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High performance n-type and ambipolar small organic semiconductors for organic thin film transistors

Ke Zhou,[1,2] Huanli Dong,[2] Hao-li Zhang[1*] and Wenping Hu[2*]

State Key Laboratory of Applied Organic Chemistry (SKLAOC), College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou, 730000, China. E-mail: haoli.zhang@lzu.edu.cn
Beijing National Laboratory for Molecular Sciences, Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China. E-mail: huwp@iccas.ac.cn

Remarkable progresses have recently been achieved in n-type and ambipolar OFETs. In this mini review, we will highlight the representative development on high performance n-type and ambipolar organic semiconductors (OSCs) especially for those n-type small OSCs with thin film mobilities >1 cm^2 V^{-1} s^{-1}, and ambipolar small OSCs with both hole and electron mobilities over 0.1 cm^2 V^{-1} s^{-1}. This overview shall provide a meaningful guideline for further development of high performance n-type and ambipolar materials and devices.

1. Introduction

Since the first organic field-effect transistors (OFETs) based on polythiophene was reported in 1980s,[1] OFETs have attracted increasing interest from both academic and industrial communities due to their attractive advantages of lightweight, low-cost, flexibility and easy processability, which make them promising for the next generation electronic circuits, such as radio-frequency identification tags (RFIDs), organic light emitting displays (OLEDs) and sensors.[2-6] Great advances have been made in the past few decades, not only on the development of high performance OFETs but also on the knowledge of understanding the intrinsic physical properties of materials. Currently, the performance of OFETs, especially for p-type OFETs, in some cases have surpassed that of amorphous silicon (α-Si) and even approaching the value of polycrystalline silicon (c-Si), and the mobility record is still being reset frequently.[7-11] For instance, a new record mobility of 43 cm^2 V^{-1} s^{-1} has recently been reported for a p-type organic semiconductor (OSC) of 2,7-dioctyl[1]benzothieno[3,2-b][1]benzothio-phene (C8-BTBT),[12] suggesting a new breakthrough in this filed. In contrast, the development of n-type and ambipolar organic semiconductors/devices is largely lag behind because of the relatively difficult synthesis of electron-transporting molecules and their unstability under ambient conditions, especially in the presence of O_2 and H_2O. While electron-transporting materials

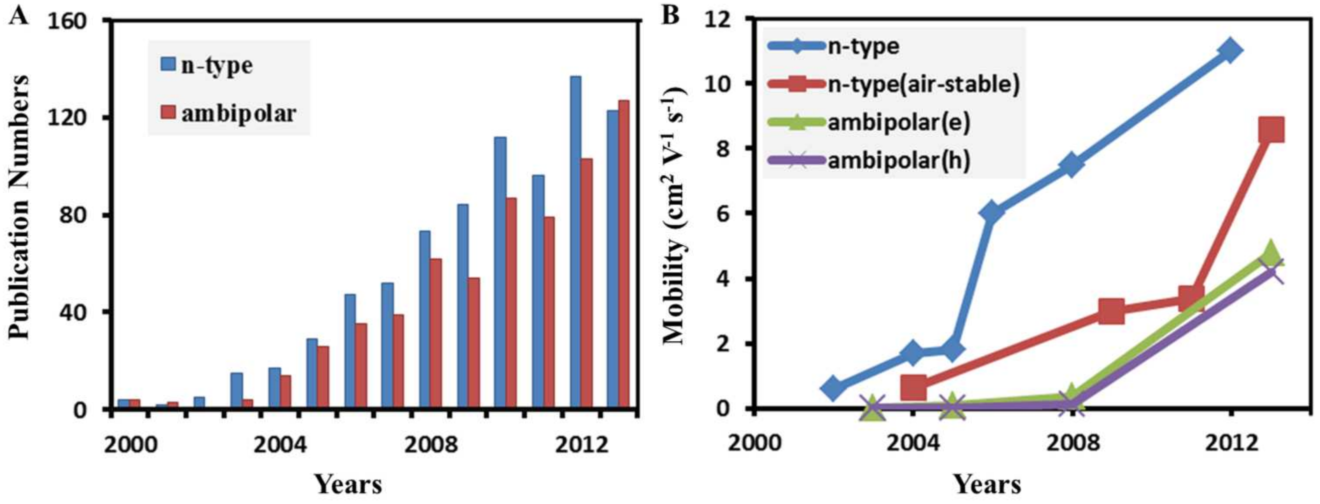


Figure 1. (A) Number of published papers on "n-type organic field effect transistor" and "ambipolar organic field effect transistors" over the past few years as counted by the Institute for Scientific Information (ISI) Web of Science. (B) Mobility dependence vs years for n-type and ambipolar small organic semiconductors.

are indispensable component for complementary integrated circuits.[13-15] Driven by the urgent demand for the development of organic electronics, much attention has recently been paid on n-type and ambipolar OFETs. According to the Web of Science citation database, the number of publications on n-type and ambipolar OFETs is indeed increased with per year over 100 in the past few years (Figure 1a). Meanwhile the electron mobility value (both in ambient and in inert atmosphere) also undergoes significant enhancements with the highest value already approaching 11 $cm^2 V^{-1} s^{-1}$ for n-type organic single crystals (Figure 1b),[16] but such excellent electron-transporting materials are still very few. In this mini review, we will highlight the remarkable progress on the development of high performance n-type and ambipolar OSCs especially for those n-type small OSCs with thin film mobilities >1 $cm^2 V^{-1} s^{-1}$, and ambipolar small OSCs with both hole and electron mobilities over 0.1 $cm^2 V^{-1} s^{-1}$. It is hoped that this review will provide a meaningful guideline for the molecular design of high performance and air-stable n-type and ambipolar small OSCs.

In principle, most of OSCs are intrinsically ambipolar and thus capable of transporting both electrons and holes, which fact has been identified by Chua *et al* through investigation on devices based on trap-free gate dielectrics.[17] Beside trap, another main reason that leads to difficulty to observe electron-transporting property in OFETs is the vulnerability of electron charge carriers to the ambient conditions, such as O_2 and H_2O, inducing serious degradation of charge transport properties.[18] Thus, from the molecular design point of view, in order to obtain excellent electron-transporting organic materials, high electron affinities (related to the lowest unoccupied molecular orbital, LUMO) as well as strong intermolecular orbital overlap is necessary for ambient stability and efficient charge injection and transport. This is generally achieved by taking a known semiconducting core molecule (including both electron-deficient and electron-rich building blocks) and adding strong electron-withdrawing groups such as –CN, -Cl, -F, $-CF_3$ and heteroatoms of N, S to construct high performance n-type and ambipolar OSCs. In the following section 2 and 3, we will systematically summarize these excellent electron and ambipolar OSC examples reported in recent years. We hope to provide some valuable guidelines for further development of n-type and ambipolar OSCs.

2. High performance n-type small molecules

As mentioned above, one direct method to construct high performance n-type materials is selecting electron-deficient building blocks with appropriate substituent groups. Perylene diimides (PDIs) and naphthalene diimides (NDIs) are the most promising electron-deficient building blocks for obtaining high performance electron transport materials due to their relatively high electron affinities, high electron mobilities and excellent chemical, thermal stability.[19-22] Moreover, the reduction potential and molecular packing of PDI and NDI blocks are also easily tuned by functionalizing at the core or end site for much lower LUMO levels and intact molecular packing structures, thus leading to ambient stability and efficient charge carrier transport. The first n-type field-effect transistors based on *N*-phenyl-substituted PDI compound was reported by Horowitz *et al.* in 1996, which only demonstrated an electron mobility of 10^{-4} $cm^2 V^{-1} s^{-1}$.[23] Since then, various PDI derivatives have been synthesized with the hope of increasing their electron transport properties and ambient stabilities by incorporating appropriate substituent at the nitrogen or core positions. Representative examples of PDI derivatives with thin film mobilities over 1 $cm^2 V^{-1} s^{-1}$ are compound **1** and **2**, with C_8H_{17} and $C_{13}H_{27}$ alkyl chains substituted at the N-positions, respectively. OTFTs based on vacuum-deposited compound **1** thin films as active layer demonstrated saturation electron mobility as high as 1.7 $cm^2 V^{-1}s^{-1}$ when using SiO_2 as substrates and tested under vacuum or reducing atmosphere conditions.[22] While the performance of compound **1** based devices were obviously decreased at ambient conditions and only 0.36 $cm^2 V^{-1} s^{-1}$ and 0.67 $cm^2 V^{-1} s^{-1}$ mobilities could be achieved for compound **1**-based OTFTs when using polymethylmethacrylate (PMMA) and cyclic olefin copolymer (COC) modified SiO_2 as substrate. OTFTs based on compound **2** thin film exhibited electron mobility of 0.58 $cm^2 V^{-1} s^{-1}$ in vacuum, which was further improved to 2.1 $cm^2 V^{-1} s^{-1}$ by an additional annealing process after the fabrication of devices, which was due to the increased molecular crystallinity and optimized film morphology.[24] Although compound **1** and **2** exhibited high electron charge transport properties, their n-channel characteristics can only be achieved under vacuum conditions. In comparison, fluorinated alkyl substituted-PDIs compound **3** exhibited good long-term air-stable operation though still with a high LUMO level of -3.85 eV, and here the good stability was largely due to the closely packed fluorocarbon chains providing a kinetic barrier to the diffusion of oxygen and moisture into the channel region. Electron mobility up to 0.72 $cm^2 V^{-1} s^{-1}$ was obtained with vapour-OTS-modified SiO_2 as substrates,[25] and this value was further increased to 1.44 $cm^2 V^{-1} s^{-1}$ and 1.24 $cm^2 V^{-1} s^{-1}$ on solution-OTS-modified substrates when measured in vacuum and in ambient conditions, respectively.[25]

Adding electron-withdrawing groups at aromatic core is an effective approach for increasing electron affinities and thus obtaining high performance and air-stable electron-transporting materials. Compound **4** is one of the most representative core-substituted PDI derivatives, which exhibits high electron mobility, excellent air stability as well as good solution processability.[26] High performance OTFTs based on crystalline thin films of compound **4** were fabricated through solution-processing method, and an electron mobility of 1.3 $cm^2 V^{-1} s^{-1}$ was achieved in ambient air.[27] Furthermore, a much higher electron mobility of 6 $cm^2 V^{-1} s^{-1}$ in vacuum and 3 $cm^2 V^{-1} s^{-1}$ in ambient condition were achieved for single crystals of compound **4**.[28] Recently, a band-like transport mechanism was observed by Nikolas *et al.* for compound **4**, where the mobility increased from 5.1 $cm^2 V^{-1} s^{-1}$ at T = 290 K to 10.8 $cm^2 V^{-1} s^{-1}$ at T =230 K.[29] This is also the first reported band-like transport mechanism for n-channel materials, indicating the high quality of single crystal for compound **4**. Compared with PDI compounds, NDI materials generally have much lower LUMO levels and better air stability. The first NDI-based OFET was also reported in 1996 by Joyce *et al.*,[30] but only very low electron mobility of 10^{-4} $cm^2 V^{-1} s^{-1}$ was achieved in that time. Actually, in the following progress, NDI has been proved to be a good electron-deficient building block for n-type OSCs. Compound **5** was one of the most successful NDI-based n-type semiconductors with excellent performance.[31] Bottom-gate, top-contact OTFTs based on compound **5** were fabricated based on OTS-modified SiO_2 substrates, and extremely high electron mobility up to 7.5 $cm^2 V^{-1} s^{-1}$ was achieved when the devices were tested after prolonged equilibration (ca. 30 min) in an argon atmosphere at low humidity. However, the mobilities were significantly degraded down to 0.41 $cm^2 V^{-1} s^{-1}$ when devices were operated in air or at higher humidity conditions.

Recently, core-chlorinated NDI compounds (**6**, **7**) with fluorinated side chains at the imide positions were reported by Oh *et al.*[32] Unlike the severe core-twisting of some other core-halogenated PDI molecules, compounds **6** and **7** demonstrated good planarity for π-conjugated core, which was beneficial to efficient charge transport. Transistors based on thin films of compounds **6** and **7** exhibited electron mobilities of 0.91 and 1.43 $cm^2 V^{-1} s^{-1}$ in air, respectively. Furthermore, under bias stress, an increased electron mobility up to

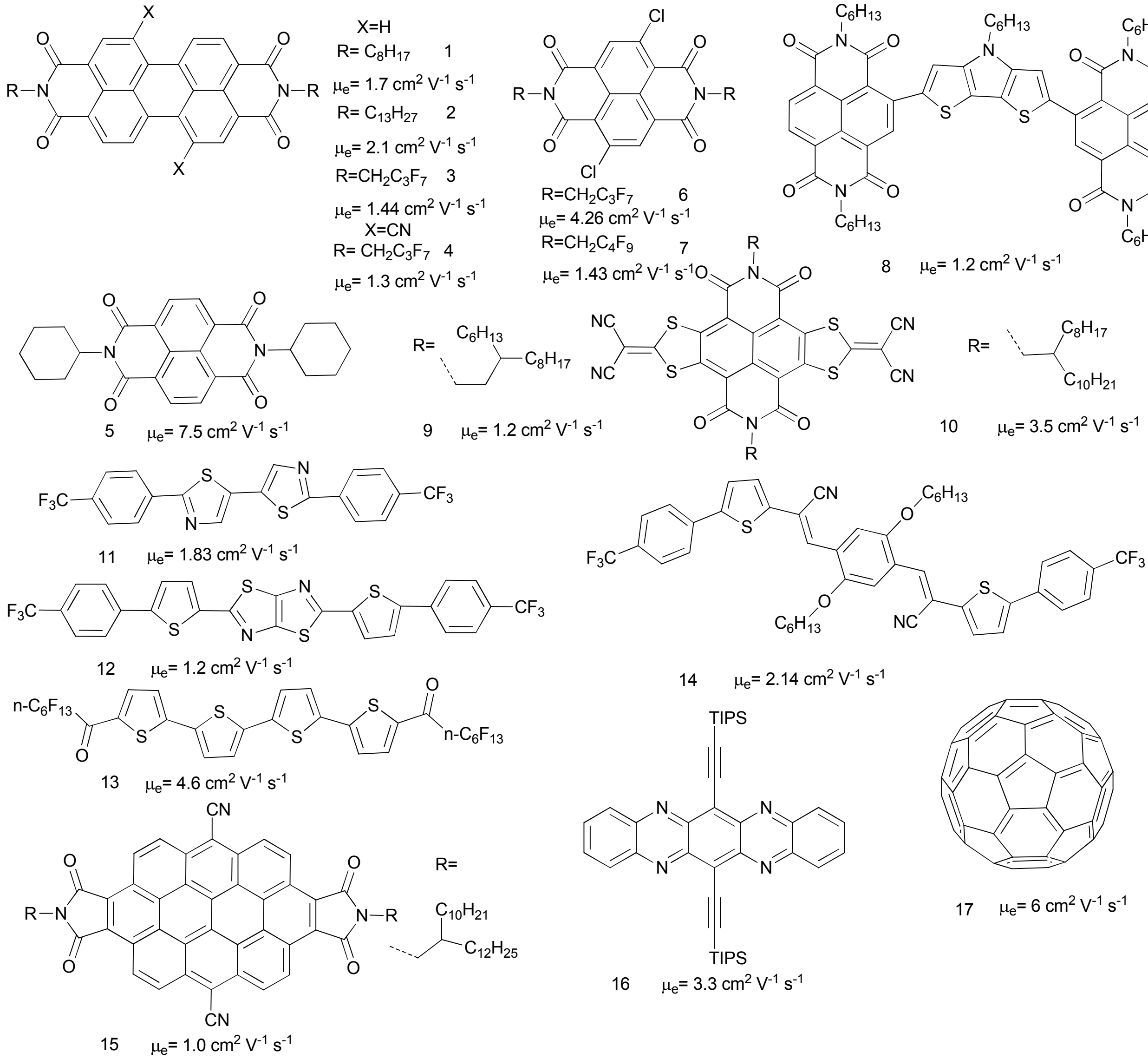


Figure 2. Chemical structures of high performance n-type small semiconductors with thin film mobility > 1cm^2 V^{-1} s^{-1}.

4.26 cm^2 V^{-1} s^{-1} was observed for compound **6**.[33] Moreover, ribbon-shaped single-crystal OFETs based on compound **6** were further fabricated with an unprecedented electron mobility of 8.6 cm^2 V^{-1} s^{-1} in air.[34] From the point of view of extending molecular conjugation, a novel conjugated donor-bridged bis-NDI derivative compound **8** was reported by Marder and co-workers.[35] High electron mobility value of 1.5 cm^2 V^{-1} s^{-1} in N_2 was achieved for this compound. Two-dimensional (2D) compounds **9** and **10** with core-expanded conjugation and good stability were further designed and synthesized by Zhu *et al*.[36, 37] An electron mobility of 1.2 cm^2 V^{-1} s^{-1} and 3.5 cm^2 V^{-1} s^{-1} in ambient was obtained for solution-processed OTFTs based on compound **9** and **10**, respectively.[38, 39]

Another effective approach for n-type organic molecules is converting the known p-type building blocks into n-type by introducing electron-withdrawing groups (such as –F, –CN, –Cl, –NO$_2$, –COO, etc.) to reduce the LUMO levels for electron injection and transport. Based on this molecular design concept, a thiazole-based oligomer with trifluoromethylphenyl groups (compound **11**) was synthesized by Yamashita *et al*.[40] The molecule has a completely planar geometry and forms a unique two-dimensional columnar structure. Electron mobility as high as 1.83 cm^2 V^{-1} s^{-1} was achieved for OFETs based on compound **11** with a top-contact configuration. Compound **12** was another example of this class materials and an electron mobility of 1.2 cm^2 V^{-1} s^{-1} with on/off ratio of 10^7 was obtained based on OTS-modified substrates.[41] Compound **13** was reported by Yoon *et al*. in 2005 with electron mobility as high as ~0.6 cm^2 V^{-1} s^{-1} on hexamethyldisilazane (HMDS)-treated SiO_2 substrates.[42] Furthermore, they found that an increased mobility of 2 cm^2 V^{-1} s^{-1} could be obtained for devices based on the polystyrene-modified SiO_2 and crosslinked-polystyrene dielectrics.[43] In another work, saturation mobility up to 4.6 cm^2 V^{-1} s^{-1} was achieved for transistors based on top-contact Au source-drain electrodes, almost two orders of magnitude higher than that with Al/LiF electrodes.[44] Compound **14** was designed and synthesized by Yun *et al*.[45] OFETs were fabricated based on 50 nm-thick films of compound **14** on OTS-treated SiO_2 substrates and a high electron mobility of 2.14 cm^2 V^{-1} s^{-1} with on/off ratios >10^6 was obtained. Recently, compound **15** with a large π-conjugated plane was further designed and synthesized, and a solution-processed OTFTs based on compound **15** exhibited an electron mobility up to 0.51 cm^2 V^{-1} s^{-1} in air and 1.0 cm^2 V^{-1} s^{-1} in N$_2$ atmosphere.[46] More importantly, the devices displayed good air stability with almost no change after storing two weeks in air. Compound **16** was the most successful acene-based n-type semiconductor, which was designed and synthesized by Miao *et al*.[47] The highest mobility obtained was 3.3 cm^2 V^{-1} s^{-1} in vacuum and 0.5 cm^2 V^{-1} s^{-1} in ambient conditions for vacuum-deposited thin films of compound **16**.[48] For solution-processed thin film, mobility of 2.5 cm^2 V^{-1} s^{-1} was achieved for compound **16** in vacuum with a phosphonic acid modified AlOy/TiOx dielectrics.[49]

Fullerene is a benchmark for n-type semiconductors. Because of the difficulty in synthesis, very few fullerene derivatives were reported until now. The first OFETs with fullerene thin films as the active layer was reported by Haddon *et al.* [50] Electron mobility of 0.08 cm^2 V^{-1} s^{-1} and on/off ratio of 10^6 were obtained based on bottom gate Si/SiO$_2$ substrates and bottom-contact Au electrodes under UHV. Anthopoulos *et al.* fabricated n-channel OFETs based on C$_{60}$ films grown by hot wall epitaxy.[51] The highest mobility up to 6 cm^2 V^{-1} s^{-1} was achieved with LiF/Al top-contact and a polymer dielectric. Furthermore, Li *et al*. prepared well-aligned C$_{60}$ needle and ribbon-shaped single crystals by a simple droplet-pinned crystallization (DPC) method, and OFETs based on aligned single crystals exhibited a high electron mobility of 11 cm^2 V^{-1} s^{-1},[16] which was also the highest electron mobility reported so far. The chemical structures of n-type semiconductors mentioned in this text are shown in Figure 2.

3. High performance ambipolar small molecules

In p-type OFETs, hole charge carrier are injected from electrode to the HOMO energy level, while in n-type OFETs the electron charge carrier are injected from electrode to the LUMO level. For ambipolar materials, both hole and electron charge carrier could be injected and transported. In principle, similar molecular design concept for n-type organic materials is also applicable for development of ambipolar materials, while except for decreasing the LUMO levels with electron-withdrawing groups, the HOMO levels of materials also should be appropriate for hole injection, that is for balanced electron and hole transport.[52-54] To date, various attempts have been made to develop high performance ambipolar semiconductors. The most successful examples for organic small ambipolar materials are constructed from excellent p-type 6,13-bis(triisopropylsilylethynyl)pentacene (TIPS-pentacene) building block by incorporating different numbers of halogen substituents (such as –F and -Cl) or nitrogen atoms at different positions of aromatic core.[55] For example, representative ambipolar compounds of **18**-**20** were initially designed and synthesized by Bao *et al*., which demonstrated 2D bricklayer molecular packing in solid state, similar to TIPS-pentacene, the most ideal molecule packing for high performance OSCs.[56, 57] Top-contact bottom-contact OFETs based on compound **18** showed typical ambipolar behavior with hole and electron mobility of 0.12 cm^2 V^{-1} s^{-1}and 0.37 cm^2 V^{-1} s^{-1}, respectively. Increased hole and electron mobility of 0.27 cm^2 V^{-1} s^{-1} and 0.68 cm^2 V^{-1} s^{-1} were observed for compound **19**. In comparison, compound **20** exhibited much balanced ambipolar behavior, with the maximized hole and electron mobility of 0.51 cm^{2}V^{-1}s^{-1} and 0.46 cm^{2}V^{-1}s^{-1}, respectively. In addition, more detailed experiments based on a series of functionalized acenes demonstrated that for Au electrode, when the LUMO level < -3.15 eV, electron injection and transport may commence; while the HOMO level > -5.6 eV, hole injection and transport may commence. Thus, ambipolar transport prevails when molecules have HOMO levels > -5.6 eV and LUMO levels < -3.15 eV. It is worthwhile to note that structural disorder or deep traps within the thin film may inhibit the observation of ambipolar behavior.[58] Zhang *et al*. found that introducing nitrogen atoms to the framework of TIPS-pentancene also could produce ambipolar compounds.[59] One representative example is compound **21**, which exhibited balanced ambipolar behavior with both electron and hole mobilites around 0.1 cm^2 V^{-1} s^{-1}. However, for molecule **22**, which contain four nitrogen atoms in the backbone of TIPS-pentacene, showed a strong electron-dominated ambipolar transport behavior, with a hole mobility of 0.22 cm^2 V^{-1} s^{-1} in air and an electron mobility of 1.1 cm^2 V^{-1} s^{-1} in vacuum.[48] This is more likely due to the presence of C–H…N hydrogen bonds, which play an important role in controlling molecular packing. Halogen substituted N-heteropententacene compounds **23** and **24** were reported by the same group.[60] Both compounds showed balanced ambipolar transport behavior with hole and electron mobilties around 0.1 cm^2 V^{-1} s^{-1}. Recently, under the assistance of theoretical calculations, a series of rubrene derivatives were developed with predicted ambipolar charge transport properties, which was further confirmed by experimental characterizations. High charge carrier mobility of 1.54 cm^2 V^{-1}s^{-1} for hole and 0.28 cm^2 V^{-1}s^{-1} for electron were achieved for single crystals of compound **25** based on Au source/drain electrodes and PMMA dielectrics,[61] which was further significantly increased to 4.8 cm^2 V^{-1} s^{-1} for holes and 4.2 cm^2 V^{-1} s^{-1} for electrons by employing carbon nanotube (CNT) electrodes for efficient charge injection, which is also the highest performance for ambiplar small organic materials reported so far.[62] The chemical structures of ambipolar semiconductors mentioned in our article with

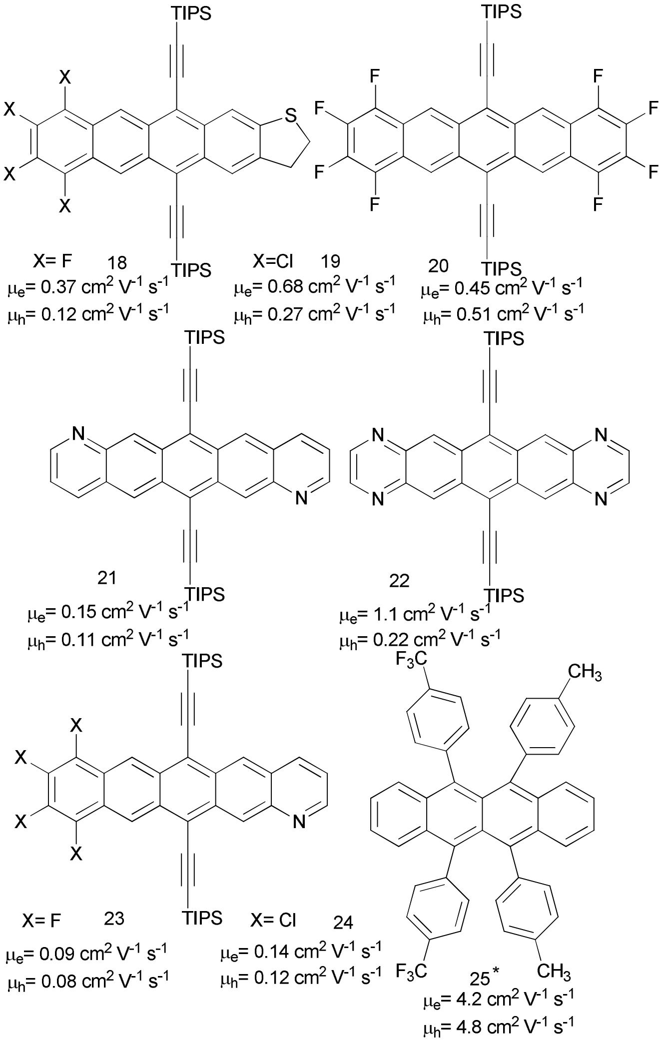


Figure 3. Chemical structures of ambipolar small semiconductors. * Single crystal

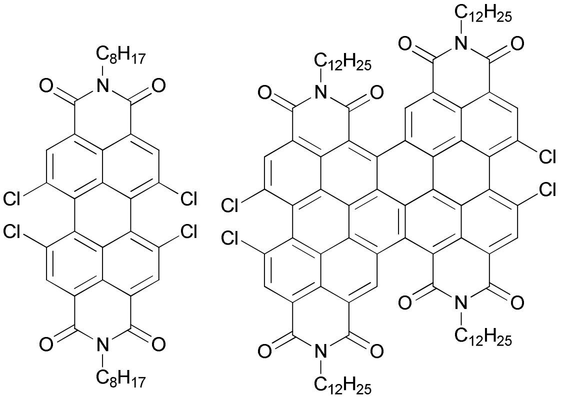
both electron and hole thin film mobilities over 0.1 cm^2 V^{-1} s^{-1} are shown in Figure 3.

4. The principles for high performance n-type and ambipolar small molecules

A crucial characteristic of OSCs is the charge transport ability. According to Marcus theory, two parameters are highly important for the mobility of organic semiconductors.[18, 63-65] One is the transfer integral, which describes the degree of molecular orbital of adjacent, and strongly dependent on π–π distance, orientation, and relative displacement distance. Another parameter is the reorganization energy, which is defined as the energy change associated with the geometry relaxation during the charge transfer, and related to molecular degrees of freedom. In this regard, rigid molecules have smaller reorganization energy values than flexible molecules. In theory, large transfer integral and small reorganization energy is favourable for high charge carrier mobility.[66-68] Both transfer integral and reorganization energy are closely related to molecular structure, as well as molecular packing in the solid states. Besides, impurities, defects, testing environment, etc. also have impacts on charge carrier mobility. In this section, molecular structure, molecular packing, electronic structure, energy alignment *etc*. will be addressed concisely.

Molecular structure

The general strategies to construct n-type and ambipolar OSCs have been discussed in section 2 and 3. Among these molecules, π-extended compounds **8**, **9**, **10**, and **15** exhibited an unprecedented mobility in ambient. Similar to NDI and PDI, π-extended molecules based on NDI and PDI show high electron affinity and good ambient stability, a higher electron affinity can be achieved by functionalized at the core with electron with-drawing groups such as –F, -CN.[69, 70] Moreover, the expansion of the π-conjugated aromatic system is believed to enhance the stacking of molecules and thus facilitates electron transport.[71, 72] For instance, Lv *et al*. reported a π-extended molecule of compound **27** (Figure 4) based on PDI, which not only exhibited low-lying LUMO level (-4.22 eV) for air stability but also efficient charge carrier transport property.[73] Electron mobility of 0.15 cm^2 V^{-1}s^{-1} was achieved for solution-processed thin film of compound **27** with silver as source/drain electrode in ambient conditions, electron mobility was further increased to 4.65 cm^2 V^{-1} s^{-1} for its single crystals. Moreover, No obvious degradation was observed for compound **27** based OFETs even after keeping in air over one and half months. However, the vacuum-deposited thin film of compound **26** exhibited very low electron mobility of 10^{-5} cm^2 V^{-1} s^{-1} in air. All these results demonstrated the extension of the π-conjugated aromatic system is an efficient strategy for high performance and air-stable n-type semiconductors. However, due to lack of crystallographic data, the precise nature of π-stacking of these molecules is unknown. More extensive π-stacking with effective overlap is believed to lead to higher mobilities.



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27

Figure 4. Chemical structures of compound **26** and **27**, and efficient charge carrier transport was achieved for the π-extended molecule of compound **27**.

Energy level alignment

Energy level alignment of OSCs is an important factor that not only determines the charge carrier injection from metal to conducting channel but also affects the electrochemical and air stability of materials. Considering the source/drain electrodes generally used in organic electronics, in order to achieve electron injection, the LUMO levels for n-type and ambipolar organic semiconductors should be below -3.0 eV. However, most of electron-transporting materials are air-instable and needs to be measured in vacuum or inert atmosphere. Various investigations demonstrated that the air instability is generally not due to the degradation of intrinsic property of materials, but arises from the charge carrier trapped under ambient conditions by H_2O or O_2.[74, 75] Recently, Nicolai *et al*. showed that the electron charge transport is limited by traps, which is identical for all polymers, and locates at an energy level of ~3.6 eV below the vacuum level.[76] They suggested that balanced trap-free charge transport can only be obtained in polymers with an electron affinity larger than -3.6 eV. Therefore, a low-lying LUMO level is essential for air-stable n-type and ambipolar materials. In general, the LUMO level of electron transport materials below -4.1 eV was believed to be air-stable. When the LUMO level in the range of -3.9 eV to -4.1 eV, the electron transport behaviour can be tested in air, but usually suffers a rapid degeneration upon the diffusion of H_2O and O_2 molecules (Figure 5A). It is worth noting that large size substituents, such as fluorocarbon substitutions, can lead to close molecular packing, which is also benefit for inhibiting the ingress of O_2 and H_2O and increase of air-stability.[19, 77] While the LUMO level above -3.9 eV, the electron transport behaviour may be concealed in air. Similarly, if the LUMO level of ambipolar OSCs is above -3.9 eV, the electron transport of ambipolar semiconductor also tend to be concealed in ambient conditions. Therefore, if both electron and hole injection and transport occurs in ambient conditions, the energy bandgap of ambipolar semiconductors should be around 1.0 eV.[14, 75, 78] However, most of the high performance ambipolar OSCs reported so far usually have an energy bandgap of ~ 2 eV, and exhibits air-instable operation behaviour. Additionally, considering the commonly used metal electrode, such as gold with a work function of ~5.1 eV, for efficient charge carrier injection, the charge carrier injection barrier should be as small as possible, which means that a lower LUMO level shall lead to a much more efficient charge injection. It is also favourable to achieve balanced ambipolar behaviour, which is also a very important requirement for ambipolar semiconductors. Summary of the energy alignments and charge carrier mobilities for organic semiconductors mentioned in this text is shown in Figure 5.

Molecular packing

The molecular packing mode is very important for analysis of the charge transport between adjacent molecules. In this respect, there is no difference between the n-type and p-type OSCs. There are four kinds of main packing motifs as shown in Figure 6.[79-81] Theoretically speaking, the cofacial lamellar packing mode is the most efficient molecular packing mode for high mobility of OSCs because it can increase the transfer integrals to the maximum and transport the charge carriers through shortest route.[82] Hence, extensive work concentrated on tailoring the molecules to obtain a perfect cofacial lamellar packing arrangement.[48, 83-85] Indeed some semiconductors with cofacial lamellar packing mode showed excellent performance such as compound **4** and **5**. However, cofacial lamellar packing arrangement is not prerequisite for high performance OSCs. For

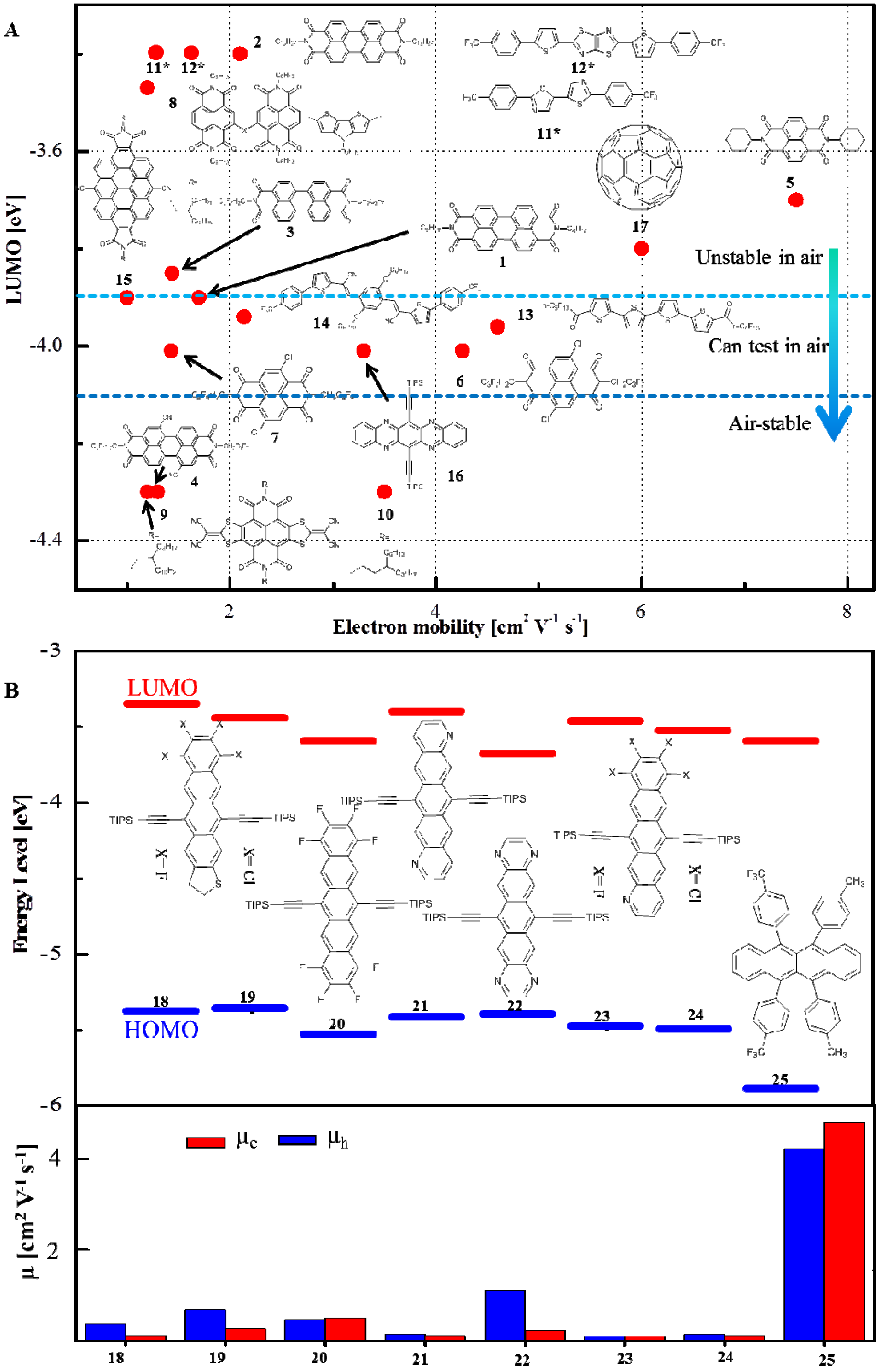

Figure 5. (A) Electron mobility and corresponding LUMO level of high performance n-type small molecules. (B) Energy level of high performance ambipolar small molecules. * LUMO level value is unknown.

instance, both cyclohexane substituted NDI and compound **5** showed similar molecular packing mode, similar molecular structure and similar HOMO/LUMO energy levels, but a dramatic improvement in field-effect mobility is demonstrated for compound **5**.[31]Another good example is TIPS-pentacene. Compared to pentacene, TIPS-pentacene showed typical 2-D π-stacking with significantly increased π-orbital overlap.[85] Theoretically, this indicated that TIPS-pentacene was more favourable for charge carrier transport. In fact, the mobilities of pentancene based OFETs were much higher than the mobilitities of TIPS-pentacene based OFETs. In addition, many OSCs with herringbone packing mode also exhibited high charge carrier mobility in experimental result such as pentacene and compound **6**.[34, 86, 87] Nevertheless, no matter what kind of molecular packing mode, a dense molecular packing and effective π-orbital overlap were believed to be crucial for high performance OSCs.

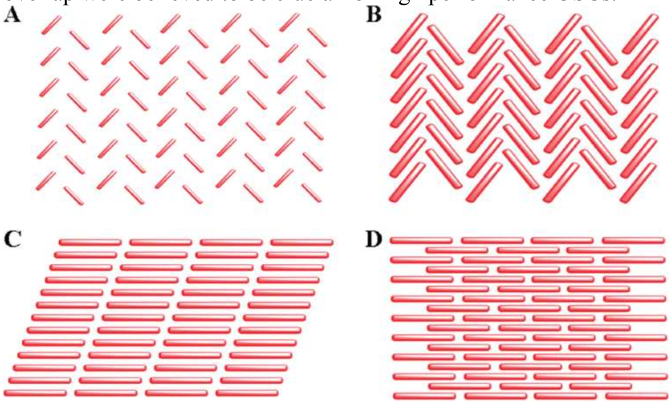

Figure 6. Molecular packing motifs in crystals. (A) Herringbone packing (face-to-edge) without π-π overlap (face-to-face) between adjacent molecules; (B) herringbone packing with π-π overlap between adjacent molecules; (C) lamellar motif, 1-D π-stacking; (D) lamellar motif, 2-D πstacking. Copyright 2012 Chemical Review.

Other factors

Many other factors are also very important for the fabrication of high performance n-type and ambipolar OFETs, such as impurities, defects, testing environment etc. Impurities in organic semiconductors may serve as defects and traps and hinder the measurement of intrinsic charge transport.[88] These organic impurities not only formed during the chemical synthesis process, but also formed during the deposition process or later degradation, and it is hard to remove. Hence, further purification processes are necessary. Multiple recrystallization and vacuum sublimation were the commonly used approach to purify organic materials. Testing environments (e.g. humidity and temperature) can also affect the charge carrier mobility. For instance, in ultrapure single crystal with a standard band-like transport mode, low temperature is favourable for high charge carrier mobility, while in disordered solid states with hopping transport, high temperature is favourable for high charge carrier mobility.[29]

5. Conclusion and Outlook

In this mini-review, we systematically summarized the high performance n-type and ambipolar organic small molecules reported in the past few years. Remarkable advances have been achieved in developing high performance n-type and ambipolar OSCs due to the urgent demand for the development of organic electronics. Till now, numerous small OSCs were designed and synthesized. Among a large set of plausible candidates, only a few small OSCs exhibited excellent performance and good air stability. It has been proved that both selecting electron-deficient building blocks (e.g. PDI, NDI) with appropriate substituent groups and converting the known p-type building blocks into n-type by introducing electron-withdrawing groups to reduce the LUMO level for electron injection and transport are promising approaches to construct high performance electron-transporting materials. Moreover, with these mentioned molecules as examples, we also give a detailed discussion on the requirements of high performance, air-stable n-type and ambipolar OSCs, that is intact extensive π-stacking with effective overlap molecular packing and appropriate energy level alignment. With the exploration of new π-conjugated system and deeper understanding of structure-property relationship of organic materials and optimization of device fabrication techniques, hopefully, remarkable breakthrough could be further achieved for n-type and ambipolar organic materials and their devices, advancing their promising practical applications in organic electronics.

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