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Development of n-Type Organic Semiconductors for Thin Film Transistors: A Viewpoint of Molecular Design

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Abstract

The past ten years have witnessed great progress of n-type organic semiconductors (OSCs) for organic thin film transistors (OTFTs), while the device performance and ambient stability of n-type OSCs are still outmatched by their p-type counterparts. The pursuit of high-performance ambient-stable n-type OSCs for OTFTs is highly desirable for realizing robust, large-area and low-cost organic integrate circuits. In this feature article, we’ll review the development of n-type OSCs for OTFTs from a viewpoint of molecular design, where more than nine molecular design strategies with > 120 representative n-type OSCs were summarized and analyzed to give some valuable insights for this significant but challenging field.
1. Introduction

As an important branch of organic electronics, organic thin film transistors (OTFTs) have attracted more and more attention for their applications in low-cost, large-area and flexible electronic products, such as flexible active-matrix displays, organic tags/memories, and chemical/biological sensors. Organic semiconductors (OSCs) are the active components of OTFTs and can be divided into p-type (hole-transporting) and n-type (electron-transporting) ones. Now, the performance of n-type OSCs is outmatched by that of the burgeoning p-type counterparts. For example, some solution-processed p-type small molecular and polymeric semiconductors have shown hole mobilities larger than 30 and 10 cm² V⁻¹ s⁻¹, respectively. However, there are still few n-type OSCs that could be compared with the performance of amorphous silicon TFTs (mobility: ~1.0 cm² V⁻¹ s⁻¹), with unsatisfied device air stability. Since both p- and n-type OSCs with comparable performance are required for ambipolar transistors, p-n junctions and organic complementary circuits, the development of high-performance ambient-stable n-type OSCs for OTFTs are highly desirable.

There is no clear boundary between p- and n-type OSCs, since field-effect (FET) electron mobilities have been generally observed in a number of common p-type polymers, such as poly(3-hexylthiophene) (P3HT) and poly(p-phenylenevinylene) (PPV), by using an appropriate hydroxyl-free gate dielectric and low-work-function electrodes. To decrease the trapping of electrons at the semiconductor–dielectric interface induced by hydroxyl groups and guarantee suitable molecular packing for charge carrier transport, the self-assembling monolayers (SAMs) of
octadecyltrichlorosilane (OTS-18), hexamethyldisilazane (HMDS), octadecyltrimethoxysilane (OTMS) or other modifying reagents on substrates are widely used for fabricating OTFTs.\textsuperscript{10} n-type OSCs are commonly electron-deficient small molecular and polymeric $\pi$-conjugated systems with the lowest unoccupied molecular orbital (LUMO) levels below $-3.0$ eV.\textsuperscript{11} Although the LUMO energy levels of most n-type OSCs are higher than $-4.0$ eV, the high work-function electrodes such as Au (5.1 eV) are still commonly used due to their much better environmental stability compared with the low work-function electrodes (Ca, Mg, Al etc). This high injection barrier could be solved by the electrode modifications and the electrode–semiconductor interface engineering.\textsuperscript{12} Since the first observation of n-channel OTFTs by using lutetium and thulium bisphthalocyanines as semiconductors in 1990,\textsuperscript{13} significant progresses in the field of n-type OSCs and n-channel OTFTs have been made and the results could be obtained from the recent reviews.\textsuperscript{3,4,11,14–20} In 2004, Newman and co-workers\textsuperscript{11} wrote an impressive review on OTFTs and n-type OSCs, and especially highlighted the molecular design for n-type OSCs. Over the past decade, hundreds of n-type OSCs for OTFTs have been synthesized with many efficient molecular design strategies. In this feature article, we’ll discuss the progress in recent ten years on n-type OSCs for OTFTs from a viewpoint of molecular design.

2. Basic overview for designing n-type OSCs for OTFTs

Compounds 1–6 (Scheme 1) are the representative n-type OSCs early developed for OTFTs and could illustrate the basic molecular design strategy. High electron
Scheme 1. Representative early stage n-type OSCs for transistors

mobility, good processability, and excellent ambient/operating device stability are the
key targets for the molecular design of n-type OSCs, of which the ambient/operating
device stability is the most challenging topic for n-type OSCs used in OTFTs due to
the vulnerable electron charge carriers that are easily trapped by ambient species, such
as O₂ and H₂O. For example, vacuum-deposited bottom-gate top-contact (BGTC)
OTFTs based on a naphthalene diimide (NDI) derivative bearing N-cyclohexyl groups
exhibited an electron mobility (μₑ) of up to 6.2 cm² V⁻¹ s⁻¹ under a positive argon
atmosphere, however, when tested in air the μₑ value was degraded to 0.41 cm² V⁻¹ s⁻¹
with a three-order lower current on/off ratios (I_on/off). What factors affect the
ambient/operating device stability of n-type OSCs for OTFTs? Generally, both the
energetic (thermodynamic) factors and the kinetic elements influence the stability of
n-type OSCs in OTFTs. For the energetic factors, the LUMO energy levels of n-type
OSC should be less than or equal to −4.0 eV (a value between −4.3 and −4.4 will be
better) for ambient stable electron injection and transport in OTFTs. For example,
solution-processed BGTC OTFTs based on a fullerene derivative [84]PCBM showed
an electron mobility (μₑ) of 0.5 × 10⁻³ cm² V⁻¹ s⁻¹ under ambient light in air and could
continue to operate even after exposure to air for several months without any noticeable degradation.\textsuperscript{27} The low-lying LUMO energy level of [84]PCBM (about \(-4.0\) eV) should be the key energetic factor for the device air stability,\textsuperscript{27} since most fullerene derivatives have the higher LUMO energies (such as [60]PCBM, about \(-3.7\) eV) and could only perform as n-channel transistors in vacuum or in inert atmosphere.\textsuperscript{27} Copper hexadecafluorophthalocyanine (F\textsubscript{16}CuPc, 1) reported by Bao et al in 1998 is the early ambient stable n-type OSC, its BGTC OTFTs showed an electron mobility of 0.03 cm\textsuperscript{2} V\textsuperscript{−1} s\textsuperscript{−1} with long-term device stability in air.\textsuperscript{28} The deep LUMO energy level (about \(-4.3\) eV estimated from the Cyclic Voltammetry results)\textsuperscript{24} and the fluorine atoms that could block moisture from penetrating through the films are respectively the energetic and kinetic factors for device stability.\textsuperscript{28} The kinetic factors that influence the n-channel OTFT stability were systematically studied by Katz et al in 2000,\textsuperscript{29,30} where OTFTs based on a NDI derivative that bears two fluorinated chains (2) showed electron mobility of up to 0.1 cm\textsuperscript{2} V\textsuperscript{−1} s\textsuperscript{−1} with good air stability, while those with alkyl chains showed no FET activity in air.\textsuperscript{29,30} Since the N-fluororalkyl groups only slightly depress the LUMO energy level of 2 (\(\Delta E \leq 0.15\) eV) relative to the alkyl chain functionalized NDIs, with the help of single crystal analysis, Katz et al. proposed that a kinetic barrier formed by the densely packed R\textsuperscript{F} groups could hinder the ambient species (O\textsubscript{2}, H\textsubscript{2}O) penetration and contribute to the electron-transport air stability.\textsuperscript{29} Besides the microstructure of thin films, the thin film morphology (crystallinity, grain size, and grain boundaries) and active layer thickness are all kinetic factors that influence the n-channel OTFT stability.\textsuperscript{31–33} Thin films with
high crystallinity, large grain size, and low density of grain boundaries favor the device air stability.

There is interplay between the energetic and kinetic factors on ambient stability of n-channel OTFTs, they oppose each other also complement each other. \(\alpha,\omega\)-Diperfluorohexylsexithiophene \(3\) and perfluoropentacene \(4\) both have fluorinated groups that might be served as the kinetic factors for device stability. However, BGTC OTFTs based on \(3\) and \(4\) only showed n-channel behaviors in \(N_2\) atmosphere or in vacuum with the electron mobility of up to 0.02 and 0.11 cm\(^2\) V\(^{-1}\) s\(^{-1}\), respectively.\(^3\),\(^4\) The device air instability might be explained by the high LUMO energy levels of \(3\) and \(4\) (\(-2.9\) and \(-3.65\) eV, respectively),\(^3\),\(^4\) and the energetic factors rather than the kinetic elements dominate the n-channel device stability of \(3\) and \(4\). Core-cyanated perylene diimides (PDI) derivative \(5\)\(^3\) is the early example designed in viewpoint of energetic factors, the deep LUMO energy of \(-4.33\) eV realized by the introduction of two electron-withdrawing cyano groups on the PDI core is responsible for the ambient stability of n-channel OTFTs of \(5\) (\(\mu_e\): \(\sim\)0.1 cm\(^2\) V\(^{-1}\) s\(^{-1}\) in air for BGTC device).\(^3\) Both the energetic and kinetic factors play an important role in improving the electron mobility and device stability of OTFTs based on a \(N\)-fluoroalkyl functionalized dicyano-PDI derivative \(6\).\(^3\) Vacuum-deposited BGTC OTFTs based on \(6\) exhibited electron mobility as high as 0.64 cm\(^2\) V\(^{-1}\) s\(^{-1}\) with current on/off ratio \((I_{on/off})\) of \(10^4\), and the devices showed excellent ambient stability with negligible degradation in mobility, threshold voltage \((V_T)\), and \(I_{on/off}\) over six months.\(^3\) The device ambient stability of \(6\) is owing to its low-lying LUMO energy
level (−4.44 eV) and a kinetic barrier formed by the short \( \pi-\pi \) interactions and the densely packed fluorinated \( N \)-groups. \(^{36}\) The spin-coated bottom-gate bottom-contact (BGBC) OTFTs based on \( \text{6} \) exhibited electron mobilities of up to 0.15 \( \text{cm}^2 \text{V}^{-1} \text{s}^{-1} \) in vacuum and 0.14 \( \text{cm}^2 \text{V}^{-1} \text{s}^{-1} \) in air with \( I_{\text{on/off}} > 10^3 \), and mobilities of \(~0.08 \text{cm}^2 \text{V}^{-1} \text{s}^{-1} \) were still measured after 20 days of continuous exposure to air. \(^{37}\) By using an improved solution processing technique and triethoxy-\( 1H,1H,2H,2H \)-tridecafluoro-\( n \)-octylsilane SAMs for substrate treatments, highly crystallized thin films of \( \text{6} \) were achieved, and BGTC OTFTs based on these crystalline films showed electron mobility of up to 1.3 \( \text{cm}^2 \text{V}^{-1} \text{s}^{-1} \) and \( I_{\text{on/off}} \) of \( 10^5 \), with excellent device air stability. \(^{38}\) In addition, single-crystal field-effect transistors (SCFETs) of \( \text{6} \) were also studied with electron mobilities of up to 6 \( \text{cm}^2 \text{V}^{-1} \text{s}^{-1} \) in vacuum and 3 \( \text{cm}^2 \text{V}^{-1} \text{s}^{-1} \) in air. \(^{39}\) Band-like electron transport in vacuum-gap SCFETs of \( \text{6} \) was observed recently with electron mobility of up to 10.8 \( \text{cm}^2 \text{V}^{-1} \text{s}^{-1} \) when measured at low temperature (230 K) in vacuum. \(^{40}\) The mobility deviations from the values measured in vacuum to those tested in air demonstrate some air sensibility of \( \text{6} \)-based SCFETs, \(^{39}\) similar phenomena were also observed for vacuum-deposited BGTC OTFTs based on \( \text{6} \) and other \( N \)-fluoroalkyl functionalized dicyano-PDI derivatives. \(^{41}\) The results demonstrate that the energetic and kinetic factors could not fully explain the ambient stability of n-channel OTFTs, and further efforts are required for clarifying the mechanism of electron-transport stability.

3. The strategies for designing n-type OSCs for OTFTs

By summarizing recent ten years’ references on n-type OSCs for OTFTs, we present
here more than nine molecular-design strategies toward high-performance ambient-stable n-channel OTFTs. In each section, the n-type OSCs with electron mobility larger than 0.5 cm² V⁻¹ s⁻¹ for vacuum-deposited OTFTs and \( \mu_e > 0.1 \) cm² V⁻¹ s⁻¹ for solution-processed n-type OSCs are highlighted (see Table 1 for details), as well as the very stable OSCs for n-channel OTFTs. The HOMO/LUMO energy levels’ control of n-type OSCs is another emphasis in the following sections.

### Table 1. Device performance of the representative n-type OSCs for OTFTs with molecular orbital energy values

<table>
<thead>
<tr>
<th>HOMO/LUMO energy (eV)</th>
<th>Optimized ( \mu_e ) (cm² V⁻¹ s⁻¹)</th>
<th>( I_{on/off} )</th>
<th>( V_T ) (V)</th>
<th>Device structure</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>−6.8/−4.5</td>
<td>0.64 (v-d, air) 1.3 (s-d, air) 6 (s-c, vacuum) 3 (s-c, air)</td>
<td>10⁴ 10⁵ 10¹⁄₂–10⁴</td>
<td>BGTC (Au)</td>
<td>36 38 39</td>
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<tr>
<td>7</td>
<td>−6.71/−3.71</td>
<td>0.7 (v-d, air)</td>
<td>10⁵–10⁶ 3–13</td>
<td>BGTC (Au)</td>
<td>44</td>
</tr>
<tr>
<td>8</td>
<td>−3.85</td>
<td>0.57 (v-d, air)</td>
<td>10⁷ 13–48</td>
<td>BGTC (Au)</td>
<td>45</td>
</tr>
<tr>
<td>12</td>
<td>−3.79</td>
<td>1.44 (v-d, N₂) 1.24 (v-d, air)</td>
<td>10⁶ 39–47 47–57</td>
<td>BGTC (Au)</td>
<td>49</td>
</tr>
<tr>
<td>13</td>
<td>−3.79</td>
<td>0.62 (v-d, N₂) 0.37 (v-d, air)</td>
<td>10⁶–10⁷ 21–29 28–39</td>
<td>BGTC (Au)</td>
<td>49</td>
</tr>
<tr>
<td>24</td>
<td>−6.13/−3.90</td>
<td>1.0 (s-d, N₂) 0.51 (s-d, air)</td>
<td>10⁴–10⁵ 10¹⁄₂–10⁴ 4–15</td>
<td>BGTC (Au)</td>
<td>61</td>
</tr>
<tr>
<td>25</td>
<td>−5.88/−4.04</td>
<td>0.16 (s-d, air)</td>
<td>10⁶ 23</td>
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<td>62</td>
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<tr>
<td>27</td>
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<td>10⁷–10⁸ 28</td>
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<td>63</td>
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<td>0.66 (v-d, N₂) 0.61 (v-d, air)</td>
<td>10⁶ 9–15 11–29</td>
<td>BGTC (Au)</td>
<td>49 69</td>
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<tr>
<td>34</td>
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<td>10⁵ 8–14 17–41</td>
<td>BGTC (Au)</td>
<td>49</td>
</tr>
<tr>
<td>38</td>
<td>−6.92/−4.01</td>
<td>0.86 (v-d, N₂) 0.91 (v-d, air) 0.95 (s-d, air) 8.6 (s-c, air)</td>
<td>10⁴–10⁶ 10⁵ 10¹⁄₂</td>
<td>BGTC (Au)</td>
<td>71 72 73</td>
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<tr>
<td>39</td>
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<td>1.26 (v-d, N₂) 1.43 (v-d, air)</td>
<td>10⁵ 15±2 23±2</td>
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<td>71</td>
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<td>10⁹ 8</td>
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<td>78</td>
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<td>Energy (eV)</td>
<td>Density (g/cm³)</td>
<td>Mobility (cm²/V·s)</td>
<td>Temperature (K)</td>
<td>Material (Au)</td>
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<td></td>
<td>TGB (Au)</td>
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<td>$10^4$–$10^6$</td>
<td>13</td>
<td>TGB (Au)</td>
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<td>3.0 (s-d, N₂)</td>
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<td>$10^1$</td>
<td>10</td>
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<td>86</td>
<td>−6.0/−4.2</td>
<td>0.10 (linear, s-d, air)</td>
<td>$10^5$</td>
<td></td>
<td>BGBC (Au)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.03 (s-d, air)</td>
<td></td>
<td></td>
<td>TGB (Au)</td>
</tr>
<tr>
<td>94</td>
<td>−5.3/−3.7</td>
<td>0.12 (s-d, N₂)</td>
<td>$10^5$–$10^6$</td>
<td>21</td>
<td>BGTC (Au)</td>
</tr>
<tr>
<td>100</td>
<td>−6.6/−3.8</td>
<td>0.34 (s-d, N₂)</td>
<td>$10^5$</td>
<td>8</td>
<td>TGB (Au)</td>
</tr>
<tr>
<td>102</td>
<td>−6.28/−3.47</td>
<td>0.19 (s-d, vacuum)</td>
<td>$10^5$</td>
<td>76</td>
<td>TGB (Au)</td>
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<tr>
<td>104</td>
<td>−6.12/−4.10</td>
<td>1.1 (s-d, air)</td>
<td></td>
<td></td>
<td>TGB (Au)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.1 (s-d, air)</td>
<td></td>
<td></td>
<td>BGTC (Au)</td>
</tr>
<tr>
<td>106</td>
<td>−6.98/−4.14</td>
<td>0.55 (s-c, N₂)</td>
<td>10⁵</td>
<td>45</td>
<td>BGTC (Au)</td>
</tr>
<tr>
<td>107</td>
<td>−6.04/−4.22</td>
<td>4.65 (s-c, air) 0.11 (s-d, air)</td>
<td></td>
<td></td>
<td>BGTC (Ag)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>BGTC (Au)</td>
</tr>
<tr>
<td>108</td>
<td>−6.14/−4.30</td>
<td>0.70 (s-d, air)</td>
<td>10⁷</td>
<td>21</td>
<td>BGTC (Au)</td>
</tr>
<tr>
<td>109</td>
<td>−6.16/−4.26</td>
<td>0.25 (s-d, air)</td>
<td>10⁵</td>
<td></td>
<td>BGTC (Au)</td>
</tr>
<tr>
<td>110</td>
<td>−6.08/−4.40</td>
<td>0.18 (s-d, air)</td>
<td>10⁵</td>
<td>0.95</td>
<td>BGTC (Au)</td>
</tr>
<tr>
<td>118</td>
<td>−5.75/−4.01</td>
<td>3.3 (v-d, vacuum) 0.5 (v-d, air) 2.5 (s-d, vacuum)</td>
<td>10⁵</td>
<td></td>
<td>BGTC (Au)</td>
</tr>
<tr>
<td>119</td>
<td>−6.45/−3.79</td>
<td>3.39 (s-c, air)</td>
<td>10⁴</td>
<td></td>
<td>TGTC (graphite)</td>
</tr>
</tbody>
</table>

*a* v-d: vacuum deposition, v-d: solution deposition, s-c: single crystal, BGTC: bottom-gate top-contact, BGBC: bottom-gate bottom-contact, TGBC: top-gate bottom-contact, TGTC: top-gate top-contact. *b* The device depositing and testing conditions. *c* Ambipolar transporting features were observed.

### 3.1 The functionalization of electron-deficient \( \pi \)-conjugated systems by using fluorine or fluorocarbon-based functional groups, a kinetic mechanism

Compounds 7–19 are shown in Scheme 2 to illustrate molecular design strategy in this section. 1,4,5,8-Naphthalene diimides (NDIs)\(^{42}\) are a class of electron-deficient \( \pi \)-functional molecules with low-lying HOMO/LUMO levels (−7.0/−3.4 eV for a model NDI molecule with \( N \)-methyl groups estimated by DFT calculations).\(^{43}\) As mentioned in section 2, Katz et al.\(^{29}\) reported ambient-stable n-channel OTFTs based on a fluorocarbon-functionalized NDI derivative 2 with \( \mu_e \) of up to 0.1 cm\(^2\) V\(^{-1}\) s\(^{-1}\).

Since the fluorocarbon-based \( N \)-groups depress the LUMO energy level of 2 slightly (\( \Delta E \leq 0.15 \) eV), a kinetic barrier formed by the densely packed fluoroalkyl chains was proposed and it could hinder the ambient species (O\(_2\), H\(_2\)O) penetration and contribute to the electron-transport air stability.\(^{29}\) Later on, a series of \( N \)-fluorocarbon (R\(^F\))-functionalized NDI derivatives 7–10 were designed and synthesized for
ambient-stable n-channel OTFTs.\textsuperscript{44–47} A \( N,N' \)-bis(3-(perfluorocetyl)propyl)-NDI derivative 7 was reported by Katz and coworkers,\textsuperscript{44} 7-based BGTC OTFTs showed \( \mu_e \) approaching 0.7 cm\(^2\) V\(^{-1}\) s\(^{-1}\) in air (\( I_{\text{on/off}} \): \( 10^5 \)–\( 10^6 \) and \( V_T \): 3–13 V),\textsuperscript{44} which is much better in performance than 2-based devices.\textsuperscript{29} In addition, the electrical stability against gate bias stress of 7-based devices is comparable to that of a-Si TFTs.\textsuperscript{44} The results demonstrate that \( N-(\text{CH}_2)_3\text{C}_8\text{F}_{17} \) group is more powerful than \( N-\text{CH}_2\text{C}_7\text{F}_{15} \) substituent for achieving high-performance NDI-based n-type OSCs. NDI derivatives bearing perfluoroalkyl benzyl \( N \)-groups were readily synthesized from commercially available starting materials, of which compound 8 presented \( \mu_e \) values of up to 0.57 cm\(^2\) V\(^{-1}\) s\(^{-1}\) in air for its BGTC OTFTs with the \( I_{\text{on/off}} \) as high as \( 10^8 \).\textsuperscript{45} Low-temperature-deposited, transparent, and ambient-operable n-channel OTFTs were demonstrated by Katz \textit{et al.} by using fluorinated phenylethylated NDI derivatives as active layers.\textsuperscript{46} The devices based on 9 showed \( \mu_e \) values of 0.1–0.31 cm\(^2\) V\(^{-1}\) s\(^{-1}\) in air with the depositing substrate temperature \( \leq 80 \) °C, and the optimized mobility for a flexible and transparent transistor of 9 was 0.23 cm\(^2\) V\(^{-1}\) s\(^{-1}\) with low hysteresis.\textsuperscript{46} BGTC OTFTs based on a 3,5-bis-trifluoromethyl aniline functionalized NDI derivative 10 displayed excellent thermally resistant and high electron mobility of up to 0.24 cm\(^2\) V\(^{-1}\) s\(^{-1}\) with a negligible decrease in \( \mu_e \) even when exposed to air for 42 days.\textsuperscript{47}

Besides NDIs,\textsuperscript{29,30,44–47} the fluorocarbon-based air barrier mechanism\textsuperscript{29} was also successfully applied to perylene diimides (PDIs), pyromellitic diimides, and other n-type molecules, affording many ambient-stable n-type OSCs for OTFTs.\textsuperscript{48–56} A
series of $N$-fluoro-phenyl functionalized PDI derivatives were studied for n-channel OTFTs by Chen, Bao and their coworkers, their-based OTFTs performed well in air with electron mobilities slightly lower than those measured in glove box, of which the

**Scheme 2.** Representative n-type OSCs designed from a fluorine- or fluorocarbon-based air barrier mechanism

OTFTs based on an $N$-pentafluorobenzene substituted NDI derivative 11 exhibited optimized $\mu_e$ values of 0.053 and 0.068 cm$^2$ V$^{-1}$ s$^{-1}$ in air and in glove box, respectively.$^{48}$ More RF functionalized PDI-based n-type OSCs were developed by Würthner, Bao and their coworkers, and were successfully applied for air-stable n-channel OTFTs.$^{49}$ A PDI derivative with two $N$-CH$_2$C$_3$F$_7$ groups (12) showed the best device performance, with electron mobilities of up to 1.44 and 1.24 cm$^2$ V$^{-1}$ s$^{-1}$ measured in N$_2$ atmosphere and in air, respectively ($I_{on/off}:10^6$).$^{49}$ OTFTs based on an $N$-pentafluorophenylethylated PDI derivative (13) also exhibited high $\mu_e$ values of
0.62 and 0.37 cm$^2$V$^{-1}$s$^{-1}$ tested in N$_2$ atmosphere and in air, respectively, with $I_{\text{on/off}}$ of $10^6$–$10^7$. R$^F$ substituted pyromellitic diimides, such as 14, were reported by Katz et al. for air-stable n-channel OTFTs, these n-type OSCs have the minimal cores but showed relatively high electron mobility of up to 0.079 cm$^2$V$^{-1}$s$^{-1}$ with $I_{\text{on/off}}$ as high as $10^6$. Zheng and co-workers applied the fluorocarbon-based functionalization on the angular-shaped 1,2,5,6-NDIs and studied their BGTC OTFTs. The R$^F$ functionalized 1,2,5,6-NDIs showed better device performance in N$_2$ atmosphere, with electron mobility of up to 0.52 cm$^2$V$^{-1}$s$^{-1}$ for 15-based OTFTs, when tested in air, the $\mu_e$ values were much lower (about $10^{-2}$ cm$^2$V$^{-1}$s$^{-1}$). The less air stability of R$^F$-1,2,5,6-NDIs-based OTFTs is due to the materials’ high LUMO energy levels (about $-3.6$ eV) that could result in electron trapping under ambient conditions, while the corresponding R$^F$-1,4,5,8-NDIs have relatively lower LUMO energy levels (about $-3.9$ eV) and better device air stability. Fullerene derivatives are a class of n-type OSCs, while most fullerenes could not exhibit n-channel OTFT characteristics in air due to the electron trapping by ambient spices. Perfluoroalkyl-substituted C$_{60}$ derivatives (such as 16) were developed by Chikamatsu et al. and the air operation for their-based n-channel OTFTs was realized, with the electron mobility of up to 0.078 cm$^2$V$^{-1}$s$^{-1}$. Since these perfluoroalkyl-substituted C$_{60}$ derivatives have the high LUMO energies of about $-3.6$ eV, the fluorocarbon-based air barrier contributes to the device air stability. Compounds 17–19 have the electron-deficient $\pi$-cores and fluorine or fluorocarbon-based groups with the LUMO energies of $-3.79$, $-3.53$ and $-3.67$ eV, respectively.
OTFTs based on 17–19 showed well n-channel FET characteristics, with electron mobilities of up to 0.39, 0.16 and 0.07 cm² V⁻¹ s⁻¹, respectively, and \(I_{\text{on/off}}\) of \(10^5-10^7\). In spite of the high LUMO energy levels (–3.5 ~ –3.8 eV) of 17–19 that go against ambient-stable electron transport, their-based OTFTs exhibited good air stability due to the fluorine or fluorocarbon-based air barrier formed by the dense molecular packing.

For compounds 7–19, most of their LUMO energy levels are higher than –4.0 eV, the fluorine or fluorocarbon-based air barrier mechanism dominates their n-channel device air stability. In addition, compounds 7–19 have relatively large HOMO–LUMO gaps and low-lying HOMO energy levels (–6.0 eV), which blocks the hole transport and makes the unipolar n-channel charge carrier transport. Therefore, the molecular design by using fluorine or fluorocarbon-based air barrier mechanism could afford promising n-type OSCs for ambient-stable, unipolar, n-channel OTFTs. However, most of fluorocarbon-functionalized n-type OSCs suffer from a low solubility in common organic solvents, which hinders their applications for solution-processed OTFTs.

3.2 The functionalization of electron-deficient π-conjugated systems by using electron-withdrawing groups, an energetic mechanism

Compounds 20–31 are displayed in Scheme 3 to illustrate the molecular design strategy in this section. The vulnerability of n-type charge carriers is due to the trapping by the most common reactive species in ambient atmosphere (H₂O and O₂). de Leeuw and co-workers first studied the issue of ambient carrier stability in n-type
OSCs and presented a thermodynamically stable model of n-type OSCs’ charge carrier transport based on solution-phase electrochemical potentials (vs SCE): a reduction potential more positive than −0.658 V is stable towards H₂O and more positive than +0.571 V is stable towards O₂, and an overpotential of about 0.5–1.0 V towards O₂ is required for electrochemical stability of n-type OSCs. In fact, n-type OSCs with first reduction potentials more positive than −0.658 V (vs SCE) are common, while it is not practical to find or synthesize electron-deficient molecules with reduction potentials higher than +0.571 V. By studying ambient/operating stability of n-channel OTFTs based on nonfluorinated arylene diimides and other n-type OSCs, Marks and co-workers presented an empirical “energetic mechanism” for air-stable electron transport in n-channel OTFTs: n-type OSCs with first reduction potentials ≥ −0.4 V (vs SCE) could operate in air without severe device performance degradation, and the ones with first reduction potentials > −0.1 V (vs SCE) could operate well in air with minimal hysteresis and performance degradation. That is, the deep LUMO energy levels of n-type OSCs could stabilize the injected charge carriers against the reactions with ambient species (H₂O and O₂) and thermodynamically determine the air/operating stability of n-channel OTFTs. An onset LUMO energy of −4.0 − −4.1 eV is essential to stabilize electrons during charge transport, and LUMO level < −4.3 is better for ambient-stable electron transport, but much lower LUMO energies (≤ −4.5 eV) may result in “always on” transistors and low I_{on/off} values due to unintentional doping. Therefore, for n-type OSCs, a LUMO energy between −4.1 and −4.4 eV would be desirable for air-stable electron

transport with minimal doping and high $I_{on/off}$ values.

The introduction of two cyano groups onto the core of electron-deficient arylene diimides is an efficient strategy to achieve n-type OSCs with deep LUMO energy levels.23,24,36 PDI-CN2 derivatives 5 and 20 have the LUMO energies of about −4.3 eV and their-based vacuum-deposited BGTC OTFTs showed optimized electron mobility of about 0.1 cm$^2$ V$^{-1}$ s$^{-1}$ in air with excellent ambient/operating stability.24,36

The solution-processed BGTC or BGBC OTFTs based on 20 exhibit $\mu_e$ values of about 10$^{-2}$ cm$^2$ V$^{-1}$ s$^{-1}$ with $I_{on/off}$ of 10$^3$–10$^5$ and $V_T$ values within ±10 V.58,59 The first

Scheme 3. Representative n-type OSCs designed from an energetic mechanism
reduction potential (vs SCE) of NDI-CN2 derivative 21 is about +0.08 V, demonstrating a very low LUMO energy level of −4.5 eV, which made 21-based BGTC OTFTs operate well in air with average electron mobility of 0.11 cm² V⁻¹ s⁻¹ and also a relatively lower $I_{on/off}$ value of $10^3$ due to unintentional doping. Moreover, dicyano anthracene diimides (ADI), pentacene diimides (PADI) and ovalene diimides (ODI) derivatives 22–24 were synthesized for n-channel OTFTs, their-based BGTC devices could operate in air with electron mobilities of up to 0.02, 0.07 and 0.51 cm² V⁻¹ s⁻¹, respectively. n-Channel OTFTs based on 22 or 23 measured in air showed comparable device performance to those tested in N₂ atmosphere due to the low-lying LUMO energies of 22 and 23 (−4.1 ∼ −4.2 eV). ODI-CN2 24 has a relatively higher LUMO level of −3.9 eV and exhibits a big deviation of device performance from ambient testing ($\mu_e$: 0.51 cm² V⁻¹ s⁻¹) to N₂ atmosphere measurement ($\mu_e$: 1.0 cm² V⁻¹ s⁻¹). Besides arylene diimides derivatives, this cyanation strategy has been applied to other electron-deficient π-systems towards ambient-stable n-type OSCs for OTFTs, such as the recently reported cyano-disubstituted dipyrrolopyrazinedione 25 whose solution-processed TGBK OTFTs showed electron mobility of up to 0.16 cm² V⁻¹ s⁻¹ in air, with $I_{on/off}$ of $10^5$–$10^6$. Tetrachloro PDI derivative 26 reported by Bao and co-workers for vapor-deposited BGTC OTFTs showed well n-channel FET behavior in air with electron mobility on the order of 0.1 cm² V⁻¹ s⁻¹. Four chlorine atoms are not enough to depress the LUMO level of 26 below −4.0 eV, and the relatively higher LUMO energy level of −3.9 eV could not explain the air stability for 26-based n-channel
OTFTs, where the good thin-film morphology (such as the large grain sizes) was thought as the kinetic factor for device air stability.\textsuperscript{31} Octachloro PDI derivative \textbf{27} was demonstrated by Würthner, Bao and their coworkers, in comparison with \textbf{26}, the doubled core-substituted chlorine atoms make \textbf{27} a deep LUMO leveled n-type OSC (LUMO: −4.23 eV).\textsuperscript{63} The \textbf{27}-based vacuum-deposited BGTC OTFTs showed comparable device performance when measured in N\textsubscript{2} atmosphere and in air, with electron mobilities of up to 0.91 and 0.82 cm\textsuperscript{2} V\textsuperscript{−1} s\textsuperscript{−1}, respectively, and \(I_{\text{on/off}}\) of \(10^{7}–10^{8}\).\textsuperscript{63} More importantly, these high \(\mu_{e}\) values and \(I_{\text{on/off}}\) ratios were almost unchanged even after exposing the devices to air for about 20 months \((\mu_{e} \approx 0.60 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} \text{ and } I_{\text{on/off}} \approx 10^7)\).\textsuperscript{63} The high electron mobility and excellent air stability of \textbf{27}-based OTFTs are probably due to the energetically low-lying LUMO level and the hydrogen-bond-directed molecular dense brickstone packing.\textsuperscript{63} Besides acting as a kinetic air barrier,\textsuperscript{29} fluorocarbon-based functional groups could also serve as electron-withdrawing moieties directly attaching on the electron-deficient \(\pi\)-cores to achieve deep LUMO leveled n-type OSCs. n-type OSCs \textbf{28–31} are the examples for this molecular design with deep LUMO levels of about −4.1 to −4.2 eV, their-based OTFTs performed well in air as n-channel transistors although the \(\mu_{e}\) values are not high \((10^{-6} \sim 0.1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})\), where the fluorocarbon-based groups might have the dual functions (kinetic and energetic factors) for realizing device air stability.\textsuperscript{64–67}

\textbf{3.3 The functionalization of electron-deficient \(\pi\)-conjugated systems by using both electron-withdrawing groups and fluorine/fluorocarbon-based functional groups, an energetic/kinetic combined mechanism}
PDI derivative 6 (Scheme 1) not only have two electron-withdrawing cyano groups on the perylene core but also bears two fluorocarbon-based $N$-groups at the six-membered imide rings, and an energetic/kinetic combined mechanism could be envisioned for ambient stability of 6-based n-channel OTFTs. The applications of 6 in high-performance ambient-stable n-channel OTFTs have been described detailedly in section 2. Compounds 32–41 (Scheme 4) are representative n-type OSCs designed by using the energetic/kinetic combined mechanism. Beside the lower $V_T$ values, higher $\mu_e$ values were found for OTFTs based on ADIF-CN2 (32, 0.06/0.04 cm$^2$ V$^{-1}$ s$^{-1}$ measured in vacuum/air) relative to the devices based on ADI-CN2 (22, 0.03/0.02 cm$^2$ V$^{-1}$ s$^{-1}$) due to the denser molecular packing induced by the $R^F$ side chains and the relatively lower LUMO energy of 32 (−4.2 eV) versus 22 (−4.07 eV) for easier electron injection.$^{23,68}$ Core-fluorinated PDI derivatives bearing $R^F$ $N$-groups 33–35 were applied for n-channel OTFTs by Würthner, Bao and their coworkers, while the electronegative fluorine atoms showed limited electron-withdrawing ability and the LUMO energies of 33–35 are still higher than −4.0 eV (−3.88 ∼ −3.94 eV).$^{49,69}$ OTFTs based on 33–35 operated well in air with the optimized $\mu_e$ values of 0.61, 0.51, and 0.031 cm$^2$ V$^{-1}$ s$^{-1}$, respectively, and the $I_{on/off}$ ratios of $10^5$–$10^7$.$^{49,69}$ the device air stability might be explained by a kinetic dominated and energetic/kinetic combined mechanism. In comparison with the LUMO energy of 35 (−3.93 eV),$^{69}$ compound 36 has a lower LUMO energy level value of −4.11 eV,$^{49}$ indicating that chlorine atom is more efficient than fluorine atom for withdrawing electron from $\pi$-systems as revealed by Bao et al.$^{70}$ Wang and coworkers reported a core-perfluoroalkylated and
R\textsuperscript{F} N-functionalized PDI derivative 37 that has the deep LUMO energy level of about −4.2 eV, and 37-based BGTC OTFTs operated well in air with $\mu_e$, $I_{on/off}$ and $V_T$ values of 0.003 cm\textsuperscript{2} V\textsuperscript{−1} s\textsuperscript{−1}, $4 \times 10^3$ and 4.7 V, respectively.\textsuperscript{64}

Scheme 4. Representative n-type OSCs designed from an energetic/kinetic combined mechanism

Core-chlorinated and R\textsuperscript{F} N-functionalized NDI derivatives 38–41 were developed by Bao, Würthner and their co-workers, and were applied for vacuum-deposited BGTC n-channel OTFTs.\textsuperscript{71} The dichloro R\textsuperscript{F} NDIs 38 and 39 exhibited comparable device performance when measured in N\textsubscript{2} atmosphere and in air, with $\mu_e$ values (N\textsubscript{2}/air) of 0.86/0.91 and 1.26/1.43 cm\textsuperscript{2} V\textsuperscript{−1} s\textsuperscript{−1}, respectively, and $I_{on/off}$ of $10^5$–$10^7$.\textsuperscript{71} After exposing the devices to air for 3 months, the average mobilities of OTFTs based on 38 and 39 could hold about 80% of the initial values, demonstrating the excellent device ambient stability.\textsuperscript{71} In comparison with OTFTs based on 38 and 39, the devices of tetrachloro R\textsuperscript{F} NDIs 40 and 41 showed much lower $\mu_e$ values (N\textsubscript{2}/air) of 0.15/0.021
and 0.44/0.04 cm² V⁻¹ s⁻¹, respectively, with about a ten-fold deviation for the values measured in N₂ and in air.⁷¹ Although 40 and 41 have relative lower LUMO energies (−4.1 eV) than 38 and 39 (−4.0 eV), 40 and 41 have the inferior device performance and air stability than those of 38 and 39, which should be ascribed to the lower packing density of the fluorinated side chains and the slightly larger π−π stacking distances of 40 and 41 relative to 38 and 39.⁷¹ Therefore, the unfavorable kinetic factors could explain the poor device air stability of 40 and 41,⁷¹ their distorted π-cores (versus the nearly planar π-cores of 38 and 39) might be the internal factors for the inferior device performance and air stability. Würtchner and co-workers demonstrated that OTFTs of 38 could be easily processed into large OTFT device arrays with appreciable homogenous performance and μₑ values of up to 0.95 cm² V⁻¹ s⁻¹ in air by solution shearing onto common SiO₂-covered silicon wafers.⁷² Recently, SCFETs based on microribbons of 38 were displayed by Würthner et al.,⁷³ with the optimized μₑ, V_T and I_on/off values of 8.6 cm² V⁻¹ s⁻¹, 9 V and 7 × 10⁷, respectively, and less than 13% degradation in mobility was observed for the microribbon-FET device of 38 in air during a period of 82 days.⁷³ Single crystal analysis of 38 indicated that the high molecular packing density (20.46 g/cm³), the close contacts between adjacent π-scaffolds (about 3.27 Å), and the densely packed fluoroalkyl chains with F···F and F···O interactions, which could explain the high device performance and excellent air/operating stability of 38-based n-channel OTFTs.⁷³

3.4 The construction of donor-acceptor (D–A) structures towards high performance n-type OSCs
π-functional materials with donor-acceptor (D–A) structures are common in organic electronics, especially for donors of bulk-heterojunction organic photovoltaic (BHJ OPV) and p-type OSCs for OTFTs due to the intramolecular charge transfer (ICT)-induced low band gap and the strong intermolecular D–A interactions. However, the construction of D–A structure for designing n-type OSCs did not cause wide attention until recently.

3.4.1 n-type D–A copolymers

Polymers 42–57 (Scheme 5) are representative n-type OSCs designed by the construction of D–A structure. In 2007, Zhan and coworkers reported a PDI-based D–A polymer (42) and applied it as n-type OSC for BGTC OTFTs (measured in N₂, \( \mu_c: 0.013 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} \), \( V_T: 4.4 \text{ V} \), and \( I_{on/off} > 10^4 \)) and organic acceptor for all polymer OPVs (a power conversion efficiency (PCE) of 1.5%). This pioneering work promotes the development of rylene diimides-based D–A polymers for n-type OSCs. By using acetylene units as linkers between PDI and dithienothiophene (DTT) segments, Zhan et al. prepared a copolymer 43, the 43-based BGTC and BGBC OTFTs performed well in air with electron mobility of 0.06 and 0.075 cm² V⁻¹ s⁻¹, respectively. The better air stability and higher electron mobility of OTFTs based on 43 (versus those of 42) are due to the densely ordered packing of the polymer chains and the lower LUMO energy (−4.0 eV) of 43 versus 42 (−3.9 eV). It is interesting that the device performance and stability changed with the device structures, the BGBC devices of 42 and 43 showed higher \( \mu_c \) values than their BGTC ones, and 42-based BGBC OTFTs operated well in air with electron mobility of 0.038 cm² V⁻¹
s$^{-1}$ rather than its air-inactive BGTC devices.$^{76}$ To further pursue air stable n-type PDI copolymers, Zhan and co-workers select fluorenone as “acceptor” or “weaker donor” to construct new PDI copolymer 44, and OTFTs based on 44 performed well in air ($\mu_e$: $0.01 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) thanks to the polymer’s low-lying LUMO energy ($\sim 4.0 \text{ eV}$).$^{77}$ A diethynylbenzene-linked PDI copolymer 45 was recently reported by Marder, Ree and their coworkers, which could form a nanowire suspension in chloroform.$^{78}$ 45-based OTFTs were fabricated by spin-coating its nanowire suspension on OTS-treated SiO$_2$/Si substrates and could performed in air as n-channel transistors. When annealed at a high temperature ($200 ^\circ \text{C}$), the BGTC devices yielded high $\mu_e$ and $I_{on/off}$ values of $0.15 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $10^6$, respectively, with a low threshold voltage (8 V) and negligible hysteresis (0.5 V).$^{78}$

The dithiophene (T2)-linked PDI/NDI D–A polymers 46 and 47 were developed by Facchetti et al, their-based BGTC OTFTs measured in vacuum showed electron mobilities of about 0.002 and 0.06 cm$^2$ V$^{-1}$ s$^{-1}$, respectively, and obvious degradations of device performance were observed for these two polymers due to their relatively higher LUMO energies ($> -4.0 \text{ eV}$).$^{79}$ However, something amazing happened when P(NDI2OD-T2) 47 was applied for top-gate bottom-contact (TGBC) OTFTs, very high electron mobilities of up to 0.85 cm$^2$ V$^{-1}$ s$^{-1}$ were achieved under ambient conditions with $I_{on/off}$ of $10^6$–$10^7$, and the TFT stability data tested in ambient conditions were excellent.$^{80}$ This excellent device air stability is probably due to the TGBC device structure where the active layer was sandwiched by the dielectric and the substrate. The thiophene-vinylene-thiophene (TVT) building block functionalized
Scheme 5. Donor–acceptor copolymers for n-type OSCs

with alkoxyal groups at the C=C linkage was applied for constructing D–A copolymer

48 by Marks, Facchetti and their co-workers,81 and 48-based BGTC and TGBG

n-channel OTFTs operated well in air with electron mobilities of up to 0.2 and 0.5

$\text{cm}^2 \, \text{V}^{-1} \, \text{s}^{-1}$, respectively, and the low-lying LUMO energy level of 48 ($-4.0 \text{ eV}$) could
explain its good device stability. By varying the number of thiophene units, Luscombe
et al. reported a series of NDI-oligothiophene-based polymers, of which PNDI-3Th

(49)-based BGTC OTFTs exhibited a maximum electron mobility of $0.076 \text{ cm}^2 \, \text{V}^{-1} \, \text{s}^{-1}$
measured in N$_2$ atmosphere.82 Later on, some fused-thiophene containing NDI-based
copolymers (such as 50) were developed, their-based OTFTs showed either n-channel
or electron-dominated ambipolar charge-transport behaviors, with electron mobilities
of about $10^{-3} - 10^{-2}$ cm$^2$ V$^{-1}$s$^{-1}$ measured in N$_2$ atmosphere.$^{83,84}$ Copolymers comprising thiophene-based strong donors and NDI acceptors usually have the low band gaps and relatively high HOMO energies (mostly higher than $-5.8$ eV), the high HOMO levels make hole transport possible and go against the unipolar n-channel charge transport.$^{84}$ When the weaker donors such as benzene and naphthalene were used for constructing NDI-based copolymers ($51$ and $52$, with HOMO energies of about $-5.9$ and $-6.1$ eV, respectively), the unipolar n-channel charge transport was achieved with electron mobilities of about $10^{-3} - 10^{-2}$ cm$^2$ V$^{-1}$s$^{-1}$ due to the low-lying HOMO energy levels that block the hole transport.$^{85}$ Copolymers based on NDI and TVT units were independently studied by Chen, Kim and their coworkers, of which polymer $53$-based TGBK OTFTs showed electron mobility of up to $1.5$ cm$^2$ V$^{-1}$s$^{-1}$ or even higher in air due to the low-lying LUMO energy levels (about $-3.9 \sim 4.0$ eV), the densely packed polymeric backbones, and good thin film morphology.$^{86,87}$ Obvious ambipolar charge transport behaviors were observed for all BGTC/BGBC/TGBK OTFTs of these NDI-TVT-based polymers,$^{86,87}$ while the unipolar n-channel charge transport could be realized for $53$-based TGBK OTFTs by using Cs$_2$CO$_3$-treated source/drain Au electrodes, with electron mobility of up to $1.8$ cm$^2$ V$^{-1}$s$^{-1}$.$^{87}$ A number of selenophene–NDI D–A polymers were developed recently,$^{85,88,89}$ and their-based BGTC OTFTs exhibited n-channel or electron-dominated ambipolar charge-transport behaviors, of which devices based on the end-capped polymer $54$ showed electron mobility of up to $0.24$ cm$^2$ V$^{-1}$s$^{-1}$.$^{89}$ This value is much higher than that of P(NDI2OD-T2,$^{47}$)-based BGTC OTFTs (0.06 cm$^2$ V$^{-1}$s$^{-1}$).
Recently, Jenekhe et al. reported a thiophene-tetraazabenzo[difluoranthene diimide based D–A polymer 55 that comprises a big acceptor unit and a small donor (thiophene) moiety.\textsuperscript{90} BGTC OTFTs based on 55 exhibited unipolar n-channel transport with electron mobility of up to 0.30 cm\textsuperscript{2} V\textsuperscript{−1}s\textsuperscript{−1} measured in N\textsubscript{2} atmosphere.\textsuperscript{90} In recent years diketopyrrolopyrrole (DPP)-based D-A polymers are mostly developed for high performance p-channel OTFTs, some of which exhibited hole mobilities larger than 10 cm\textsuperscript{2} V\textsuperscript{−1}s\textsuperscript{−1}.\textsuperscript{6,7} The efforts in developing DPP-based copolymers for n-channel OTFTs are eye-catching, for example, the BGTC OTFTs based on electron-deficient DPP D–A polymers 56 and 57 showed electron mobilities of up to 3 and 2.36 cm\textsuperscript{2} V\textsuperscript{−1}s\textsuperscript{−1}, respectively.\textsuperscript{91,92} The 57-base n-channel OTFTs also displayed excellent air stability, with the electron mobility decreasing from 2.36 to 1.88 cm\textsuperscript{2} V\textsuperscript{−1}s\textsuperscript{−1} after a 7-month storage under ambient conditions, the device stability and high electron mobility might be attributed to the polymer’s low-lying LUMO energy level of −4.18 eV and the unique edge-on/face-on orientations in thin films.\textsuperscript{92} However, even the electron-deficient DPP-based copolymers 56 and 57 still could not completely shut down the hole transport in their OTFTs due to their relatively higher HOMO energy levels (≥ −5.65 eV).\textsuperscript{91,92}

3.4.2 n-type small molecules with D–A structures

As mentioned in section 3.2, the functionalization of electron-deficient π-conjugated systems by electron-withdrawing groups could afford n-type OSCs with deep LUMO levels for ambient-stable OTFTs. While the introduction of electron-donating
\(\pi\)-conjugated moieties to the electron-deficient \(\pi\)-backbones is usually thought to be not conducive to obtain ambient-stable n-type OSCs for OTFTs due to the limited changed LUMO energies. Now, this opinion seems to be changing. Usta \textit{et al.} reported a D–A small molecule 58 that has a deep LUMO energy level of \(-4.32\) eV, this value is even slightly lower than that of the parent acceptor backbone (\(-4.30\) eV), and the solution-processed BGTC OTFTs based on 58 exhibited an electron mobility of 0.16 cm\(^2\) V\(^{-1}\) s\(^{-1}\) and an \(I_{\text{on/off}}\) ratio of \(10^7\)–\(10^8\), with excellent air stability.\(^{25}\) Zhang and co-workers introduced the electron-donating sulfur-rich rings to the NDI core and obtained a D–A small molecule 59.\(^{93}\) It is surprising that compound 59 has a much lower LUMO energy level (\(-4.4\) eV) than the parent NDI derivative (about \(-3.8\) eV).\(^{93}\) The solution-processed BGTC OTFTs based on 59 performed well in air as n-channel transistors, with \(\mu_e\) and \(I_{\text{on/off}}\) values of 0.05 cm\(^2\) V\(^{-1}\) s\(^{-1}\) and \(10^7\), respectively.\(^{93}\) A thiophene-fused NDI derivative 60 was reported recently by Takimiya \textit{et al.},\(^{94}\) its LUMO energy level (\(-4.0\) eV) is just slightly lower than the parent NDI compound (\(-3.9\) eV). The vacuum-deposited BGTC OTFTs of 60 showed electron mobility of about 0.05 cm\(^2\) V\(^{-1}\) s\(^{-1}\) in vacuum and 0.02 cm\(^2\) V\(^{-1}\) s\(^{-1}\) in air.\(^{94}\)

**Scheme 6.** Donor–acceptor small molecules for n-type OSCs
Marder and coworkers demonstrated that the conjugated donor-bridged bis-NDI derivatives (61–64) were excellent n-type OSCs for high-performance solution-processed OTFTs. The D–A structures make 61–64 much higher HOMO energies relative to the parent NDI compound, while their LUMO energy values were almost unchanged versus NDI (ΔLUMO ≤ 0.12 eV). TGBC OTFTs based on 61 showed electron-dominated ambipolar-transport behaviors with hole and electron mobility of up to 0.0098 and 1.5 cm² V⁻¹ s⁻¹, respectively, the relatively higher HOMO energy of 61 (about −5.4 eV) could explain its hole-transport behavior. TGBC devices based on 62–64 exhibited unipolar n-channel transport with electron mobilities > 0.1 cm² V⁻¹ s⁻¹, of which 64-based flexible OTFTs displayed electron mobility of up to 0.17 cm² V⁻¹ s⁻¹ with good air/operating stability.

3.5 Naphthalene diimides fused with sulfur heterocycles and end-capped with electron-withdrawing groups towards high-performance ambient-stable n-type OSCs

The results from sections 3.1–3.4 demonstrate that promising NDI-based n-type OSCs for OTFTs could be designed by the introduction of RF N-substituents, the electron-withdrawing groups, both RF N-substituents and electron-withdrawing groups, or conjugated electron donors to NDI skeleton at imide rings (only for RF) and/or naphthalene core. In this section, a different molecular design strategy will be introduced by using a series of core-expanded NDIs (c-eNDIs) 65–76 (Scheme 7, 71, 73 and 74 are the mixtures of cis/trans isomers) that were used in n-channel OTFTs. c-eNDIs 65–76 were designed and synthesized by Gao and
co-workers,\textsuperscript{97–100} the inspiration of molecular design comes from the previous research experiences\textsuperscript{104–106} and Yamashita \textit{et al.}’s pioneering work on organic acceptors.\textsuperscript{107} The molecular design strategy for these c-eNDIs (such as 65–76) are as follows: (i) the expansion of NDI core by sulfur heterocycles could promote the intermolecular $\pi$--$\pi$ stacking and/or S...S interactions in solid state, which is crucial for achieving high charge mobility; (ii) the end-cap of lateral $\pi$-conjugated structure by electron-withdrawing groups (such as C≡N group) can depress molecular LUMO energies, which benefits for the ambient-stable electron injection and conduction; (iii) the long and branched N-alkyl chains and the expanded $\pi$-conjugation could realize a balance of good solubility, strong and efficient intermolecular interactions in solid state, high crystallinity, and good film formation.\textsuperscript{98} c-eNDIs 65–76 have good solubility in common organic solvents and low-lying LUMO energy levels of about $-4.0 \sim -4.6$ eV.\textsuperscript{97–100} The good solubility and deep LUMO energies make these c-eNDIs possible for solution-processed ambient-stable n-channel OTFTs. The solution-processed OTFTs based on 65–76 all displayed positive amplification and performed as air-stable n-channel transistors with well-defined linear/saturation regimes, and the $\mu_e$ values were in the range of $10^{3}$--$3.5$ cm$^2$ V$^{-1}$ s$^{-1}$,\textsuperscript{97–103} demonstrating the effectiveness of the molecular design strategy of these c-eNDIs towards solution-processable, ambient-stable n-channel OTFTs. Compounds 65–69 are a class of NDI derivatives fused with two 2-(1,3-dithiol-2-ylidene)malononitrile groups (NDI-DTYM2), their-based n-channel OTFTs showed the best device performance among those based on c-eNDIs 65–76. As the excellent n-type OSCs
used in solution-processed OTFTs, NDI-DTYM2 derivatives 65–69 will be highlighted in this section.

NDI-DTYM2 derivatives 65–68 were designed and synthesized for studying the side-chain influence on their OTFT device performance. OTFTs based on 65–68 were fabricated by spin coating their respective chloroform solutions on OTS-treated SiO₂/Si substrates (for BGBC and BGTC devices) or poly-(perfluorobutenylvinylether)/glass substrates (for TGBK devices). Compounds 65 and 66 bear the 2-branched C₁₂,₈ and C₁₀,₆ N-alkyl chains, respectively, with the

Scheme 7. Core-expanded NDIs for n-type OSCs
deferent side-chain length (carbon atom numbers: 20 vs 16). BGTC/BGBC/TGBK OTFTs base on 65 and 66 showed the optimized average electron mobility (μₑ,av) of about 0.15–0.5 cm² V⁻¹ s⁻¹ and 0.08–0.2 cm² V⁻¹ s⁻¹, respectively, with a 1–2-fold
deviation, demonstrating the limited side-chain influence on device performance. Compounds 66–68 have the 2-, 3-, and 4-branched N-alkyl chains, respectively, with the comparable chain length (carbon atom numbers: 16–18). The 3-branched compound 67 exhibited the optimized \( \mu_{e,av} \) values of 3.0, 2.5, and 0.65 cm\(^2\) V\(^{-1}\) s\(^{-1}\) for its BGBC, BGTC and TGBC devices, respectively, while OTFTs based on 2-branched compound 66 showed the corresponding mobility values of 0.2, 0.12, and 0.08 cm\(^2\) V\(^{-1}\) s\(^{-1}\), respectively, leaving a 7–20 times’ gap for device performance of 66 and 67. In addition, OTFTs based on 66 and 67 showed a positive mobility response to the thin-film annealing temperature (even up to 180 °C), while a negative mobility response to the thin-film annealing temperature was found in OTFTs based on 4-branched compound 68, the \( \mu_e \) values of 68-based devices decreased from the as-deposited (or low-temperature annealing \( \leq 80 \) °C) about 0.2 cm\(^2\) V\(^{-1}\) s\(^{-1}\) to a minimum value of 0.001 cm\(^2\) V\(^{-1}\) s\(^{-1}\) after annealing at a temperature \( > 100 \) °C. The results indicate that the branch-point position of side N-alkyl chains significantly affects the device performance of NDI-DTYM2 derivatives. This finding together with Pei and co-workers’ work on alkyl chain branching p-type polymers demonstrate that besides the popular work on new \( \pi \)-backbones, the variation of alkyl chain branching point of known or new \( \pi \)-systems is a powerful strategy for achieving high charge carrier mobility through fine tuning molecular packing in solid state. A versatile one-pot synthesis of NDI-DTYM2 derivatives was developed in our lab, which afforded an unsymmetrically \( N \)-substituted NDI-DTYM2 derivative 69. The solution-processed BGTC OTFTs based on 69 showed electron mobility as high as
0.7 cm$^2$ V$^{-1}$s$^{-1}$ in air, demonstrating that both the symmetrically and unsymmetrically $N$-substituted NDI-DTYM2 are promising n-type OSCs for OTFTs.$^{99}$ Moreover, unsymmetrically $N$-substituted 69 has been successfully used in ultra-thin-film ($\leq 10$ nm) n-channel OTFTs$^{103}$ and n-channel thin-film phototransistors.$^{109}$ In a word, the high electron mobility (0.1–3.5 cm$^2$ V$^{-1}$s$^{-1}$), high current on/off ratios ($10^5$–$10^8$), low threshold voltages (< 15 V), as well as the excellent air/operating device stability make NDI-DTYM2 derivatives (such as 65–69) a class of the most promising n-type OSCs for OTFTs.$^{97–99,101–103}$ Besides c-eNDIs 65–76 mentioned above, some new c-eNDIs bearing the symmetrical or unsymmetrical π-rings on the naphthalene core were developed by Zhang’s group and applied in solution-processed, ambient-stable, n-channel OTFTs, with the electron mobility ranging from $10^{-3}$ to 0.22 cm$^2$ V$^{-1}$s$^{-1}$.110–112

3.6 Quinoidal thiophene derivatives terminated with cyano-containing methylenes towards high-performance ambient-stable n-type OSCs

7,7,8,8-tetracyanoquinodimethane (TCNQ) is a typical n-type OSC with low-lying LUMO energy level of about $-4.8$ eV. In 1994, Brown and co-workers reported OTFTs based on TCNQ, while the electron mobility is very low (about $10^{-5}$ cm$^2$ V$^{-1}$s$^{-1}$) as well as the low $I_{on/off}$ values.$^{113}$ Later on, Uemura et al.$^{114}$ prepared the air-stable n-channel single-crystal transistors based on TCNQ, the devices showed high $\mu_e$ values of up to 0.5 cm$^2$ V$^{-1}$s$^{-1}$ with negligible threshold gate voltages, demonstrating the great potential of quinoidal derivatives in n-channel OTFTs.

As shown in Scheme 8, quinoidal thiophene derivatives terminated with
cyano-containing methylene are becoming a class of promising n-type OSCs for OTFTs.\textsuperscript{115–123} A dicyanomethylene-terminated quinoidal terthiophene derivative 77 was first applied in n-channel OTFTs by Pappenfus \textit{et al.},\textsuperscript{115} electron mobilities of about $10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$ were achieved for both vacuum-deposited and solution-processed BGTC (Ag source/drain contacts) devices.\textsuperscript{115} A much higher $\mu_e$ value of about 0.2 cm$^2$ V$^{-1}$ s$^{-1}$ and a high $I_{on/off}$ ratio of $10^6$ were realized in 77-based vacuum-deposited BGBC (Au source/drain contacts) OTFTs, where the substrates were held at 130 °C during the deposition of thin film of 77 and the devices were measured in high vacuum due to the device air sensitiveness.\textsuperscript{116} A series of cyano-containing methylene-terminated quinoidal thiophene derivatives such as 78–80 were developed by Takimiya \textit{et al.} and applied in n-channel OTFTs.\textsuperscript{117–119} The solution-processed BGTC OTFTs based on 78–80 all displayed ambient-stable...
n-channel FET behaviors with electron mobilities of up to 0.16, 0.015, and 0.06 cm^2 V^{-1}s^{-1}, respectively, and the low-lying LUMO energy levels of 78–80 (about −4.2 eV) could explain their device air stability. 117–119 Li and co-workers reported a dicyanomethylene-substituted fused tetrathienoquinoid derivative 81 and applied it in solution-processed n-channel OTFTs. 120 In comparison with OTFTs based on dicyanomethylene-end-capped quinoidal oligothiophenes (such as 77–80), 81-based OTFTs exhibited a much higher electron mobility of about 0.9 cm^2 V^{-1}s^{-1} with good air/operating stability. 120 A number of dicyanomethylene-substituted 2,5-di(thiophen-2yl)thieno-[3,2-b]thienoquinoid derivatives with different alkyl chain positions on the π-backbone were reported by in Li et al., 121 of which the 3,3′-alkylated compound 82 showed the best OTFT performance, with the electron mobility of up to 0.22 cm^2 V^{-1}s^{-1} and I_{on/off} ratios of 10^4–10^5 measured in air, indicating that the alkyl chain location has significant influence on device performance. Compounds 81 and 82 have the comparable LUMO energy levels of about −4.3 eV, which contributes to the device air stability of their-based n-channel OTFTs. 120,121 Recently, diketopyrrolopyrrole(DPP)-containing dicyanomethylene-terminated quinoidal thiophene derivatives 83 and 84 were developed in Zhu’s lab, 122 their-based BGTC OTFTs showed ambient-stable n-channel FET behaviors, with electron mobilities of up to 0.55 (vacuum-deposited device) and 0.35 cm^2 V^{-1}s^{-1} (solution-processed device), respectively, as well as high I_{on/off} ratios (10^5–10^6) and excellent air/operating device stability. Compounds 83 and 84 are the first examples for DPP-based OSCs with unipolar electron-transport
characteristics in FET devices. Compound 85, with the same \( \pi \)-backbone of 83 and 84 but different side chains, was reported by Heeney and coworkers for small-molecule/polymer blended n-channel OTFTs,\textsuperscript{123} high electron mobilities of 0.5 \( \text{cm}^2\text{V}^{-1}\text{s}^{-1} \) and \( I_{\text{on/off}} \) ratios of \( 10^2 \sim 10^3 \) were achieved for 85-based TGBC devices. The deep LUMO energy levels of 83–85 (about \( -4.2 \sim -4.5 \text{eV} \)) might explain their excellent device stability in ambient and operating conditions.\textsuperscript{122,123}

3.7 Ladder-type small molecules and polymers synthesized by condensation reactions for n-type OSCs

As shown in Scheme 9, ladder-type polymers (86 and 87) and small molecules (88–96) are typical n-type OSCs for OTFTs, which could be readily synthesized by condensation reactions. Poly(benzobisimidazobenzophenanthroline) (BBL, 86), a

![Scheme 9. Ladder-type small molecules and polymers for n-type OSCs](image-url)
conjugated ladder polymer, was the first class of n-type polymers used for OTFTs, its BGBC OTFTs spin coated from methanesulfonic acid solution showed electron mobility of up to 0.1 cm\(^2\) V\(^{-1}\)s\(^{-1}\). More importantly, 86-based n-channel OTFTs exhibited long-term ambient stability over 4 years with negligible changes for \(\mu\), \(I_{\text{on/off}}\) and \(V_T\) values. The long-term device air stability could be explained by the energetic and kinetic factors, i.e. the deep LUMO energy level of 86 (about 4.0–4.2 eV) and its high crystalline films with the densely packed polymeric chains (about 3.4 Å). A ladder-type polymer 87 was recently reported by Luscombe and coworkers, its spin-coated BGTC OTFTs showed electron mobility as high as 0.0026 cm\(^2\) V\(^{-1}\)s\(^{-1}\) that was measured in an inert atmosphere due to the high LUMO energy of 87 (−3.54 eV). 3,4,9,10-perylenetetracarboxylic bis-benzimidazole (PTCBI, 88) was an old n-type OSC that was used in early-stage photovoltaic cells by Tang. Dhagat et al. reported the vacuum-deposited BGTC OTFTs based on 88, giving electron mobility of up to 0.05 cm\(^2\) V\(^{-1}\)s\(^{-1}\) in N\(_2\) atmosphere. Compounds 89\(^{129}\) and 90\(^{130}\) are the almost smallest NDI-based ladder-type molecules, but their-based vacuum-deposited BGTC OTFTs showed electron mobilities of up to 0.35 and 0.10 cm\(^2\) V\(^{-1}\)s\(^{-1}\) (measured in vacuum but with somewhat air stability), respectively, demonstrating their great potential in n-channel OTFTs. Ladder molecules 91\(^{131}\) and 92\(^{132}\), bearing larger \(\pi\)-systems than 89 and 90, were recently reported for n-channel BGTC OTFTs, and showed comparable electron mobility of about 0.05 cm\(^2\) V\(^{-1}\)s\(^{-1}\), 91-based devices exhibited excellent air and operating stability due to the low-lying LUMO energy
level of 91 (−4.2 eV). A series of tetraazabenzodifluoranthene diimide (BFI) derivatives 93–96 (LUMO levels: −3.6, −3.7, −3.5 and −4.3 eV, respectively) were developed by Jenekhe et al., which share a large rigid ladder-type π-backbone and were applied for solution-processed n-channel OTFTs. Bottom-gate devices based on 93–96 were measured in N2 atmosphere and showed electron mobilities of up to 0.03, 0.12, 0.05, and 0.021 cm2 V−1 s−1, respectively.

3.8 The construction of acceptor–acceptor (A–A) or acceptor–linker–acceptor (A–L–A) structures for high performance n-type OSCs

As discussed in section 3.4, the construction of donor–acceptor (D–A) structures could afford excellent n-type OSCs for OTFTs, while most n-type OSCs with D–A structures usually have low band gaps and high HOMO energies that make hole transport possible. To achieve pure electron-transporting OSCs, the construction of acceptor–acceptor (A–A) and acceptor–linker–acceptor (A–L–A) structures for n-type OSCs is highly desirable. Scheme 10 presents the representative n-type OSCs (97–110) for OTFTs with A–A or A–L–A structures, the linkers (L) are double bond (104), triple bond (105), benzene ring (51 and 106), or fused benzene ring (107–110). These linkers could be regarded as weaker donors relative to the common electron-donating thiophene and its derivatives. Polymer 97 (BBB) was the early A–A polymer used for n-channel OTFTs, its BGBC devices exhibited a very low electron mobility of about 10−6 cm2 V−1 s−1. Luscombe and co-workers prepared the NDI-based A–A polymers 98126 and 9982 that have the HOMO/LUMO energies of −3.54/−5.90 and −3.76/−6.50 eV, respectively. The deep HOMO energy levels of 98...
and 99 resist the hole transport and make their-based OTFTs pure n-channel transport. The BGTC OTFTs based on 98 and 99 measured in N₂ atmosphere showed low electron mobilities of about $4 \times 10^{-7}$ and $6 \times 10^{-4}$ cm² V⁻¹s⁻¹, respectively.²⁻¹²⁶ NDI A–A oligomers 100 and 101 with LUMO levels of about −3.8 eV and HOMO energies < −6.5 eV were synthesized by Marder and coworkers,¹³⁴ their-based solution-processed TGB OTFTs showed electron mobilities of up to 0.34 and 0.014 cm² V⁻¹s⁻¹, respectively. A–A polymers 102¹³⁵,¹³⁷ and 103²⁵ were prepared by Marks et al. and were applied for n-channel OTFTs. BGTC devices based on 102 showed molecular weight-dependent mobility, the high and low-molecular-weight 102 samples afforded the different $\mu_e$ values of about 0.038 and 0.011 cm² V⁻¹s⁻¹, respectively, and TGB OTFTs based on high-molecular-weight 102 exhibited electron mobility of up to 0.189 cm² V⁻¹s⁻¹.¹³⁶ In comparison with devices of 102, 103-based BGTC OTFTs showed a much lower $\mu_e$ value of about $0.5 \times 10^{-4}$ cm² V⁻¹s⁻¹ in N₂ atmosphere.²⁵

Recently, Pei and coworkers designed and synthesized an electron-deficient PPV-like polymer 104,¹³⁷ which possesses the A–L–A structure feature, with benzodifurandione-based oligo(p-phenylene vinylene) (BDOPV) as the acceptor (A) and double bond as the linker (L). TGB OTFTs based on 104 displayed high electron mobility of up to 1.1 cm² V⁻¹s⁻¹ under ambient conditions, the low-lying HOMO/LUMO energy levels of 104 (−6.12/−4.10 eV) contribute to its pure ambient-stable electron transport.¹³⁷ In comparison with the TGB devices, 104-based BGTC OTFTs exhibited 10-fold-lower electron mobility of about 0.1 cm²
V⁻¹s⁻¹ in air.¹³⁷ As a whole, this electron-deficient PPV derivative (104) showed comparable or even better device performance (in mobility) relative to the

![Chemical structures](image)

**Scheme 10.** n-Type OSCs with acceptor–acceptor or acceptor–linker–acceptor structures

well-studied n-channel polymer P(NDI2OD-T2) (46).⁷⁹,⁸⁰ A pyromellitic diimide–ethynylene-based A–L–A polymer 105 with HOMO/LUMO energies of about −6.41/−3.84 eV was recently reported by Katz *et al.*,¹³⁸ its TGBC OTFTs exhibited unipolar charge transport with electron mobility of about 2 × 10⁻⁴ cm² V⁻¹s⁻¹, making this class of simplest n-channel polymers great potential in organic electronics. Compound 106 containing A–L–A structure feature with benzene as the
linker, is a typical n-type OSC due to its low-lying HOMO/LUMO levels ($-6.98/-4.14$ eV). The 106-based SCFETs and vacuum-deposited OTFTs showed electron mobilities of up to 0.55 and 0.34 cm$^2$V$^{-1}$s$^{-1}$, respectively, demonstrating the excellent pure electron-transporting property. The fused bis-PDI derivatives 107 and 108, and the NDI/PDI mix-fused derivatives 109 and 110 were developed by Wang and coworkers, these compounds also have the A–L–A structure features where the linkers could be regarded as the fused benzene rings. Compound 107 with the n-C$_{12}$H$_{25}$ side chains has the low-lying HOMO/LUMO energy levels ($-6.04/-4.22$ eV), its single-crystal FETs showed high electron mobility of up to 4.65 cm$^2$V$^{-1}$s$^{-1}$ in air, which is much higher than the mobility of the corresponding solution-processed thin-film devices (about 0.14 cm$^2$V$^{-1}$s$^{-1}$ measured in air). Compound 108 shares the same π-backbone with 107 but has the different N-alkyl chains. The solution-processed BGTC OTFTs based on 108 that bears the n-C$_{18}$H$_{37}$ chains exhibited electron mobility as high as 0.7 cm$^2$V$^{-1}$s$^{-1}$ and a high current on/off ratio of $4 \times 10^7$ with excellent device ambient stability. The NDI/PDI mix-fused derivatives 109 and 110 have the enlarged π-systems and deep HOMO/LUMO energy levels of $-6.16/-4.26$ and $-6.08/-4.40$ eV, respectively, which makes 109 and 110 promising n-type OSCs for transistors. The solution-processed BGTC OTFTs based on 109 and 110 operated well in air with electron mobilities of up to 0.25 and 0.18 cm$^2$V$^{-1}$s$^{-1}$, respectively ($I_{on/off}: 10^5-10^7$).

3.9 Electron-deficient metal complexes for potential n-type OSCs

Electron-deficient metal complexes are a class of potential n-type OSCs for transistors...
(Scheme 11, 111–116), although they are less studied relative to the common small molecular and polymeric n-type OSCs discussed above. As mentioned in section 2, copper hexadecafluorophthalocyanine (F₁₆CuPc, 1) is an excellent n-type OSC for ambient-stable n-channel OTFTs.²⁸ Yan and coworkers reported two tin (IV)-Pc-based n-type OSCs SnCl₂Pc (111)¹⁴⁴ and SnOPc (112)¹⁴⁵ with the LUMO energy levels < −4.0 eV and applied them to vacuum-deposited n-channel OTFTs. The BGTC devices based on 111 and 112, with the modified substrates by a thin film of para-sexiphenyl (< 10 nm), showed electron mobilities of up to 0.44 and 0.3 cm² V⁻¹ s⁻¹, respectively, with good device air stability.¹⁴⁴,¹⁴⁵

Scheme 11. Electron-deficient metal complexes for n-type OSCs

In 1993, a nickel-(dimt)₂ complex 113 was applied to n-channel OTFTs by using Langmuir-Blodgett technique, affording an electron mobility as high as 0.2 cm² V⁻¹ s⁻¹.¹⁴⁶ Later on, some nickel bis(dithiolene) complexes such as 114–116 were developed for n-type OSCs used in transistors.¹⁴⁷–¹⁴⁹ Mori and coworkers synthesized a number of tetraphenyl nickel bis(dithiolene) complexes (such as 114) and applied...
them to n-channel OTFTs, some of which could performed in air as n-channel transistors but the $\mu_e$ (about $10^{-6}$–$10^{-5}$ cm$^2$ V$^{-1}$ s$^{-1}$) and $I_{on/off}$ ($\leq 10^2$) values were very low.$^{147}$ In comparison with 114, a simpler complex 115 was developed by Qin and coworkers, 115-based vacuum-deposited BGTC OTFTs showed an electron mobility of 0.11 cm$^2$ V$^{-1}$s$^{-1}$ and $I_{on/off}$ of $2 \times 10^6$, with good device air stability.$^{148}$ The solution-processed BGTC OTFTs based on a tetraphenyl nickel bis(dithiolene) complex 116 were studied by Cho et al.$^{149}$ affording an electron mobility of $1.3 \times 10^{-3}$ cm$^2$ V$^{-1}$s$^{-1}$ with $V_T$ and $I_{on/off}$ values of 4.6 V and $10^5$, respectively. Neutral complexes 114–116 have the low-lying LUMO energy levels of about $-4.1 \sim -4.6$ eV due to the electron-deficient tetravalent Ni ion, which contributes to the device air stability.$^{147,148}$ Phthalocyanine metal complexes and the metal dithiolene complexes have been well studied for organic conductors,$^{150-152}$ their uses for OSCs especially for n-type ones should draw more attention.

3.10 Other molecular design for n-type OSCs

Besides the strategies mentioned above, there are some molecular systems designed for n-type OSCs. As shown in Scheme 12, the electron-deficient pentacene-like small molecules$^{153-156}$ and the side-chain polymers with pendant PDI units$^{158,159}$ are two classes of n-type OSCs for OTFTs. A series of $\pi$-deficient pentacenequinones were developed by Miao and coworkers.$^{153}$ It was found that replacing H atoms of pentacenequinone with F atoms or replacing C atoms with N atoms (117) could lower the LUMO energy level of pentacenequinone to yield n-type OSCs with electron mobilities higher than 0.1 cm$^2$ V$^{-1}$s$^{-1}$ (measured in vacuum). Vacuum-deposited
OTFTs based on silylthynylated N-heteropentacene \textbf{118} showed $\mu_e$ values in the
\begin{align*}
\begin{array}{c}
\text{117} \\
\text{118} \\
\text{119} \\
\text{120} \\
\text{121} \\
\text{122}
\end{array}
\end{align*}

\textbf{Scheme 12.} Electron-deficient pentacene-like derivatives and side-chain polymers with pendant PDI units for n-type OSCs

range of 1.0–3.3 cm$^2$ V$^{-1}$s$^{-1}$ (in vacuum), when the devices were tested in air, the $\mu_e$ values decreased to 0.3–0.5 cm$^2$ V$^{-1}$s$^{-1}$.$^{154}$ High-surface-energy self-assembled monolayers (SAMs) of phosphonic acids with oxygen-containing long alkyl chains have been applied for solution-processed n-channel OTFTs of \textbf{118} by Miao \textit{et al.}, leading to a high electron mobility of up to 2.5 cm$^2$ V$^{-1}$s$^{-1}$ and an on/off ratio of 6×10$^5$ when tested in vacuum.$^{155}$ It is worth noting that single-crystal FETs based on 5,7,12,14-tetrachloro-6,13-diazapentacene (\textbf{119}) exhibited a very high electron mobility of 3.39 cm$^2$ V$^{-1}$s$^{-1}$ when measured in ambient, although the LUMO energy of \textbf{119} is relative high ($\sim$3.79 eV).$^{156}$ Overall, n-channel OTFTs based on electron-deficient pentacene-like derivatives exhibited unsatisfied device air stability.
due to the relative higher LUMO energy levels (≥ −4.0 eV), more electron-deficient pentacene-based n-type OSCs would be the next focus. As shown in Scheme 12, side-chain polymers with pendant PDI units (120–122) were designed for n-channel OTFTs by Thelakkat, Marder and their respective coworkers,157–159 with electron mobility of up to $1.2 \times 10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$ (measured in inert gas).158 The side-chain polymers with pendant π-deficient building blocks (such as PDI, NDI or core-modified PDI/NDI) would attract more attention for their uses in n-channel OTFTs and OPVs (as organic acceptors).

4. Synthesis of n-type OSCs

Synthesis is crucial for developing n-type OSCs and directly determines the cost of the materials. Herein, we choose to highlight some important synthetic strategies for n-type OSCs mentioned above. Aromatic diimides with fluororcarbon-based $N$-groups (2, 6–15, and 33–41) are a class of important n-type OSCs for OTFTs and could be prepared by the imidization reactions from commercially available or core-modified bisanhydrides and fluororcarbon-based primary amines. These imidization reactions are typically carried out at elevated temperature in high boiling solvents such as propionic acid, DMF, NMP, quinoline or imidazole, the catalysts (such as zinc acetate dehydrate and acetic acid) are usually used for amines with steric hindrance and electron deficient.24,29,49,160 Compounds 5, 6, 20–25 and 32 are air-operable n-channel materials due to the core-attached cyano groups that deep the LUMO energy to a suitable level. The core-cyanations were achieved by the Pd-catalyzed reaction of the dibromo precursor of 5, 6, 23 or 24 with Zn(CN)$_2$ or CuCN in the hot dioxane
solution (Pd$_2$(dba)$_3$:dpff as the catalyst),$^{36,60,61,161}$ or by the uncatalyzed reaction of the dibromo precursor of 20–22, 25, 32 or 96 with CuCN in the refluxing DMF solvent.$^{24,57,62,68,133}$ It should be noting that Diels-Alder reactions are usually used for synthesizing the five-membered-ring acene diimides, such as 22–24 and 32.$^{60,61,68}$ Compounds 33–36 were obtained by the Halex reactions of the corresponding dibromo or tetrachloro PDIs with potassium fluoride in sulfolane and in the presence of 18-crown-6 or $N,N'$-dimethylimidazolidino-tetramethylguanidinium (CNC') fluoride as catalyst.$^{49}$ Octachloro PDI 27 and tetrachloro NDIs 40 and 41 were synthesized by the electrophilic reactions of the corresponding core-unsubstituted PDI and NDIs with chlorine in chlorosulfonic acid at 80–85 °C (iodine as catalyst).$^{63,71}$ Perfluoroalkylation via copper coupling reactions of dibromo PDIs with perfluoroalkyl iodides in DMSO gave excellent yields of core-perfluoroalkylated PDIs 28 and 37.$^{64}$

The aryl-aryl coupling reactions are widely used for synthesizing OSCs, of which the Stille coupling reaction is the most usual method for synthesizing π-functional materials.$^{162}$ D–A polymers 42, 46–50, 53–55, 57 and A–L–A polymers 104 and 105 were all prepared by the Stille coupling reactions, where the Pd-catalysts are usually Pd(PPh$_3$)$_4$ (sometimes with CuI),$^{75,138}$ Pd(PPh$_3$)$_2$Cl$_2$, $^{79,80}$ or Pd$_2$(dba)$_3$ with P(o-tolyl)$_3$ ligand (commonly used),$^{81–89}$ the solvents are anhydrous toluene (commonly used), chlorobenzene, THF, DMF or the mixed solvents, and the reaction temperatures are usually among 80–130 °C depended on the reaction solvents. In addition, the Stille coupling reactions were applied for the syntheses of 17, 29, 30, 58, 61–64, 87, 94, 95.
The Suzuki-Miyaura coupling reactions were used for synthesizing 31, 44, 51, 52 and 56, the Pd(PPh₃)₄ was commonly used as catalyst with K₂CO₃ or other basic salt in toluene, of which Pd₂(dba)₃, P(o-tolyl)₃ ligand, K₃PO₄ and toluene (as solvent) were applied for synthesizing copolymer 56. Copolymers 43 and 45 containing triple bonds were prepared by the Sonogashira coupling reactions with CuI, Et₃N, and Pd-catalyst Pd(PPh₃)₄ or Pd(PPh₃)₂Cl₂ in toluene or THF solvent. In addition, the Sonogashira coupling reaction was also used for synthesizing compound 60. Yamamoto polycondensations were successfully utilized for preparing A–A polymers 99, 102 and 103, with Ni(COD)₂ (catalyst), COD and 2,2′-bipyridyl (ligands) in toluene, DMF or their mixed solvent. The fused bis-PDIs 107 and 108 were synthesized by the home-coupling reactions of tetrachloro PDIs with CuI as the catalyst, L-proline as the ligand, and K₂CO₃ as the base in DMSO, which involves the traditional Ullmann coupling reaction and C–H transformation with relative lower yields (< 20%). The NDI-PDI hybrid rylene arrays 109 and 110 were prepared by the cross-coupling reactions between tetrachloro PDI and monostannyl NDIs, the synthesis undergoes the Stille coupling reaction and C–H transformation using Pd(PPh₃)₄ and CuI as catalysts in toluene, giving the moderate yields of 20–46%. The nucleophilic aromatic substitution (SNAr) reactions were successfully used for preparing c-eNDIs 59 and 65–76, the SNAr reactions are very simple with 2,3,6,7-tetra bromonaphthalene diimides (TBNDIs) and dithiolate salts reacting in polar solvents such as THF and DMF. Gao and coworkers developed the synthetic
methods for TBNIDs by using a dehydrohalogenation-based imidization reaction.\textsuperscript{106,163} Now, TBNDIs have become the key precursors for preparing c-eNDIs.\textsuperscript{93,97,98,100,111,112,164–167} It should be noting that NDI-DTYM2 derivatives\textsuperscript{65–69} could be achieved by a mild one-pot synthesis from 2,3,6,7-tetrabromonaphthalene dianhydride, sodium 1,1-dicyanoethylene-2,2-dithiolate, and primary amines in DMF, this one-pot synthesis undergoes a S$_2$AR reaction and then an imidization reaction, allowing an easy and low-cost access to diverse n-type OSCs.\textsuperscript{99}

The quinoidal thiophene derivatives\textsuperscript{77–85} were usually prepared by a Pd-catalyzed (such as Pd(PPh$_3$)$_4$) Takahashi coupling reaction from the corresponding dibromo precursor and the cyano-methylene derivative, with the base (e.g. NaH) in organic solvents (e.g. THF and DME), followed by an oxidation reaction with Br$_2$, air or other oxidants.\textsuperscript{117–123} The condensation reactions were utilized in the syntheses of n-type OSCs\textsuperscript{86–93, 97, 98 and 106}, of which the condensations of ortho-arylenediamine and dianhydride, anhydride, tetracarboxylicacid, dicarboxylicacid or 1,2-diketone usually performed in the heated organic solvents such as acetic acid, trifluoroacetic acid, polyphosphoric acid, ethanol, n-BuOH, imidazole, or HMPA.\textsuperscript{129–133,168,169}

5. Relationship between the thin-film structure and the device performance

For OTFTs, the study on the relationship between the thin film structure and the device performance is very important and also quite challenging. Since this topic is beyond the scope of this review, we only choose to highlight some key points for the
relationship of the thin film structure and the device performance of n-type OSCs: (i) The molecular packing (the microstructure of thin film) and the thin film morphology play an important role in the air stability of n-channel OTFTs, and the dense molecular packing, good thin-film morphology with high crystallinity, large grain sizes, and low density of grain boundaries are positive kinetic factors for realizing ambient-stable n-channel OTFTs even the energetic factors of n-type are negative due to the high LUMO energies (> −4.0 eV).29-33 (ii) There would be interplay between energetic and kinetic factors on the ambient stability of n-channel OTFTs, as revealed by Bao and coworkers for the active layer thickness-dependent device stability.33 (iii) The combination of energetic factors (e.g. LUMO < −4.0 eV for n-type OSCs) and kinetic elements (e.g. dense molecular packing in solid state and good thin-film morphology) could realize long-term air stability for n-channel OTFTs.36,125 (iv) The crystallinity and crystallite-growth direction of active thin film significantly affect the electron mobility and other device characteristics of n-channel OTFTs, the highly crystallized thin film with large domains, ordered grain orientation, and the dense molecular packing are highly desired for achieving high electron mobility.22,37,38,102

6. Conclusion and outlook

In the last decade, the development of n-type OSCs for OTFTs has witnessed great progress, hundreds of n-type small molecular and polymeric materials were designed and synthesized, some of which exhibited electron mobility comparable to or even higher than the mobility of amorphous silicon (0.5 ~ 1.0 cm² V⁻¹ s⁻¹). Molecular design is the basic motive for developing n-type OSCs. We summarized more than
nine molecular design strategies and used the representative n-type OSCs to demonstrate each one. These molecular design strategies are generally effective for obtaining high-performance ambient-stable n-type OSCs for OTFTs, where the energetic and kinetic factors were considered for realizing the ambient-stable electron injection and transport. We envision that some new molecular design strategies would emerge in the future, but these strategies will continue to promote the development of n-type OSCs in the field of OTFTs.

There are still some problems and challenges for the development of n-type OSCs for OTFTs, and special attention should be paid to these issues. (i) What govern the air/operating stability of n-channel OTFTs? The energetic/kinetic factors and their combination are still not enough to solve this problem. (ii) The pursuit of low-lying LUMO energy levels of n-type OSCs (such as $<-4.0$ eV) is not the only task for realizing ambient-stable n-channel OTFTs, since the HOMO energies should also be controlled (such as $<-6.0$ eV), otherwise the hole transport would appear, which goes against the pure n-channel charge transport. (iii) The device performance of current n-type OSCs is still lower than that of their p-type counterparts with unsatisfied device air/operating stability, especially for the pure electron-transport polymeric OSCs, where the performance was relied on the sandwiched TGBC device structure and/or the inert-atmosphere or vacuum testing conditions; the main indexes for next generation n-type OSCs for OTFTs would be $\mu_e \geq 5 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$, $I_{on/off} \geq 10^6$ and $\left| V_T \right| \leq 10 \text{ V}$ with easy processing property and excellent air/operating device stability. The following three points are important for both n-type OSCs and p-type ones: (iv) Most
solution-processed high-performance OTFTs depend on the utilization of chloro-carbon solvents such as chloroform, chlorobenzene and dichlorobenzene, while these chlorinated solvents are harmful to humans and the environment, the green non-chlorinated solvents are highly desirable for the real use of OSCs in printing electronics. (v) Solution-processable OSCs towards printing electronics do not always mean “the real low cost”, the synthetic cost of the material itself should also be considered, facile and low-cost synthesis of OSCs with simple purification is also a significant topic in organic electronics. (vi) The integrated circuit technology using both n- and p-type OSCs is the most challenging topic, which is badly in need of the development of matching dielectric/electrode/substrate/interface-modification materials and techniques with current OSCs.

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TOC

More than nine molecular design strategies with > 120 representative n-type organic semiconductors were summarized and analyzed.