic semiconductors

Pentacene (compound (**2**) in **Scheme 1a**) OFETs have received particular attention since they have shown hole mobilities of up to 5 cm^2 V^{-1} s^{-1} with on/off current ratios of up to 10^8 in some cases. However, pentacene is only moderately stable to oxygen as a dense solid and is unstable under illumination. Pentacene also has a very high melting point and is virtually insoluble, even in hot aromatic solvents. Hexacene (**3**) has received some attention and appears in the solid state to follow a homologous series with tetracene (**1**) and pentacene (**2**).[5] However, like pentacene, this molecule has proven to be unstable, being highly reactive in the 6- and 15- positions due to π electron localization.

Sulfur-rich annulated oligomers and polymers have attracted growing interest owing to their desirable characteristics (electronic, optical, and magnetic properties) for fabricating electronic and optical devices. In particular, thiophene-based conjugated oligomers and polymers have been shown to be environmentally stable and robust in nature. Oligothienoacenes (*n*TA: fully fused

oligothiophenes, (**4**)–(**7**)) and thiophene-based acenes are among the most frequently studied organic semiconducting materials. The advantages of these molecules have been attributed to their unique structural features: all the sulfur atoms are positioned at the molecular periphery, facilitating multiple short intermolecular S···S contacts which increase the effective dimensionality of the electronic structure with the result that they may possess enhanced transport properties.

2.2 Field-effect transistors based on linear compounds

2.2.1 Pentathienoacene

Condensed derivatives of thiophenes have attracted considerable interest as building blocks for electrically conducting polymers. Their low oxidation potential, high degree of conjugation achieved using fused blocked aromatic rings and high degree of rigidity favor an enhanced π···π overlap in the solid state, leading to efficient intra- and interchain charge transport, resulting in high charge carrier mobilities. Ring fusion can also induce changes in molecular packing, for instance, from a less favorable herringbone packing to the desired π-stacking.

Pentathienoacene (compound (**5**) in **Scheme 1a**), the thiophene equivalent of pentacene (**2**), is one of the latest additions to the family of organic crystal semiconductors with great potential for use in OFETs. Recently an improved synthesis of pentathienoacene (**5**) and extension of the series to make heptathienoacene (**7**) has been reported by Zhang and co-workers.[6] These oligothienoacenes show molecular packing in the desired face-to-face π-stacking motif, rather than the herringbone packing typical of nonfused oligothiophenes or pentacene. Pentathienoacene (**5**) was successfully developed as an active semiconducting material for OFETs by our group via synthetic routes in **Scheme 1b** in 2005. The best mobility achieved was 0.045 cm^2 V^{-1} s^{-1} with pentathienoacene (**5**) as the substrate at a temperature of 80 °C.[7] Hexathienoacene (**6**) and

octathienoacene, consisting of an even number of thiophene rings, have also been synthesized although somewhat later than pentathienoacene (**5**) and heptathienoacene (**7**), mainly due to their limited solubility during the synthetic steps.[8]
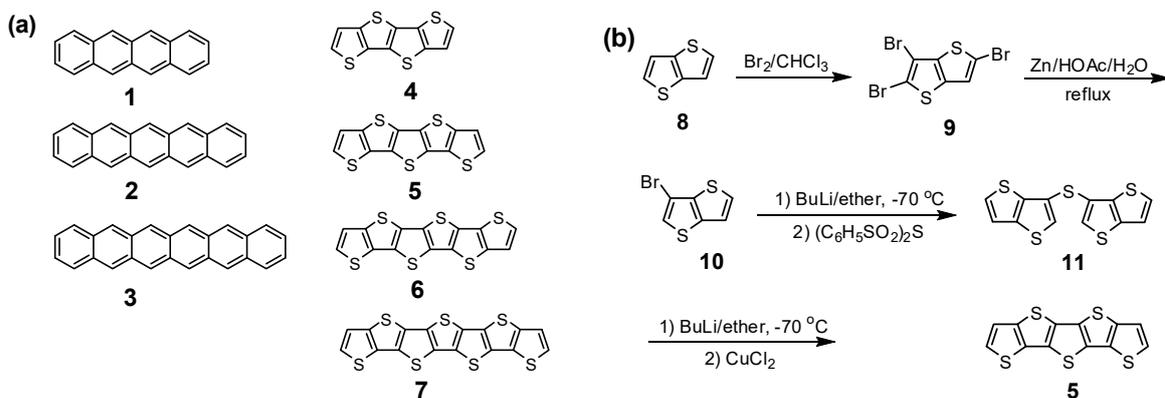
Scheme 1. (a) Chemical structure of acenes and fused-ring oligothiophenes. (b) Synthetic routes for pentathienoacene (**5**) (Reprinted with permission from ref. 7. © 2005, American Chemical Society).

By using density functional theory and gas-phase ultraviolet photoelectron spectroscopy, Kim et al. investigated the microscopic charge transport parameters of pentathienoacene crystals.[9] They found that the valence band exhibited a stronger dispersion than those in pentacene and rubrene (5,6,11,12-tetraphenylnaphthacene) single crystals, with marked uniaxial characteristics within the molecular layer due to the presence of one-dimensional π-stacks; a small hole effective mass was also found along the direction perpendicular to the molecular layers. In the conduction band, strong intermolecular sulfur–sulfur interactions gave rise to a significant inter-stack electronic coupling whereas the intra-stack dispersion was greatly reduced. The intra-molecular vibronic coupling (reorganization energy) was found to be stronger than that in pentacene but comparable to that in sexithiophene (which contains six non-fused thiophene moieties); it was also found to be larger for holes than for electrons, as a result of low-frequency modes induced by the sulfur atoms.

2.2.2 Thieno[3,2-b]thieno[2',3':4,5]thieno[2,3-d]thiophene derivatives

Thieno[3,2-*b*]thieno[2',3':4,5]thieno[2,3-*d*]thiophene (tetrathienoacene, **TTA**, (**4**) in **Scheme 1a**) is a conjugated four thiophene-fused system. Novel materials with good performance can be obtained by introducing **TTA** moieties into molecules. We synthesized a series of functionalized thieno[3,2-*b*]thieno[2',3':4,5]thieno[2,3-*d*]thiophene derivatives ((**12**)–(**14**) in Figure 2a) that are composed of a tetrathienoacene core and symmetrically substituted phenyl, biphenyl, or naphthyl groups.[10] OFETs based on (**12**) demonstrated the best performance with a mobility of 0.14 $cm^2 V^{-1}$ s^{-1} and an on/off ratio of up to 10^6. The crystal structure of (**12**) shows both $\pi\cdots\pi$ stacking and intermolecular S$\cdots$S contacts (see Figure 2a (right)). The molecules are packed to form a sheet-like array in the *ac* plane in which the side-by-side intermolecular S$\cdots$S contact distances are 3.42 Å. The molecular sheets form a columnar stacking in the *a*-axis direction with an interplanar separation of 2.22 Å. Between the stacks, the interaction is reinforced by close intermolecular S$\cdots$S contacts.
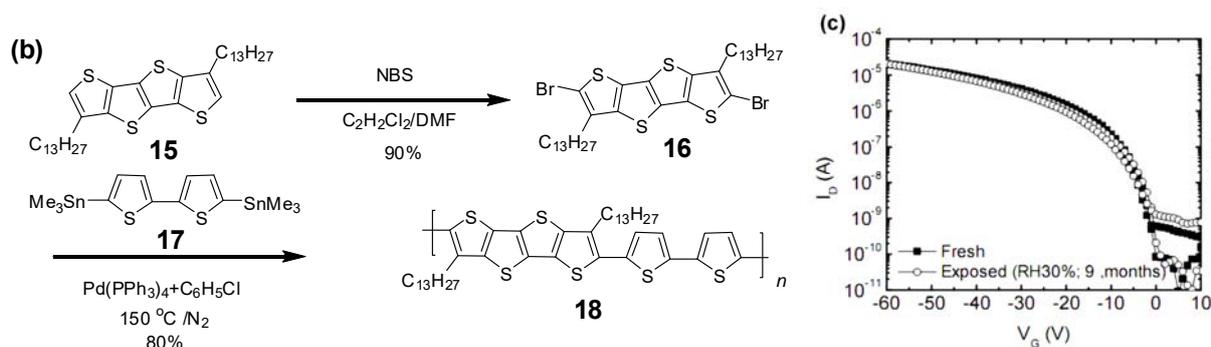
Fig. 2 (a) Chemical structures of thieno[3,2-*b*]thieno[2',3':4,5]thieno[2,3-*d*]thiophene derivatives (**12**)–(**14**) (left), and the stacking structure of (**12**) along the *b*-axis direction (right) (ref. 10. © Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission). (b) Synthetic scheme for poly(2,5-bis(thiophene-2-yl)-(3,7-ditri-decanyltetrathienoacene), **P2TDC13FT4**, (**18**). (c) Transfer characteristics of a **P2TDC13FT4** OFET measured immediately after fabrication and 9 months later (Reprinted with permission from ref. 11. © 2008, American Chemical Society).

Introducing both extended π-conjugated fused thiophene moieties and single thiophene units into the backbone of polymers, which reduces the π⋯π overlap between adjacent thiophene rings and increases the rotational freedom of the main chains, can inhibit delocalization and thereby lead to enhanced stability and retention of high charge mobility. Fong et al. reported[11] a member of the family of dialkylated tetrathienoacene copolymers (Figure 2b), namely poly(2,5-bis(thiophene-2-yl)-(3,7-ditri-decanyltetrathienoacene) (**P2TDC13FT4**, (**18**)), that can be deposited from solution to afford highly ordered films with a field-effect hole mobility exceeding 0.3 cm^2 V^{-1} s^{-1}. Moreover, a device with an octyltrichlorosilane (OTS) modified gate dielectric showed no significant degradation in its output characteristics over nine months when stored at 30% relative humidity (Figure 2c), indicating the excellent environmental stability of **P2TDC13FT4**. These advantages of environmental stability and straightforward solution processing make **P2TDC13FT4** particularly attractive for applications in large-area, mechanically flexible

electronics.

2.2.3 Dithieno[3,2-b:2',3'-d]thiophene derivatives

Other condensed derivatives of thiophenes, e.g. dithieno[3,2-b:2',3'-d]thiophene (**DTT**, compound (**19**) in **Scheme 2**), have also received considerable interest as building blocks for electrically conducting oligomers and polymers. Indeed, α-dimeric **DTT** (**biDTT**, (**20**)) has been used as the active component in OFETs showing interesting device characteristics[12], e.g. relatively high mobility (0.05 $cm^2 V^{-1} s^{-1}$) and large on/off ratios (~10^8), which have been attributed to the closely packed face-to-face stacking and the wide energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the material. Iosip et al.[13] have synthesized and characterized an OFET material (**22**) based on dithieno[3,2-b:2',3'-d]thiophene and thiophene units, and obtained stable, high-mobility semiconductors with highest field-effect mobility of 2×10^{-2} $cm^2 V^{-1} s^{-1}$ and an on/off ratio greater than 10^6.

We have also designed, synthesized and characterized a series of new oligomers ((**21**), (**23**), and (**24**)) based on dithieno[3,2-*b*:2',3'-d]thiophene units.[14] Compound (**23**) exhibits an excellent field-effect performance with a high mobility of 0.42 $cm^2 V^{-1} s^{-1}$ and an on/off ratio of 5×10^6 and shows high environmental stability. Later on, a benzannulated **DTT**, dibenzo[*d,d'*]thieno[3,2-*b*:4,5-*b'*]-dithiophene (**25**) with a very low-lying HOMO level of –5.60 eV and a large band gap of 3.46 eV, was investigated and showed not only promising semiconducting properties (mobility of 0.51 $cm^2 V^{-1} s^{-1}$ and an on/off ratio larger than 10^6), but also high thermal and photostability, as well as ease of synthesis.[15]
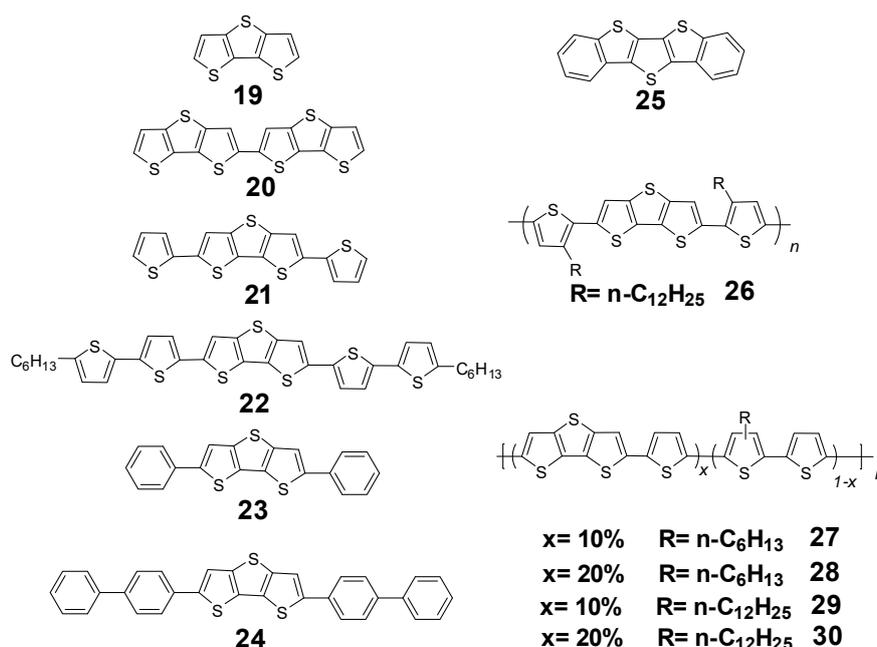
Scheme 2. Organic semiconductors based on dithieno[**3,2-*b*:2',3'-d**]thiophene moieties for high-performance and stable OFETs.

Another successful strategy toward increased mobility and ambient air stability is manipulation of band energy levels by inserting dithieno[3,2-*b*:2',3'-d]thiophene units into a polythiophene backbone.[16] Ong and coworkers described the synthesis of the copolymer, poly(2,6-bis(3-alkylthiophen-2-yl)dithieno-[3,2-*b*;2′,3′-*d*]thiophene) (**PBTDT**, (**26**)), an excellent solution-processed semiconductor for OFETs with a mobility of 0.3 $cm^2\,V^{-1}\,s^{-1}$ and a very high current on/off ratio larger than 10^7. We have synthesized a series of air stable copolymers ((**27**)–(**30**)) incorporating rigid **DTT** moieties and single thiophene units into the thiophene main chain, adopting random polymerizing configuration.[17] The best resulting hole mobility afforded was 0.028 $cm^2\,V^{-1}\,s^{-1}$ with an on/off ratio of 2×10^4 in the saturation regime. Furthermore, all the devices exhibited high environmental stability against oxygen doping and relatively high ambient humidity (~30%).

2.2.4 Thieno[3,2-b]thiophene derivatives

Incorporating fused thiophenes into oligoacene frameworks is a promising strategy in the development of novel air stable organic semiconductors since fused thiophene moieties can improve the extent of intermolecular $\pi\cdots\pi$ overlap in the solid state, a feature that is closely related to charge carrier mobility. Takimiya et al. have focused their attention on the thieno[3,2-b]thiophene ((31) in Figure 3a) derivative 2,7-diphenyl[1]benzothieno[3,2-*b*][1]-benzothiophene (**DPh-BTBT**, (**32**)) and successfully developed a series of excellent organic semiconductors for OFETs (Figure 3a).[18] The HOMO energy level of **DPh-BTBT** (–5.41 eV) is lower than that of pentacene and is comparable to that of anthracene. The best devices afforded impressive mobilities as high as 2.0 $cm^2\,V^{-1}\,s^{-1}$ and an on/off ratio of 10^8. Furthermore, the superior device characteristics were preserved for long periods of time (~250 days) without any significant change (Figure 3b). Later on, the same group found[19] that thin films prepared from 2,7-dialkyl[1] benzothieno[3,2-*b*][1]benzothiophenes (**C***n***-BTBT**, (**33**)) are stable toward oxidation and exhibit hole mobilities up to 2.75 $cm^2\,V^{-1}\,s^{-1}$. The crystal assumes a "layer-by-layer" structure consisting of alternately stacked aliphatic layers. In the **BTBT** core layer, the molecules adopt a herringbone packing which facilitates 2-D carrier transport properties. In addition, a network of intermolecular interactions through short $S\cdots S$ contacts (3.54 and 3.63 Å) exists. The high mobilities of **C***n***-BTBT**-based FET devices can be attributed to these structural aspects, since the existence of 2-D semiconducting layers with strong intermolecular overlap is considered to be one of the prerequisites to realizing high-performance OFET devices.
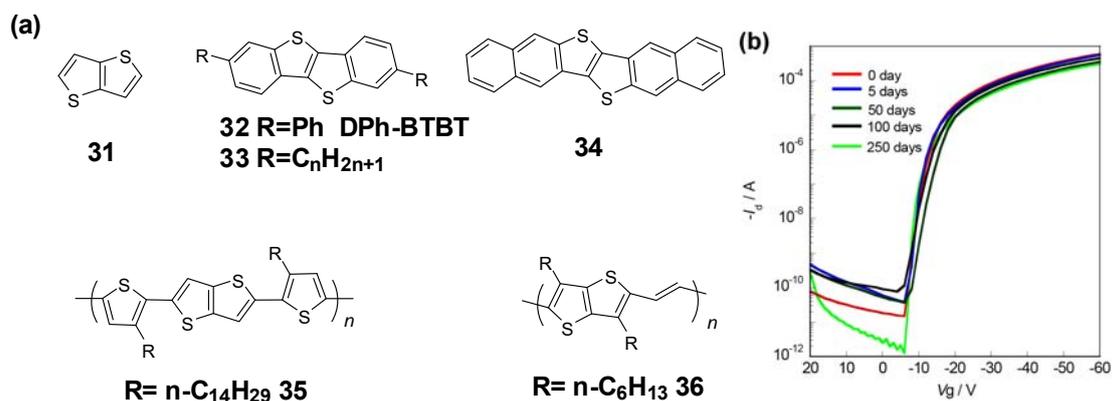
Fig. 3 (a) Organic semiconducting materials based on thieno[3,2-b]thiophene (**31**) for OFETs. (b) Transfer characteristics (V_d = –60 V) of OFETs based on **DPh-BTBT** (**33**) on an octyltrichlorosilane (OTS) treated substrate (T_{sub} = 100 °C) (Reprinted with permission from ref. 18. © 2006, American Chemical Society).

Expansion of the π-framework has the potential to provide even more durable high-performance organic semiconductors. A further compound that Takimiya et al. designed with this idea in mind is dinaphtho[2,3-b:20,30-f]thieno[3,2-b]thiophene (**DNTT**, (**35**)4) with six fused aromatic rings.[20] The calculated HOMO and LUMO levels for this compound are –5.19 and –1.81 eV, respectively. The molecules are almost planar with a small standard deviation of 0.058 Å and form a layer-by-layer structure in the crystal of **DNTT**. In a preliminary examination, a device fabricated with **DNTT** operated in air and showed a very high hole mobility of 2.9 cm^2 V^{-1} s^{-1}, close to the record level for thin film pentacene, and the on/off ratio of 10^7 was also excellent. Recent efforts have shown that pentaceno[2,3-*b*]-thiophene, another compound with six fused aromatic rings, is also useful for application in OFETs.[21] These two compounds are the most conjugated acene-based systems to be used in device applications, overcoming the instability of hexacene that renders it impractical for application in thin-film transistors.

The incorporation of partially planarized fused thiophene-based units into the polymer backbone

is an alternative approach towards improving conjugation and optimizing solid-state properties. McCulloch and co-workers reported the synthesis of poly(2,5-bis(3-alkylthiophene-2-yl)thieno[3,2-*b*]thiophene) (**PBTTT**, (**35**)), which incorporates thieno[2,3-*b*]thiophene with sulfur atoms in the *anti* position.[22] **PBTTT** exhibits a liquid crystalline phase that enables the fabrication of films with high crystallinity. OFETs fabricated with **PBTTT** showed the highest mobility reported to date, 0.6−1.0 cm^2 V^{-1} s^{-1}. **PBTTT** crystallizes with lamellae of π-stacked polymer chains on both surfaces. The crystalline domains are well-oriented relative to the substrate in the as-spun state and become highly oriented and more ordered with thermal annealing in the liquid crystalline mesophase. We prepared poly(3,6-dihexyl-thieno[3,2-b]thiophene vinylene) (**DH-PTTV**, (**36**)) by Pd-catalyzed Stille coupling.[23] The highest FET hole mobility of **DH-PTTV** after thermal annealing at 180 °C for 30 min reached 0.032 cm^2 V^{-1} s^{-1} with an on/off ratio of 10^5. The transfer characteristics of **DH-PTTV** show near-zero turn-on voltage and a small threshold voltage, indicating its high air stability due to its low HOMO (–5.04 eV) energy level.

2.2.5 Tetrathiafulvalenes

Tetrathiafulvalene (TTF) is a planar non-aromatic 14 π-electron system. Recently, various tetrathiafulvalene (TTF) derivatives were shown to exhibit excellent OFET performances both in single crystals and thin films.[24] Mas-Torrent et al. found a clear correlation between crystal structure and charge carrier mobility in OFETs based on single crystals of tetrathiafulvalene derivatives[25], by studying organic single-crystal FETs based on materials related to dithiophene-TTF, **DT-TTF** (**39**).
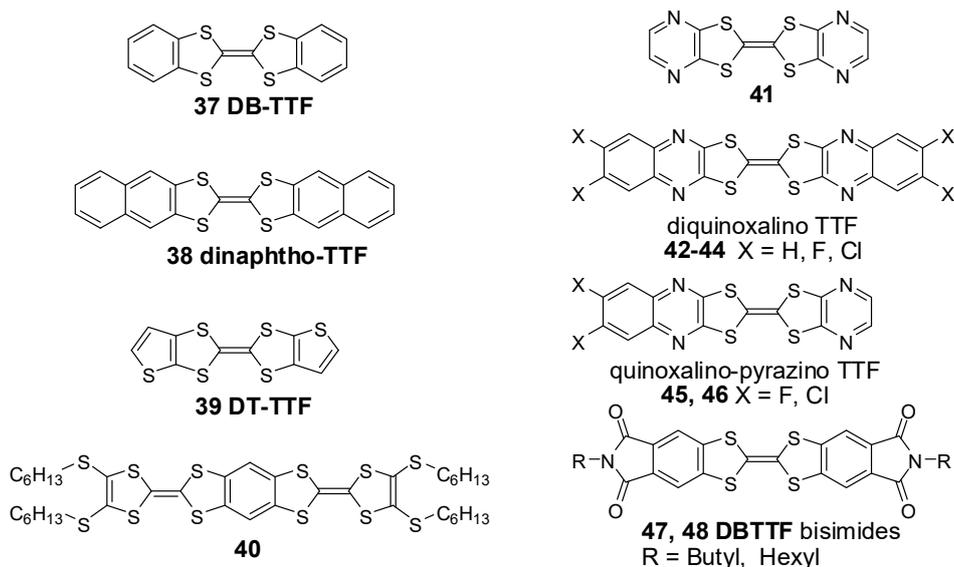
Scheme 3. Tetrathiafulvalene derivatives for OFET applications.

In spite of the high mobility, tetrathiafulvalene compounds also showed some poor OFET characteristics, such as large off-current at zero gate voltage V_G, low on/off ratio and non-saturating behavior. For example, high mobility but poor stability were obtained with **DB-TTF (37)**, **dinaphtho-TTF (38)**, **DT-TTF (39)** and the linear benzene-fused **bis(TTF) (40)**.[26] It has been found that a decrease in the electron donating properties is necessary in order to enhance the air stability of TTF derivatives. The following methods can be used: (1) attaching fused aromatic rings (benzene, naphthalene, pyrazine, or quinoxaline rings) onto the TTF skeleton; (2) attaching electron-withdrawing groups onto the fused TTF skeleton. After such modifications, high-performance TTF-based FET devices can be obtained. For example, after introducing quinoxaline rings, the first oxidation potential of the resulting (**42**) (1.15 V) was much higher than that of **dinaphtho-TTF (38)** (0.72 V), which led to its high oxygen stability and high current on/off ratios (up to 10^6) (under an O_2 pressure of 760 Torr, the mobility was little increased and the off-current was unchanged).[27] It should be noted that compound **DB-TTF (37)**, the dinaphtho-TTF derivative (**38**), and the dipyrazino-TTF derivative (**41**) all have herringbone packing. In contrast,
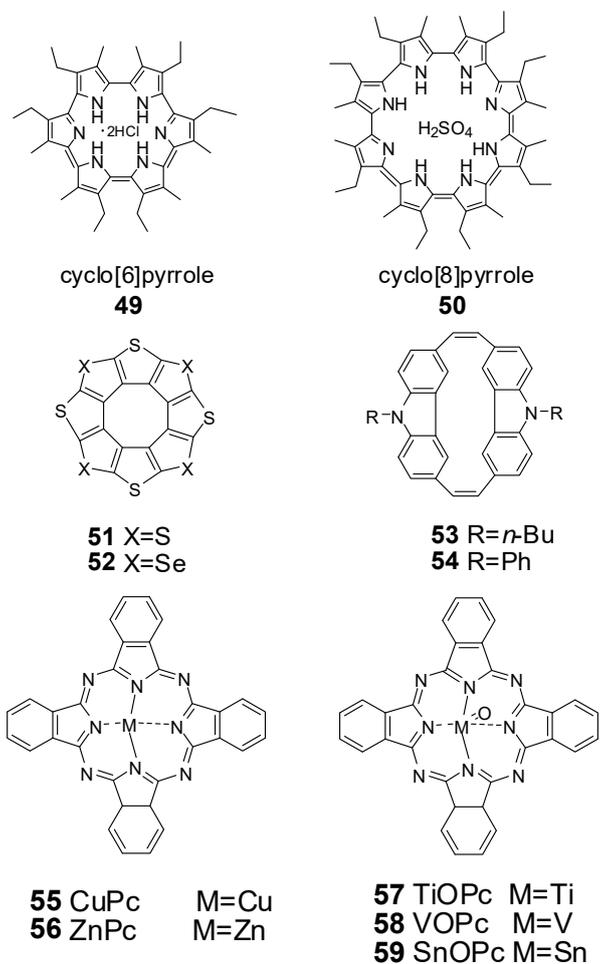
the quinoxalino derivative (**42**) has a face-to-face π-stacking motif, where the interplanar distance is about 3.41 Å and the shortest intermolecular S···S distance is 3.58 Å. The 1,3-dithiole rings overlap with the pyrazine rings, suggesting the presence of intermolecular charge transfer interactions which might induce the face-to-face π stacking.

Our group developed TTF/bisimide derivatives **DB-TTF** bisimides ((**47**) and (**48**)) by attaching imides as electron-withdrawing groups.[28] The resulting planar π-expanded molecules had lower-lying HOMO levels (–5.4 eV) relative to that of **DB-TTF (37)** (–4.97 eV). OFET devices based on (**47**) and (**48**) were fabricated at room temperature and measured in air, showing high hole mobility up to 0.094 cm^2 V^{-1} s^{-1} and 0.40 cm^2 V^{-1} s^{-1}, respectively, with high on/off ratios on the order of 10^6–10^8 as well as good stability to oxygen.

2.3 Field-effect transistors based on molecules with macrocyclic architecture

As illustrated above, the most common approach for increasing the mobility of π-conjugated *p*-type organic semiconductors is to add several benzene (or thiophene) rings in a linear fashion. A far less explored possibility is to extend the conjugation by linking the aromatic units in a macrocycle, as in circulenes. Macrocyclic molecules with extended π-conjugation represent a new class of functional organic materials with novel electrical, optical and structural properties.[29] In particular, the cyclic structure of these compounds represents an infinite well-defined π-conjugated chain excluding perturbing end-effects. The higher symmetry of such molecules (as compared to linear, star-shaped or dendrimeric structures) is potentially more favorable in terms of solid-state packing. The cyclic nature of the compounds changes their coordination behavior and structural features, which may improve the molecular ordering in the solid state and facilitate charge carrier transport. They can be designed to give materials with tailored properties for applications in

molecular electronics. Our initial interest in such macrocycles as the active components in OFETs started from our observations of high charge carrier mobility in Langmuir–Blodgett films of cyclo[6]pyrrole ((**49**) in **Scheme 4**)[30] and cyclo[8]pyrrole (**50**)[31].

cyclo[6]pyrrole
49

cyclo[8]pyrrole
50

51 X=S
52 X=Se

53 R=*n*-Bu
54 R=Ph

55 CuPc   M=Cu
56 ZnPc   M=Zn

57 TiOPc M=Ti
58 VOPc   M=V
59 SnOPc M=Sn

Scheme 4. Molecules with macrocyclic architecture for application in OFETs.

2.3.1 Octathio[8]circulene

Introducing heteroatoms, such as S or Se, on the periphery of the circulene core, can induce intercolumnar interactions and, possibly, improve the charge carrier mobility in the resulting π-conjugated organic semiconductors. Recently the first all-heterocyclic, highly symmetric

octathio[8]circulene, the so called "sulflower" (**51**), was synthesized.[32] With eight thiophene rings, (**51**) can be considered as a thiophene oligomer with a special cyclic structure, which differentiates it from the commonly studied thiophene oligomers. Molecular modeling and X-ray diffraction studies have indicated that this molecule has an almost planar geometry with nearly D_{8h} symmetry. In both the solid state and in thin films it packs in columns held together by close S$\cdots$S contacts (~3.25 Å), which could facilitate 3-D charge transport. The extremely close packing of the sulflower molecules in the solid state suggests strong intermolecular interactions both within layers and between adjacent layers. Such interactions should increase the chance of its future use as an electron donor in OFETs and other materials science applications.

Dadvand et al. demonstrated the applicability of sulflower (**51**) and its selenium analogue tetraselenotetrathio[8]circulene (**52**) (selenosulflower) as organic semiconductors by fabricating thin-film transistors with these materials.[33] OFETs with sulflower (**51**) as the organic semiconductor showed a hole field-effect mobility of about 9×10^{-3} cm^2 V^{-1} s^{-1} and on/off current ratio of 10^6. A rather high threshold voltage, ranging from –40 to –46 V was measured for these devices. This can be explained (at least partially) by the very low HOMO of (**51**) (–5.7 eV) and the resulting hole injection barrier at the Au electrode (workfunction 5.1 eV). Selenosulflower (**52**) OFETs showed a lower mobility of about 1×10^{-3} cm^2 V^{-1} s^{-1}, albeit with a much lower threshold voltage of –10 V, in accordance with the higher HOMO of (**52**) (–5.2 eV). High device stability and on/off ratio were also observed for this organic semiconductor.

2.3.2 Carbazolenevinylene oligomers

Quantum chemical calculations showed that cyclic compounds possess smaller HOMO–LUMO gaps and more extended conjugation than acyclic analogs. We synthesized another two cyclic carbazolenevinylene dimers (**53**) and (**54**) by McMurry coupling reactions.[34] The design of such

structures was based on the following considerations. Firstly, a high degree of molecular alignment and a molecular orientation that is favorable for intermolecular charge migration are needed for efficient charge transport and thus for good device performance. Secondly, vinylene was chosen as the linker, because the introduction of double bonds into organic conductors is known to reduce the band gap and tune the electrical properties by giving an extended π-conjugated length.

The X-ray crystal structure of (**54**) showed partial $\pi\cdots\pi$ overlap between adjacent molecules. Thin films of (**53**) and (**54**) were fabricated by the vacuum-deposition method on Si/SiO$_2$ substrates. Multicrystalline thin films were obtained from compounds (**53**) and (**54**), whereas only amorphous thin films could be obtained for their linear analogs. Another important difference between the cyclic and linear compounds is the reduced reorganization energy for the cyclic compounds. These two factors resulted in improved field-effect mobilities for the cyclic compounds compared with the linear compounds. FET devices based on (**54**) gave the highest mobility of 0.013 cm^2 V^{-1} s^{-1}. These results showed that carbazole derivatives with cyclic structures might allow improved OFETs to be fabricated.

2.3.3 Phthalocyanine derivatives

As a class of macrocyclic planar aromatic molecules, phthalocyanines (**Pc** in **Scheme 4**) represent one of the most promising candidates for ordered systems. They are formed by a π-conjugated aromatic ligand, consisting of a porphyrin macrocycle surrounded by four benzene rings. In its central cavity, the ligand can accommodate cations of over seventy different elements. Most of the cations do not cause a significant distortion of the macrocycle and many metal phthalocyanine (MPc) molecules are planar (e.g. CuPc, CoPc, FePc, MnPc, NiPc, and ZnPc). Of these, copper phthalocyanine (CuPc, (**55**)) is one of the most widely used molecules for OFETs

with a maximum field-effect mobility of 0.02 cm^2 V^{-1} s^{-1}. The electronic properties of the MPc molecule depend strongly on both the central metallic element inside the cavity of the ligand and the phase. The different modes of intra-stack packing as well as the different orientation of the molecular stacks with respect to the crystallographic axes, give rise to several polymorphic forms of MPcs. Some nonplanar axially oxygen substituted metal phthalocyanines such as TiOPc (**57**)[35], and VOPc (**58**)[36] have been discovered to possess high *p*-type field-effect properties. In contrast, it should be noted that tin (IV) phthalocyanine oxide (SnOPc, (**59**)) was found to be an interesting air-stable *n*-type OFET material which contains no electron-withdrawing groups.[37]

2.4 Field-effect transistors based on star shaped molecules

As we have seen, organic semiconductors based on low-dimensional π-conjugated systems such as oligothiophenes have highly anisotropic electronic properties. Another possible way to improve the mobility of organic semiconductors is to reduce the anisotropy of electronic properties (and hence the need to control molecular orientation) by increasing the dimensionality of the elemental unit. Among various kinds of organic semiconducting materials, star-shaped crystalline molecules have been highlighted because of their strong potential applications in OFETs and organic photovoltaic devices. Actually, the most famous star shaped OFET molecule is rubrene (**60**), a material well known for its large carrier mobility as high as 20 cm^2 V^{-1} s^{-1} in single crystal form.[38] Compared with linear organic conjugated oligomers and polymers used, star-shaped molecules offer a number of advantages when used in OFETs, including the ability to demonstrate multifunctionality in a single molecule.
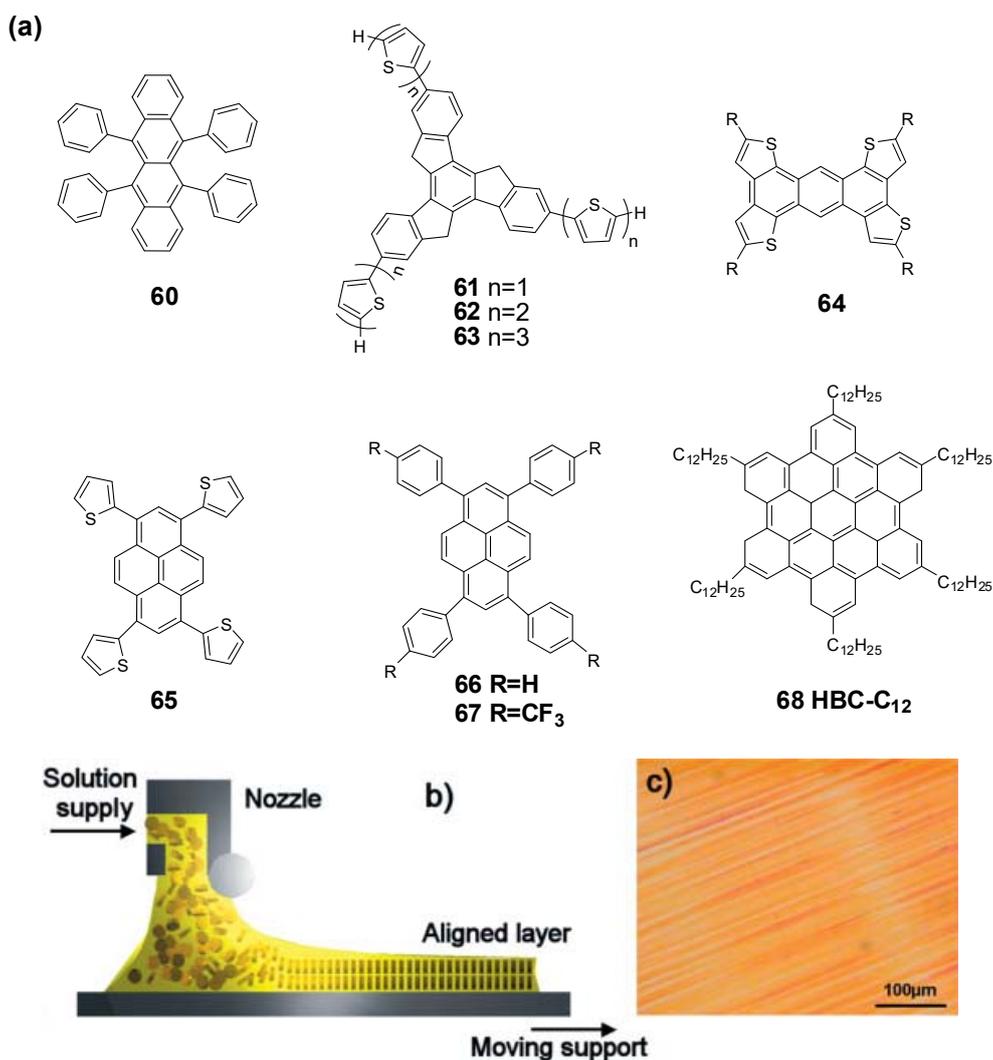
Fig. 4. (a) Chemical structures of some star-shaped compounds for FET applications. (b) Schematic presentation of the zone-casting technique. (c) An optical microscopy image taken in reflection mode for a zone-cast **HBC-C$_{12}$** (**68**) layer on a silicon substrate (ref. 43. © Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission).

2.4.1 Oligothiophene-functionalized truxenes

Ponomarenko et al. first reported the synthesis of three-armed star-shaped oligothiophenes, which demonstrated successful semiconducting characteristics for solution-processible OFETs.[39] Recently, the star-shaped molecules (**61**)–(**63**) have been developed as an interesting class of semiconducting

materials. OFET devices containing (**61**) fabricated by spin coating displayed the highest mobility of up to 1.03×10^{-3} cm^2 V^{-1} s^{-1}, which is one order of magnitude higher than that first reported by Ponomarenko et al. It was also found[40] that an increase in the oligothiophene length of the star-shaped molecules from n=1 (**61**) to n = 3 (**63**) led to a dramatic decrease in mobility to 2.2×10^{-4} cm^2 V^{-1} s^{-1} for the latter compound.

2.4.2 Anthra[1,2-b:4,3-b':5,6-b'':8,7-b'''] tetrathiophenes

Liu et al. devised a simple synthesis of two sulfur-rich anthra-[1,2-*b*:4,3-*b'*:5,6-*b''*:8,7-*b'''*]tetrathiophene-based heteroarenes with favorable $\pi\cdots\pi$ interactions. Both molecules tend to self-associate through $\pi\cdots\pi$ stacking in solution and in films.[41] A hole mobility of 0.012 cm^2 V^{-1} s^{-1} was obtained for (**64**) after thermal annealing. Such notable enhancement of hole mobility after annealing demonstrates the heat-driven change in the morphology of the films from less ordered to highly ordered structures. The good performance was retained over a period of 14 days, indicating the high stability of such transistors. The results shed important light on the strategies needed to develop air-stable, high-performance organic semiconductors.

2.4.3 Pyrene-based star-shaped molecules

We synthesized the two butterfly pyrene derivatives (**65**) and (**67**) functionalized with thienyl and trifluoromethylphenyl groups, respectively, in the 1-, 3-, 6- and 8-positions of pyrene cores by Suzuki coupling reactions, investigated their crystal structures and optical and electrochemical properties.[42] Both molecules display an inner flat, symmetric molecular geometry, while the peripheral thienyl and trifluoromethylphenyl units adopt twisted forms, connecting with the pyrene

core like a flying butterfly. Both compounds (**65**) and (**67**) dissolve in common organic solvents, allowing these semiconductors to be easily purified by a combination of recrystallization and gradient sublimation. An OFET device using (**65**) as the active material exhibited *p*-type performance; the mobility was 3.7×10^{-3} cm^2 V^{-1} s^{-1} with an on/off ratio of 10^4, and the threshold voltage was –21 V. Compound (**67**) was designed with the aim of obtaining an *n*-type material, however, it did not show any FET performance in ambient air.

2.4.4 Discotic star-shaped molecules

As an alternative to solution casting, thin-film devices based on discotic dodecyl-substituted hexa-*peri*-hexabenzocoronene molecules **HBC-C₁₂** (**68**) were fabricated by zone-casting onto hydrophobic substrates to form semiconducting columnar structures. The resulting films showed the presence of long-range ordering and a highly crystalline nature. These films showed excellent FET performance with saturation mobilities of up to 0.01 cm^2 V^{-1} s^{-1}, an order-of-magnitude improvement compared with that of devices prepared by solution casting.[43] The improved FET performance of the devices may be attributed the improved high-quality thin films obtained by the zone-casting technique. As shown in Figures 4b and 4c, the zone-casting technique is a one-step method for preparing large-area-oriented films of solution-processable materials without using a pre-oriented substrate, which involves supplying a solution of an organic material through a stationary flat nozzle onto a moving substrate. The fact that large-area well-oriented films of (**68**) were prepared from solution makes these devices suitable for low-cost and large-area-coverage electronics.

3. π-Conjugated *n*-type organic semiconductors

Organic materials should intrinsically be able to exhibit ambipolar behavior (i.e. they should be both *n*-type as well as *p*-type semiconductors), but very often *p*-type behavior has been found to dominate—as we have described above, the vast majority of organic-based semiconductors display hole-transporting (*p*-type) behavior in transistors. However, one important type of OFET circuit, known as a complementary circuit, requires an *n*-type semiconductor material in addition to a *p*-type semiconductor material. Appropriate design of an organic electronic system to allow the formation of either an *n*-type or *p*-type material is therefore desirable.

3.1 Molecular design of *n*-type organic semiconductors

Ideal systems are those where the *n*- and *p*-type materials have similar electrical and physical properties but possess different charge carriers. Electron transporting (*n*-type) materials should be selected from materials with a low-lying LUMO (high electron affinity). In the case of hole-transporting (*p*-type) materials the HOMO energy is important. Tuning of the energy levels of organic materials may be achieved by a chemical tailoring of the molecular structure. The electron affinity of an organic semiconductor can be increased by introducing strongly electron-withdrawing substituents onto its conjugated backbone. As fluorine is the most electronegative of all the elements and relatively small (hydrogen < fluorine < carbon), perfluorination is an effective way to convert a *p*-type organic semiconductor into an *n*-type one without changing the molecular size greatly.[44] Strongly electron-withdrawing groups such as fluorine atoms pull electron density away from the core of the π system, essentially lowering the energy of the LUMO and facilitating electron injection.

It should be pointed out, however, that it is not necessary to fully fluorinate a molecule and that

the location of the fluorine atoms on the π system may be important. Attaching strongly electron-withdrawing groups to aromatic core does not necessarily result in *n*-type materials, however. In some cases, unsymmetrical molecular structures with electron-withdrawing groups on one side only, showed *p*-type OFET performance (such as the TTF derivatives (**45**) and (**46**) discussed above).[45] Calculations have shown that the introduction of an electron-withdrawing substituent onto conjugated cores lowers both the HOMO and the LUMO energy of the cores. So electron-deficient heterocyclic compounds such as pyrazine and quinoxaline (e.g. the TTF derivatives (**41**) and (**42**)), tend to be building blocks for electron-transport (*n*-type) materials as they have low-lying LUMO levels. However, some systems, especially containing strong electron donors such as benzene-fused TTF, actually still display *p*-type FET performance after attaching electron-withdrawing groups (e.g. the **DB-TTF** bisimides, (**47**) and (**48**)). This is because the LUMO level is not sufficiently low for electron charge injection, although the lowered HOMO energies (–5.4 eV) do result in an increased oxidation potential and enhanced stability against photo-oxidation.

Generally, most transistors based on *n*-type organic semiconductors operate properly only in vacuum or an inert atmosphere, apparently because certain species present in ambient air, such as oxygen or water, easily diffuse into the semiconductor and destabilize or trap the negative charge carriers in the channel. Based on solution-phase electrochemical potentials, a reduction potential more positive than ~ −0.66 V vs. a standard calomel electrode (SCE) is thought necessary to stabilize the charge carriers in *n*-type organic materials with respect to H_2O oxidation.[46]

3.2 π-Conjugated *n*-type organic semiconductors

3.2.1 Perylene dianhydride-based *n*-type semiconductors

In 1997, Katz et al. observed *n*-type behavior in the directions along the molecular planes within crystals of perylene-3,4,9,10-tetracarboxylic dianhydride, **PTCDA ((69)** in **Scheme 5)**, with electron mobilities of 10^{-5}–10^{-4} cm^2 V^{-1} s^{-1} in vacuo.[47] The properties of derivatives of the closely related perylene diimide (**PDI**) may be modulated by appropriate functionalization of the parent molecule. Two main methods have been adopted to achieve chemical modification of **PDIs**. One is to introduce substituents at the N atoms of the imide groups, which does not significantly affect the optical and electronic properties. In 2000, Struijk el al. measured the mobilities of **PDI-C18 (72)** by the pulse radiolysis time-resolved microwave technique, and found mobilities of 0.1 cm^2 V^{-1} s^{-1} in the liquid crystalline phase, and 0.2 cm^2 V^{-1} s^{-1} in the crystalline phase.[48] They ascribed the high charge carrier mobility to a very stable columnar arrangement of closely packed perylene cores in both the crystalline solid and liquid crystalline phases. **PDI-C8 (70)** and **PDI-C13 (71)** films were also found to be high mobility *n*-type materials. The high mobilities were attributed to the high degree of order obtained through the self-assembly process driven by interdigitation of the alkyl chain substituents.

Another way is to introduce substituents into the perylene core of **PDI**, i.e. the bay position; with either electron-donor or electron-acceptor groups, such modification will greatly change the properties of **PDIs**. Marks and his coworkers constructed OFETs from compounds (**73**) and (**74**), which displayed mobilities of 0.10 and 0.64 cm^2 V^{-1} s^{-1} and on/off ratios of 10^5 and 10^4, respectively, under ambient atmosphere.[49] The good charge transport properties were proposed to arise from considerable intermolecular π···π overlap with a minimum interplanar spacing of 3.40 Å. The ambient stability results from the electron-withdrawing fluorinated chains, which promote close packing through fluorocarbon self-segregation and provide a steric barrier to oxygen and moisture. We successfully synthesized 1,6,7,12-tetrabromoperylene-3,4,9,10-tetracarboxylic acid

bisanhydride and the corresponding tetrabrominated perylene diimide (**75**) in high yields.[50] The presence of four bromide leaving groups in these compounds will provide more synthetic possibilities and should significantly broaden and facilitate research into **PDI** derivatives.
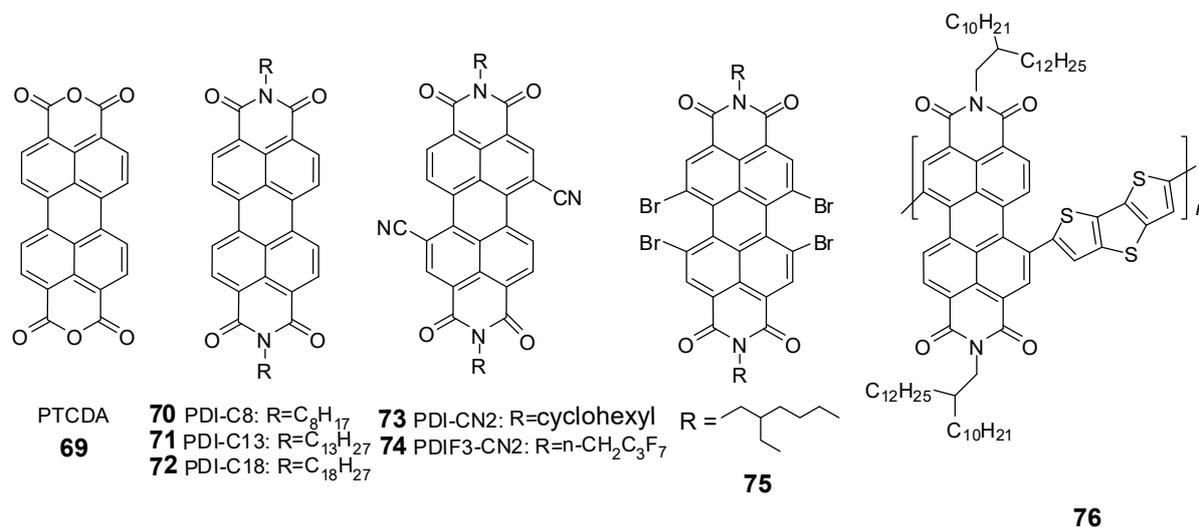
Scheme 5. Stuctures of perylene-3,4,9,10-tetracarboxylic dianhydride **PTCDA** (**69**), and perylene dianhydride-based *n*-type semiconductors.

3.2.2 Naphthalene dianhydride-based *n*-type semiconductors

Naphthalene-1,4,5,8-tetracarboxylic acid diimides (**NTCDIs**) are important compounds for materials and supramolecular chemistry. Due to their *n*-type semiconducting properties, core-unsubstituted **NTCDIs** bearing alkyl or fluorinated alkyl groups in the imide positions are of interest as the active layer in OFETs. In 1996 Katz and coworkers built OFETs from naphthalene-1,4,5,8-tetracarboxylic acid dianhydride **NTCDA** (**77**) and **NTCDI** (**78**) at a substrate temperature of 55 °C in vacuum, achieving electron mobilities of 10^{-3} and 10^{-4} cm^2 V^{-1} s^{-1}, respectively.[51] Later, they also used N-substitituted **NTCDI** derivatives to fabricate OFETs. A mobility of 0.1 cm^2 V^{-1} s^{-1} and an on/off ratio of 10^5 were recorded[52] in air for (**79**) after deposition

at 70 °C.

An alternative method to achieve chemical modification of **NTCDIs** is to functionalize the naphthalene core. These syntheses mostly used 2,6-dichloronaphthalene diimide (**DCNDI**, (**81**)) or 2,6-bromonaphthalene diimide (**DBNDI**, (**82**)) as precursors. Recently, Roger et al. and our group synthesized a hitherto unknown 2,3,6,7-tetrabromonaphthalene diimide (**TBNDI**, (**86**)) almost at the same time, completing the series of previously reported di- and trifunctionalized **NTCDI** derivatives.[53, 54] Nucleophilic substitution of (**81**), (**82**), (**85**) and (**86**) can afford a series of core-substituted **NTCDIs**, (**80**), (**83**), (**84**) and (**87**) for high performance *n*-type OFETs.

77

78 NTCDI: R=H
79 NTCDI-C8: R=C_8H_{17}

80 X=F
81 X=Cl
82 X=Br
83 X=CN

84 X=F
85 X=Cl
86 X=Br
87 X=CN

88 BBL

89 BBB

90
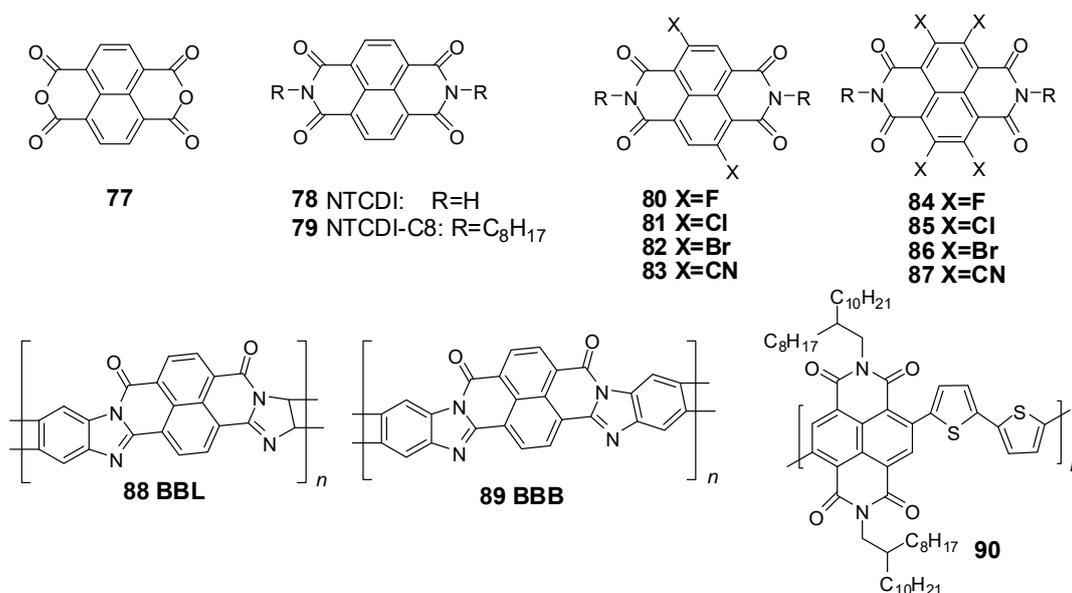
Scheme 6. Structures of naphthalene-1,4,5,8-tetracarboxylic acid dianhydride (NTCDA, (**77**)) naphthalene-1,4,5,8-tetracarboxylic acid diimide (NTCDI, (**78**)) and naphthalene dianhydride-based materials for OFET applications.

The realization of high-performance, ambient-stable *n*-channel polymeric semiconductors still remains a challenge, however. The ladder-type polymers **BBL** (**88**) and **BBB** (**89**) were very early

examples[55] of electron transport materials for OFETs, exhibiting mobilities of ~0.001–0.1 cm^2 V^{-1} s^{-1}. However, they suffered problems of low stability and poor solubility meaning that films needed be processed using the hazardous methanesulphonic acid as the solvent. Zhan et al. synthesized an electron-transport polymer with good solution processability, excellent thermal stability, and high electron affinity based on alternating perylene diimide and dithienothiophene units ((**76**) in **Scheme 5**).[56] Electron mobilities as high as 1.3×10^{-2} cm^2 V^{-1} s^{-1} were measured. Recently, Yan et al. demonstrated the realization of top-gate OFETs based on a high-performance, stable and readily processable electron-transporting naphthalene-bis(dicarboximide) (**NTCDI**) polymer (**90**) in combination with several polymeric dielectric materials.[1] This finding shows that both high performance *p*-type and *n*-type thiophene-based polymers with benchmark charge carrier mobility of >0.5 cm^2 V^{-1} s^{-1} have now been achieved, which is a major step towards commercialization of polymeric circuit technologies.

4. π-Conjugated ambipolar organic semiconductors

Conventional organic semiconductors tend to exhibit ambipolar transport with non-balanced field-effect hole and electron mobilities because of their wide band gaps (usually between 2 and 3 eV). Previous attempts to fabricate ambipolar OFETs centered on blends or bilayer structures with *p*- and *n*-type materials, or the combination of trap-free gate dielectrics with asymmetric contacts. Recently, however, ambipolar OFETs based on a single-component semiconductor have been reported.

Meijer et al.[57] first pointed out that high-performance ambipolar OFETs with balanced hole and electron mobilities require the use of semiconductors with a very narrow band gap of less than 1.8 eV. In this case, the injection barrier for both charge carriers is lowered and efficient ambipolar

transport can take place. The most attractive ambipolar transistors in terms of fabrication and performance consist of a single layer that can be simply solution-processed from a low-bandgap-material that allows electron and hole injection from one single type of electrode, as has been demonstrated with poly(3,9-di-*tert*-butylindeno[1,2-*b*]fluorene) (**PIF**, (**93**) in **Scheme 7**) (which has a band gap energy of 1.55 eV).
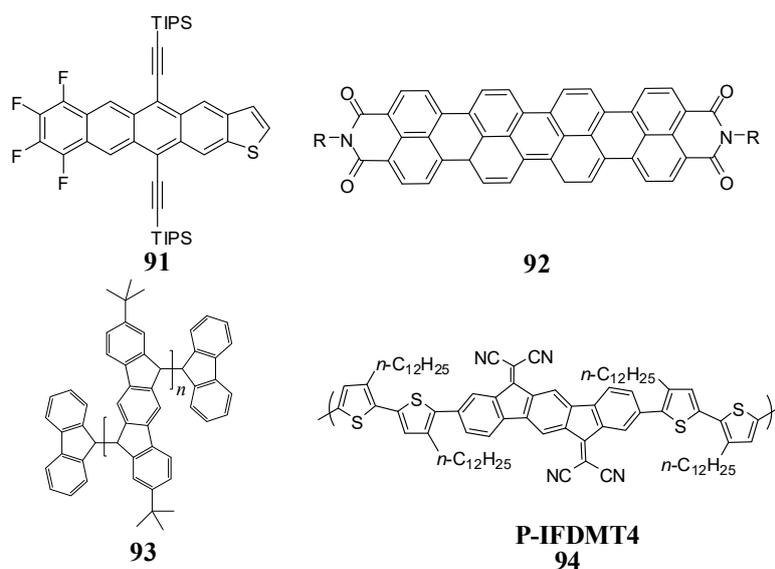
Scheme 7. Selection of recently demonstrated materials showing ambipolar transport in OFETs.

Tsao et al. utilized swallow-tailed quaterrylene tetracarboxdiimide (**SWQDI**) (**92**) as an active layer in ambipolar thin film transistors.[58] This is because on extension of the perylene core to give such rylene dyes, the LUMO remains essentially unchanged whereas the HOMO energy level increases. Tang et al. showed that 7,8,9,10-tetrafluoro-5,12-bis(TIPS ethynyl)tetraceno-tetraceno[2,3-*b*]thiophene, (**91**) (TIPS = triisopropylsilyl) is a high performance, ambipolar material for OFETs. This compound is soluble and stable, with hole mobility (μ_h) and electron mobility (μ_e) of up to 0.12 and 0.37 cm^2 V^{-1} s^{-1} in air and in nitrogen, respectively.[59]

In polymers, the aromaticity of the monomeric units results in a competition between confinement of the π-electrons within the aromatic rings and delocalization along the π-conjugated chain. Therefore, to obtain a low band gap energy it is desirable to induce coplanarity of the building blocks along the π-conjugated chain—which can be achieved by an appropriate choice of fused ring systems—or the introduction of additional covalent bonds to rigidify the conjugated backbone in so-called step-ladder or ladder-type structures. Usta et al. reported the synthesis and characterization of the first example of an air-stable, ambipolar polymer (**P-IFDMT4, (94)**) based on indenofluorenebis(dicyanovinylene).[60] In this polymer, the highly electron-deficient, ladder-type indenofluorenebis(dicyanovinylene) skeleton is utilized to depress the LUMO energy, providing ambient stability to the gate field-induced electron carriers. Furthermore, the donor–acceptor backbone enhances core rigidity and π-conjugation, affording a low band gap semiconductor. **P-IFDMT4**-based devices are ambipolar, having electron and hole mobilities of ca. 2×10^{-4} cm^2 V^{-1} s^{-1} with excellent ambient stability.

5. Conclusion and outlook

Organic electronics has attracted increasing attention as a newly emerging field of science and technology that covers chemistry, physics, and material sciences. The design and synthesis of new materials, elucidation of their structures and properties, and the fabrication of devices have been the major subjects of recent extensive studies. Much effort has been directed towards the optimization of materials for the active layers of OFETs, including π-conjugated small molecules and polymers. The charge carrier mobility of π-conjugated molecules is clearly important in defining product characteristics. At present, the best small molecules and polymers show sufficiently high mobilities for practical application (around 0.5–1 cm^2 V^{-1} s^{-1}).

Besides 1-D (linear) and 2-D (macrocyclic or star shaped) molecular structures, possible strategies for increasing the dimensions towards 3-D small molecular architectures, or 2-D and 3-D polymers with bridge linkers can be explored. This may have the advantage of achieving a further increase in the structural long-range order, as such molecular architectures may result in interactions with adjacent stacks that can lead to 2-D or 3-D electronic coupling in the solid. Care must be taken, however, that when increasing the dimensions of the molecules the substituents introduced do not significantly disrupt the formation of an ordered solid-state structure with optimal intermolecular interactions, since these interactions are critical for charge carrier transport in electronic devices.

There are many other challenging subjects remaining to be studied, including expansion of the scope of π-conjugated molecular materials to those containing elements other than nitrogen, boron, sulfur, and selenium and to various types of metal complexes other than phthalocyanines, elucidation of the microstructures including short-range ordering and orientation of molecules, the correlation between morphologies and properties, and the search for novel air stable n-type and ambipolar semiconductors for practical applications. It is projected that in the near future, organic semiconductors will lead to low-cost, light-weight, and high-performance electronic devices.

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