Recent interest in flexible electronics has led to a paradigm shift in consumer electronics, and the emergent development of stretchable and wearable electronics is opening a new spectrum of ubiquitous applications for electronics. Organic electronic materials, such as π-conjugated small molecules and polymers, are highly suitable for use in low-cost wearable electronic devices, and their charge-carrier mobilities have now exceeded that of amorphous silicon. However, their commercialization is minimal, mainly because of weaknesses in terms of operational stability, long-term stability under ambient conditions, and chemical stability related to fabrication processes. Recently, however, many attempts have been made to overcome such instabilities of organic electronic materials. Here, an overview is provided of the strategies developed for environmentally robust organic electronics to overcome the detrimental effects of various critical factors such as oxygen, water, chemicals, heat, and light. Additionally, molecular design approaches to π-conjugated small molecules and polymers that are highly stable under ambient and harsh conditions are explored; such materials will circumvent the need for encapsulation and provide a greater degree of freedom using simple solution-based device-fabrication techniques. Applications that are made possible through these strategies are highlighted.

1. Introduction

Wearable electronics are regarded as one of the key technologies for the Internet of Things era. For instance, wearable sensors are expected to enable people to constantly monitor their health, exercise, and environment in their daily lives. However, wearable devices cannot easily be fabricated using conventional inorganic materials because of their mechanical fragility and relatively high cost. In this regard, organic electronic materials, including π-conjugated small molecules and polymers, have received considerable attention because of their various advantages, which include good mechanical flexibility, low-cost solution processability, and property tunability through molecular design, which make them highly suitable for use in wearable devices.[1–3]

First-generation π-conjugated organic materials have been used for many purposes, such as in corrosion protection,[4] organic dielectric layers,[5] electromagnetic interference shielding,[6] antistatic coatings,[7] and electronic window shades.[8] Those changes the amount of light transmitted.[9] The applications of second-generation π-conjugated organic materials have included organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs), and lasers with further applications, such as in integrated circuits, flat-panel screens, and light-harvesting devices.[9]

To demonstrate the technological advances and competitiveness of organic electronic materials in the current market compared with those of inorganic-based devices, organic electronic materials such as semiconductors, dielectrics, and conductors would have to be assembled into complete commercial products. However, critical issues remain to be resolved with regard to meeting all of the requirements of environmental long-term stability and operational stability. Particularly, unprotected organic electronic devices suffer from degradation because they are typically susceptible to the environmental factors present under ambient conditions. Thus, encapsulation is a necessary technique used to maintain the electrical functionality of these devices and to protect them from harsh environments.[10,11]

Organic electronic devices are unstable to a certain degree, and their characteristics tend to degrade gradually, unlike inorganic-based electronic devices.[12] Most inorganic semiconductors are intrinsically stable and not sensitive to external environmental factors such as oxygen and light. Potential locations for degradation in organic electronic devices are the π-conjugated active layers, the electrodes, and their interfaces. In addition, the degradation of organic electronics is highly complicated and related to multiple mechanisms. The lifetime of a device fabricated using organic electronic materials is still substantially shorter than that of the one fabricated using inorganic electronic materials. For example, silicon-based photovoltaic devices can last more than 25 years under outdoor conditions. By contrast, without an encapsulation layer, many organic photovoltaic (OPV) devices significantly lose their initial performance within 10 h. The development of OPV devices with long lifetimes is still in its infancy.
Conventionally, barrier films are applied to most organic electronics to impede degradation due to external environmental factors. Most barrier films for organic electronics are considered in terms of the oxygen transmission rate and water-vapor transmission rate.\[13\] Several barrier architectures for printed electronics have been investigated, including (i) depositing the barrier onto a flexible lid and sealing the device, and (ii) directly depositing the barrier film onto the device. Recently, metal-oxide films such as Al\textsubscript{2}O\textsubscript{3},\[14,15\] titanium dioxide (TiO\textsubscript{2}),\[16\] and zirconium oxide (ZrO\textsubscript{2})\[17\] fabricated using atomic layer deposition (ALD) have gained attention as effective water-vapor barriers because they form dense and conformal coatings. These ALD barrier films, usually a few nanometers thick, have been grown in various combinations: as monolithic barrier layers in combination with other inorganic films (such as silicon nitride (SiN\textsubscript{x})) grown by plasma-enhanced chemical vapor deposition (CVD),\[18\] as nanolaminates with other ALD metal oxides, and as polymer layers to create tortuous pathways to extend the lag time of the water-vapor permeation.\[19\] In these studies, the performance of the various barrier films was studied using techniques such as the direct encapsulation of an OLED and visual inspection through measuring the number of dark spots formed over a period of time.\[20\]

Generally, environmental factors, such as oxygen, water, chemicals, heat, and light, that may trigger accelerated degradation pathways represent extrinsic degradation sources. If these external factors are regulated rationally, device lifetimes might be greatly increased. The most common approach used thus far has been the encapsulation or lamination of devices to protect them from oxygen,\[21\] water,\[22\] chemical species,\[13,23\] heat\[24\] and light\[25,26\] in the surrounding environment. For example, the use of ultraviolet (UV) filters substantially reduces the photodegradation of organic electronic materials.\[27,28\] However, the introduction of an encapsulation or lamination process increases fabrication costs and reduces the degree of freedom in the fabrication process.\[23,29\] More importantly, this type of encapsulant is neither flexible nor stretchable (except polymer barriers, which exhibit poor performance). Thus, encapsulation techniques are not yet fully applicable to organic flexible and stretchable electronic devices.\[10\] Thus, a need exists to develop intrinsically stable organic electronic materials with excellent flexibility and stretchability. In addition, understanding the degradation mechanisms of organic electronic materials is very important to realize the commercialization of organic electronic devices.

Here, we report an overview of the approaches to environmentally robust organic electronics that can overcome the detrimental effects of five representative environmental factors, i.e., oxygen, water, chemicals, heat, and light, as schematically shown in Figure 1. We also introduce applications that have been made possible through these strategies, i.e., water-stable chem/biosensors, liquid-type chemical sensors, and photolithographic patterning. The stability and degradation of OPVs\[31–39\] and OLEDs\[35,40,41\] have been discussed extensively in previous publications. Here, we extend the range of organic electronic devices to OFETs and OFET-based chem/biosensors, focusing on their stability and degradation mechanisms. A brief list of keywords, which are related to the approaches used to achieve organic electronic devices robust against each environmental factor, obtained from a literature survey is shown in Figure 1, organized according
to each factor. These factors, classified as chemical and morphological degradations, cause the organic electronic materials to undergo a chemical reaction and/or change their morphology, respectively. Generally, light, heat, and chemical species can give rise to the diffusion of degradation factors into interlayers and electrodes, morphological changes of the organic electronic materials, and unwanted interactions between the metal electrode and the organic material.

In Section 2, we discuss recent studies on specific environmental factors that are detrimental to each type of organic electronic device. First, in Section 2.1, a literature survey of ambient oxygen as a degradation factor is presented. Because numerous studies regarding ambient oxygen as a degradation factor in organic semiconductors have been reported, we subdivide this section into four parts based on molecular bulkiness and charge transport types: Section 2.1.1 on p-type small molecules, Section 2.1.2 on p-type polymers, Section 2.1.3 on n-type small molecules, and Section 2.1.4 on n-type or ambipolar polymers. In Section 2.2, organic electronic materials that are intrinsically stable under harsh aqueous conditions are discussed. The molecular strategies behind their stability under high humidity and even marine conditions are introduced. In Section 2.3, we focus on the chemical interference aspect of device fabrication using inexpensive solution-based processes. Organic electronic materials that are chemically stable are organized on the basis of the target application, such as OLEDs, OPVs, OFETs, and OFET-based chem/biosensors. Section 2.4 is dedicated to a survey of thermally stable organic electronic materials. Their heat-resistant molecular structures and the corresponding energy-level issues are discussed. In Section 2.5, the fundamentals of the photo-oxidation of both small-molecule and polymer semiconductor organic electronic materials are discussed. Section 3 presents an overview of the applications of environmentally stable organic electronic materials in advanced architectures or systems to summarize progress in this field. Water-stable organic chem/biosensors, liquid-type chemical sensors with enhanced repeatability, and the fine patterning of organic electronic materials with conventional photolithography techniques are discussed in Section 3.1–3.3, respectively. In Table 1, as a quick overview, we tabulate various environmental factors that degrade organic electronic materials and representative approaches to robustness against the environmental factors.

Here, we aim to set out the current understanding of the degradation pathways that affect most organic electronics, including OPVs, OLEDs, OFETs, and OFET-based chem/biosensors, on the basis of recent studies. We then present an overview of the approaches toward achieving environmentally robust organic electronics to overcome the detrimental effects of the degradation factors; we also briefly introduce potential applications.
Table 1. Representative examples of highly stable organic electronic devices (mainly, OFETs) with regard to various environmental factors and their applications.

<table>
<thead>
<tr>
<th>Factor</th>
<th>Approach to robustness</th>
<th>Molecular name as active materials (type)</th>
<th>Performance</th>
<th>Application</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen</td>
<td>Amorphous fluoropolymer dielectric</td>
<td>Pentacene (p-type)</td>
<td>( \Delta V_{th} &lt; 1.1 \text{ V at } V_{g} = -20 \text{ V} ) for 10 000 s</td>
<td>–</td>
<td>[53]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pentacene (p-type)</td>
<td>Gain~250 maintained after 6 months</td>
<td>Complementary inverter</td>
<td>[54]</td>
</tr>
<tr>
<td>Lowering HOMO level</td>
<td>PQT (p-type)</td>
<td>Similar mobility, no hysteresis after 1 month</td>
<td>–</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>IIDDT, IIDT (p-type)</td>
<td>Stable with 4 month exposure</td>
<td>–</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>TPD polymers (p-type)</td>
<td>( \Delta \mu_{th}/\mu_{th} &lt; 2% after 2 month storage and 1000 times of on/off cycles )</td>
<td>–</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Detaching solubilizing</td>
<td>PTA (p-type)</td>
<td>Similar mobility (( \sim 4.2 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} )), maintaining ( l_{n}/l_{n_{th}} ) of both ( &gt;10^4 )</td>
<td>–</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Siloxane side chain</td>
<td>PI2T-Si (p-type)</td>
<td>( \Delta \mu_{th} &lt; 1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} ) for 30 d (RH = 40-45%)</td>
<td>–</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lowering LUMO level</td>
<td>PDI-CN_2, PDI-FCN_2 (n-type)</td>
<td>Negligible difference of ( \mu_{th} ) measured in vacuum and air</td>
<td>–</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>PDI-F/\text{FBr}_2/\text{FCN}_2 (n-type)</td>
<td>( \mu_{max} = 1.26 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} ) (measured in N_2)</td>
<td>–</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Core-chlorinated NDIs with fluoroalkyl substituents (n-type)</td>
<td>( \mu_{max} = 1.43 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} ) (measured in air)</td>
<td>–</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Device encapsulation</td>
<td>PNBO (n-type)</td>
<td>Maintain mobility after 70 d in ambient condition</td>
<td>–</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Energy level tuning</td>
<td>PNDI-mT(BZ)mT (ambipolar)</td>
<td>Maintain mobility after 3 months in ambient condition</td>
<td>–</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td>Long alkyl side chain with close packing</td>
<td>DDDFTTF (p-type)</td>
<td>( \Delta \mu_{th} &lt; 0.01 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} ), ( \Delta l_{n}/l_{n_{th}} = 3, \text{ constant } V_{th} ) after 10^4 cycles under DI water</td>
<td>Chemical sensors detecting trinitrobenzene, glucose, cysteine, methylphosphonic acid, pH solution</td>
<td>[65]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( \Delta \mu_{th} &lt; 0.03 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} ) during exposure to DI water</td>
<td>Chemical sensors detecting trinitrotoluene, cysteine</td>
<td></td>
<td>[66]</td>
</tr>
<tr>
<td></td>
<td>Siloxane side chain</td>
<td>PI2T-Si (p-type)</td>
<td>( \Delta V_{th} = 20 \text{ mV d}^{-1} ) in DI water</td>
<td>Sensors for selective detection of Hg(^{2+}) in seawater</td>
<td>[47]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( \Delta V_{th} = 15 \text{ mV d}^{-1} ) in seawater</td>
<td>Sensors for selective detection of Hg(^{2+}) in seawater</td>
<td></td>
<td>[49]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PDDTTT-SiCl_2 (p-type)</td>
<td>( \mu_{th}/\mu_{th} = 0.79 ) after 12 h in saturated humidity atmosphere</td>
<td>Potential of chemical sensor application</td>
<td></td>
</tr>
<tr>
<td>Chlorine substitution</td>
<td>P(NDI2HD-T2Cl_2) (p-type)</td>
<td>( \Delta \mu_{th} &lt; 0.01 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} ), ( \Delta V_{th} &lt; 21 \text{ V} ), maintain ( l_{n}/l_{n_{th}} ) after 3 weeks exposure to DI water</td>
<td>–</td>
<td></td>
<td>[67]</td>
</tr>
<tr>
<td>Hydrophobic</td>
<td>PDPPPDBTE</td>
<td>( \Delta \text{Efficiency} = 0.8% over 1000 h under humid condition )</td>
<td>Perovskite solar cells</td>
<td></td>
<td>[68]</td>
</tr>
<tr>
<td>Passivation layer</td>
<td>CuPc</td>
<td>( \Delta \mu_{th} &lt; 0.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} ) for 30 min in aqueous media</td>
<td>Label-free chemical sensors detecting biotin, pH, sodium dodecyl sulfate</td>
<td></td>
<td>[69]</td>
</tr>
<tr>
<td>Chemicals</td>
<td>Chemical crosslinking</td>
<td>Sensor with crosslinked films: ( \Delta \text{signal intensity} = 36.2 % ) (methanol), ( = 35.8 % ) (toluene)</td>
<td>Chemical sensors detecting liquid-phase methanol, ethanol, DI water, toluene, n-hexane, pH solutions (pH 3–9)</td>
<td></td>
<td>[48]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>With non-crosslinked films: ( \Delta \text{signal intensity} = 85.0 % ) (methanol)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>X-PTPA-5 (hole-transporting materials for OLED)</td>
<td>EQE = 11.8%, power efficiency = 10.4 \text{ lm W}^{-1}, luminous efficiency = 43.7 \text{ cd A}^{-1} ) (without X-PTPA-5: 6.2%, 5.2 \text{ lm W}^{-1}, and 22.3 \text{ cd A}^{-1}, respectively)</td>
<td>Patterning micrometer-sized pixel OLED arrays by photolithography</td>
<td></td>
<td>[52]</td>
</tr>
</tbody>
</table>
Table 1. Continued.

<table>
<thead>
<tr>
<th>Factor</th>
<th>Approach to robustness</th>
<th>Molecular name as active materials (type)</th>
<th>Performance</th>
<th>Application</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Siloxane side chain</td>
<td>Introducing a hindered phenol-type radical scavenger</td>
<td>PTDPPSe-SiC4 (p-type)</td>
<td>$\mu_{\text{avg}}$: 1.4, 1.08, 1.02, 0.61, 0.7 $\mu_{\text{avg}}$: 0.113, 0.11, 0.069, 0.079, 0.075 (cm$^2$/V s$^{-1}$), as-fabricated, after soaking in DI water, ethanol, acetone, and chlorobenzene for 24 h</td>
<td>Chemical sensors detecting vaporized acetone</td>
<td>[50]</td>
</tr>
<tr>
<td>Heat</td>
<td>Dense packing structure</td>
<td>DBTTT</td>
<td>$\mu_i$ and $V_{th}$ maintained after 140 °C heating</td>
<td>–</td>
<td>[70]</td>
</tr>
<tr>
<td></td>
<td>Energy level tuning</td>
<td>PCDTBT</td>
<td>$\mu_i$ maintained after 150 °C heating</td>
<td>–</td>
<td>[71]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Dph-BBTNDT</td>
<td>$V_{th}$, $I_{on}/I_{off}$ maintained after 300 °C heating</td>
<td>–</td>
<td>[72]</td>
</tr>
<tr>
<td></td>
<td>Device encapsulation</td>
<td>DNTT encapsulated with parylene</td>
<td>$\Delta \mu_i \leq 25%$ after 200 °C heating</td>
<td>–</td>
<td>[73]</td>
</tr>
<tr>
<td>Light</td>
<td>Cyanation of molecules</td>
<td>PDIF-CN$_2$ (n-type)</td>
<td>No changes under bright illumination and O$_2$ atmosphere for 10 min</td>
<td>–</td>
<td>[75]</td>
</tr>
<tr>
<td></td>
<td>Introducing metal NPs</td>
<td>P3HT:PCBM (Bulk heterojunction)</td>
<td>–</td>
<td>–</td>
<td>[76–81]</td>
</tr>
<tr>
<td></td>
<td>Introducing a hindered phenol-type radical scavenger</td>
<td>PPV-type polymers</td>
<td>Radical transfer reaction from the polymer backbone to the added compound</td>
<td>–</td>
<td>[82]</td>
</tr>
</tbody>
</table>

2. Approaches to Overcome the Instability Caused by Degradation Factors

2.1. Approaches to Oxygen Robustness

2.1.1. p-Type Small-Molecule Semiconductors

The stability of p-type organic semiconductors under oxygen-abundant conditions is a primary consideration for robust organic electronics. For example, oxygen greatly influences the device lifetime and the on/off currents in OFETs because of the introduction of bulk charge carriers through oxygen doping resulting in an increase in the conductivity of organic semiconductors when the gate voltage is off. The thermodynamic stability of p-type organic semiconductors is mostly dependent on the energetically high-lying highest occupied molecular orbital (HOMO) level of π-conjugated small molecules or polymers. A redox electrochemical reaction with oxygen from the surrounding environment induces the loss of electrons from the HOMO, provided that the HOMO energy level is above $-4.97$ eV ($+0.57$ V vs SCE, where SCE stands for saturated calomel electrode). Thus, the rational molecular designs of small molecules or polymers for p-type charge transport are required to lower the HOMO energy level to below $-4.97$ eV.\[88\]

Azenos, polycyclic aromatic hydrocarbons (PAHs) with linearly fused benzene rings, such as naphthalene, anthracene, and tetracene, are regarded as promising electronic materials because of their excellent hole-transporting characteristics. The reactivity of azenes has been studied intensively.\[84\] The reactivity of bulky azenes under ambient conditions (oxygen in air) is a topic of great interest in various research fields, including materials science, chemistry, and biology (all PAHs are carcinogenic). Pentacene has drawn substantial attention because of its high charge-carrier mobility among the azenes. One of the limitations to the practical application of pentacene in OFETs is its instability under ambient conditions.\[85\] Generally, as the conjugation length of an acene increases, the acene becomes more reactive. Additionally, the central ring of an acene is typically the most reactive location, and a biradical mechanism has been found to occur at this position in the reaction with oxygen molecules.\[84\]

The effects of oxygen on the device operation of pentacene thin-film transistors were investigated using in situ electrical measurements to check the stability under oxygen-abundant conditions.\[86,87\] When a pentacene film was exposed to oxygen in the air, a huge shift toward positive gate voltages in the subthreshold voltage was observed in the transfer curve. Consequently, the subthreshold slope for 50 nm thick dielectrics increased from 0.2 to $>0.5$ V decade$^{-1}$. Additionally, the degradation mechanism might be dominated by polar water molecules.\[88,89\] Specifically, the water molecules might diffuse into the pentacene active layer and generate several traps in the grain boundaries, leading to performance degradation.

The air stability of acene-based OFETs can be enhanced through the use of hydroxyl-free and amorphous fluoropolymers as gate dielectrics.\[51,90,54\] Tokiyoshi et al.\[53\] used cyclized transparent optical polymer (CYTOP) (commercially available amorphous fluoropolymer from Asahi Glass Co.) thin films from as gate dielectric layers in pentacene OFETs. The leakage current densities of the CYTOP thin films were less than $10^{-8}$ A cm$^{-2}$, and the electric fields for breakdown were greater than $5$ MV cm$^{-1}$ (Figure 2a). The CYTOP dielectric layers are hydrophobic because of the fluorinated functional groups and hydroxyl-free characteristics; thus, crosslinks in its chemical structure are not required. The small hysteresis (Figure 2b,c) and the small threshold voltage ($V_{th}$) shifts obtained in the
OFETs are attributable to these advantages under ambient conditions.

Intrinsically air-stable p-type organic semiconductors can be summarized as 2,6-bis[2-(4-pentylphenyl)vinyl]anthracene (DPPVAnt),[91] 2,7-diphenyl[1]benzothieno[3,2-b][1]benzothiophene (DPh-BTBT),[92] 2,6-diphenylbenzo[1,2-b:4,5-b']dichalcogenophenones (DPh-BDS with a fused selenophene and DPh-BDTe with a fused tellurophene),[93] dinaphtho[2,3-b:2',3'-f]thieno[3,2-b]thiophene (DNTT),[94–96] and dinaphtho[2,3-b:2',3'-f]selenopheno[3,2-b]selenophene (DNSS).[97] These intrinsically air-stable p-type organic semiconductors possess densely packed crystal structures along with a well-ordered thin-film morphology and relatively low HOMO levels and large HOMO–LUMO energy gaps to prevent oxidation reactions under ambient conditions (Figure 3).

2.1.2. p-Type Polymer Semiconductors

After exposure to ambient conditions containing a large amount of oxygen and a small amount of water vapor, organic electronic devices tend to exhibit degraded performance, including $V_{th}$ shifts, increases in the subthreshold slope, reductions in mobility, and increases in off current and hysteresis.[98] In recent years, to prevent such adverse effects of air exposure, researchers have devoted extensive effort to the development of semiconducting polymers that assure a sufficiently high hole mobility with acceptable ambient stability. Ong et al. introduced a new method to obtain highly stable polymer semiconductors that intrinsically overcome oxidative doping by increasing the ionization potential or lowering the HOMO level.[99] They newly synthesized solution-processable regioregular polythiophenes, poly(3,3”-dialkyl-quaterthiophene) (PQT), and showed that controlled $\pi$-conjugation length enhanced the air stability of p-type polymer semiconductors, inhibiting delocalization by sterically reducing $\pi$-overlap or breaking the extension of conjugated pathways.[99] Lei et al. reported two isoindigo-based polymers with bithiophene (IIDDT) and thiophene (IIDT), which were used as active layers for highly stable OFET devices with good electrical performance under ambient conditions.[99] In comparison with conventional thiophene or fused thiophene-based polymers, both polymers exhibit much deeper HOMO levels of $-5.7$ and $-5.8$ eV for IIDDT and IIDT, respectively, because of their electron-deficient isoindigo core. Because of their lower HOMO levels, both polymers were stable for more than 4 months under ambient conditions, maintaining a good hole mobility of up to 0.79 cm$^2$ V$^{-1}$ s$^{-1}$ (Figure 4a).

Guo et al. reported new p-type semiconducting polymers with an electron-deficient thieno[3,4-c]pyrrole-4,6-dione (TPD) building block, achieving HOMOs of 0.24–0.57 eV.
lower than that of poly(3-hexylthiophene) (P3HT) and ultimately realizing ambient stable OFETs. They synthesized various TPD-based polymers with various numbers of thiophene donor co-units in the polymer backbone; the thiophene co-units, with consecutive S···O interactions, enhanced the backbone planarity, which consequently decreased the band gap. The fabricated OFETs exhibited an oxygen-robust performance, with only minor changes in carrier mobility values, \(I_{on}/I_{off}\) ratios, and \(V_{th}\), even after exposure to ambient conditions for longer than 5 months. They also tested the operational stability by checking the on–off cycles of the devices exposed to air; the devices delivered static operations for 1000 cycles, showing excellent air robustness (Figure 4b).

Together with lower-lying HOMOs, the detachment of solubilizing groups such as alkyl side chains (oxygen radicals formed by external factors such as heat or light can attack C–H bonds of a long alkyl side chain, causing step-by-step degradation) has been shown to further enhance oxygen robustness. Schmoltnzer et al. reported a new air-stable p-type heterotriangulene polymer (PTA). The presence of the dimethylmethylene bridging groups enabled excellent solubility in common organic solvents even without side chains, and improved conjugation was observed because of the enhanced electron delocalization and planarization. Additionally, air stability was provided by the relatively low-lying HOMO level of \(-5.1\) eV with a wide band gap of \(2.9\) eV. The excellent ambient stability of the PTA polymer was demonstrated by comparing the transfer characteristics with those of regioregular P3HT as a function of air-storage time. The PTA-based OFETs did not show significant device performance changes, whereas the P3HT-based OFETs showed a shift in \(V_{th}\) and a decrease in the on/off current ratio and mobility (Figure 4c).

Mei et al. introduced another method to enhance the air stability of polymer semiconductors. They focused on designing new solubilizing groups with a siloxane block as a part of the solubilizing chain that can enhance solubility and even function as a potential crosslinking site. Compared with the reference polymer with an alkyl side chain (PII2T-Ref), the newly synthesized polymer with a siloxane side chain (PII2T-Si) showed stronger intermolecular interactions, resulting in an unusually high hole mobility of \(2.00 (±0.49) \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}\) relative to PII2T-Ref-based devices with a hole mobility of \(0.33 (±0.13) \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}\). Moreover, the adoption of the siloxane-based side chain affected device stability, which demonstrated only a slight degradation in performance after exposure to ambient conditions (relative humidity (RH) \(≈ 45\%\)) for a month (Figure 4d).

### 2.1.3. n-Type Small-Molecule Semiconductors

Historically, n-type organic semiconductors have been investigated less than p-type organic semiconductors because the electrical properties of n-type organic semiconductors usually degrade when the materials are exposed to ambient conditions because of the oxidation of electrons by ambient oxidants such as oxygen, ozone, and water vapor. However,
for the fabrication of complementary circuits or p–n-junction-based electronic devices that use both p- and n-type semiconductors, developing high-performance n-type semiconductors is important.

In general, two main approaches have been developed to impart n-type organic semiconductors with air stability: approaches based on: i) thermodynamic aspects and those based on ii) kinetic aspects. In terms of the thermodynamic aspects, the molecular design of organic semiconductors with low LUMO levels is a key approach for enhancing air stability of n-type semiconductors. To lower the LUMO level of organic semiconductors, substitutions with strong electron- withdrawing or hydrophobic functional groups such as alkanoyl,[103] perfluorobenzene,[104] fluoroalkyl groups,[105–107] F,[108,109] CN,[60] and Cl[110] have been found, according to molecular orbital energetics, to make π-conjugated cores of organic semiconductors electron deficient (electron accepting). This substitution method could lower the LUMO of the n-channel semiconductors, enabling them to resist oxidation under ambient conditions. de Leeuw et al. reported on the relationship between the redox potential of n-type semiconducting materials and air stability.[81] They elucidated that the LUMO level of n-type semiconductors should be lower than −3.74 eV (−0.66 V vs SCE) to avoid oxidation by humidity in an ambient atmosphere (Figure 5a). In the case of oxygen, the air stability could be secured with a LUMO level below −4.37 eV, which is slightly higher than the redox potential of oxygen (−4.97 eV, +0.57 V vs SCE) because of an overpotential for the reaction between oxygen and electrons.

Kinetic aspects such as packing structures and side chain modifications of organic semiconductors also strongly affect the air stability of OFETs based on n-type organic semiconductors. The introduction of bulky and electrostatically negative side chains to π-conjugated core molecules can promote air stability. Katz et al. reported on the steric barrier effect of the fluoroalkyl-substituted naphthalene diimide (NDI) molecules.[105] Oxygen intrusion into the π-conjugated core was reduced by the narrow spacing between the adjacent side chains of the fluoroalkyl-substituted NDI (~2 Å) compared with the available spacing of the alkyl-substituted NDI molecules (~4 Å). Jones et al. investigated the effects of steric barrier effects of the fluorinated side chain of perylene diimide (PDI)-based n-type organic semiconductors (Figure 5b).[61] The authors gave an account of the air-stable operation behaviors of 1H,1H-perfluorobutyl-substituted PDI derivatives (i.e., PDI-F and PDI-FBr₂), which are LUMO/charge-carrier energetics placed in an air-unstable region (reduction potentials of PDI-F and PDI-FBr₂ are −0.33 V and −0.24 V vs SCE, respectively), resulting from the steric barrier effect by the dense fluoroalkyl-based packing structures.

Several groups have demonstrated the relationship between the LUMO level and air stability based on side chains in PDI-based semiconductors.[60,101,107,111] Empirical results from previous studies show the relationship between the LUMO level and the air stability of n-type organic semiconductors (Figure 6). Typically, organic semiconductors with a LUMO level higher than −3.8 eV exhibit n-channel operation but not air stability because of oxidation by humidity or oxygen in the ambient atmosphere. The onset of air stability in n-type organic semiconductors starts with a LUMO level below −3.8 eV, and both air stability and a low off-current are observed when the LUMO level is below −4.0 eV. However, current modulation is difficult to control when the LUMO level of the semiconductor is below −4.4 eV because of the substantial doping. In the case of N-alkyl PDIs, n-channel device operation was observed with a LUMO level of −3.70 eV, but it showed poor air stability, with a $V_{th}$ of 75 V, because the high-lying LUMO level could not effectively prevent oxidation.[112] Jones et al. reported two core-cyanated PDI derivatives (i.e., PDI-CN₂ and PDI-FCN₂) with high air stability.[69] Low-lying LUMO levels were acquired by substituting the side chain of core-cyanated PDI derivatives with cyclohexyl and N-fluoroalkyl groups, and the resultant materials exhibited air stability under ambient conditions. However, the $V_{th}$ values of PDI-CN₂ (~15 V) and PDI-FCN₂ (~20 to ~30 V) differed. The substantially shifted $V_{th}$ for PDI-FCN₂-based OFETs yielded “always on” operating behaviors, presumably because of the highly electron-deficient nature of PDI-FCN₂ resulting from unintentional doping. Schmidt et al. reported the synthesis and characterization of air-stable n-type organic semiconductors based on PDI functionalized using fluorinated imide substituents.[107] Various fluorinated PDIs were investigated in terms of energy levels, molecular packing structure, electrical performance, and air stability. PDIs fluorinated with up to two

![Figure 5](https://www.advancedsciencenews.com/articles/1703638/figures/5a.png)

**Figure 5.** a) Energy level diagram representing redox potentials of water and oxygen, and the ranges of LUMO levels of n-type organic semiconductors required to achieve stability toward humidity and oxygen. SCE and $E_{\text{r ank}}$ stand for saturated calomel electrode and vacuum energy level, respectively. b) Molecular structures and the space-filling models of air-unstable alkyl-PDI (N,N’-pentyl-PDI, left) and air-stable fluoroalkyl-PDI (PDI-FCN₂, right). “Channel” at alkyl-PDI indicates the possible pathway where ambient oxidants (charge-trapping materials) penetrate into the film. In the case of fluoroalkyl-PDI, the “channel” is blocked by the barrier of bulky fluoroalkyl bay, facilitating the enhancement of air stability. Reproduced with permission.[61] Copyright 2007, American Chemical Society.
fluorine substituents showed a planar aromatic core without distortion, resulting in molecular packing that is denser than that of PDIs with four fluorine substituents (Figure 2a). PDIs with a flat aromatic core also demonstrated improved electrical performance (electron mobility as high as 1.44 cm² V⁻¹ s⁻¹). The long-term air stability of the fluorinated PDIs was investigated and compared with that of PDIs without a fluorinated side chain. Superior air stability, for ≈2 months, was observed with the fluorinated PDIs, whereas a 91.3% mobility degradation was observed in PDIs without fluorinated side chains (Figure 7b). The enhanced air stability of the fluorinated PDIs was due to several factors, including the LUMO level, molecular packing distance, and morphology of the films. NDI derivatives have also been used as active layers for air-stable n-type OFETs. Oh and co-workers reported on highly air-stable core-chlorinated tetracarboxylic NDI derivatives (Figure 7c).[110,62] The NDIs with two chlorine substituents showed a herringbone packing structure with close π-plane distances and a large π-stack overlap (3.3–3.4 Å and a slipping angle of ≈62°, respectively) and a mobility as high as 1.43 cm² V⁻¹ s⁻¹ under ambient conditions (Figure 7d,e).[62]

The interplay between thermodynamic and kinetic factors should also be considered when attempting to achieve ambient stability of n-type OFETs. Oh et al. found that the optimization of active-layer thickness (kinetic factor) was important for air stability in the case of two PDIs with distinctly different LUMO levels, i.e., PDI-CN₂ (LUMO, −4.33 eV) and PDI-FCN₂ (LUMO, −3.84 eV) were at the air-stable region and at the onset region for air stability, respectively, according to thermodynamic aspects.[101] An enhanced ambient stability was observed for thicknesses greater than 10 monolayers (ML) in the case of air-unstable PDI-F OFETs. By contrast, the PDI-CN₂ OFETs, which were regarded as “air-stable” devices in terms of thermodynamic aspects, were unstable in air when the thickness of PDI-CN₂ was less than 4 ML. This result indicates that the optimization of the thickness of n-type organic semiconductors and

![Figure 6](image-url) Energy level diagram indicating the relationship between LUMO levels and air stability and the reported results of representative n-type semiconductor PDI derivatives (alkyl-PDI, PDI-CN₂, PDI-FCN₂).

![Figure 7](image-url) a) Side view of the aromatic systems of molecules 1a–1e in panel (b) (from left to right), showing the twisted perylene cores. b) Percentage drop of average mobility (Δμ, %) after exposing the PDI OFETs to air (RH ≈ 50%) for 1 h as a function of the LUMO level of PBI molecules. The blue squares and red circles represent substrate condition as OTS-S and OTS-V, respectively. Reproduced with permission.[107] Copyright 2009, American Chemical Society. c) Synthesis scheme of core-chlorinated NDIs. d,e) Transfer and output characteristics of OFETs based on compound 3b in N₂ (d) and air (e) conditions, respectively. Reproduced with permission.[62] Copyright 2010, Wiley-VCH.
consideration of the LUMO level, film growth mode, and film morphology are necessary for achieving air stability in n-type OFETs.

2.1.4. n-Type and Ambipolar Polymer Semiconductors

Takeda et al. reported the synthesis of a highly fluorinated air-stable n-type semiconducting conjugated polymer, poly[2,3-bis(perfluorohexyl)thieno[3,4-b]pyrazine] (PPFHTP) (Figure 8a).[113] Thermogravimetric analysis revealed that PPFHTP started to decompose at 337 °C in air, indicating high air and thermal stability of PPFHTP. Top-gated OFET devices fabricated using the PPFHTP semiconductor showed a saturation-regime electron mobility of 2.15 × 10⁻⁶ cm² V⁻¹ s⁻¹, and the device did not show significant changes in electrical properties after storage under ambient conditions for ~1 month (Figure 8b). Because of the high electron affinity resulting from the electron-withdrawing nature of fluorine, electron injection and stabilization were enhanced. Additionally, fluorinated alkyl chains are effective in enhancing thermal and air stability because of the formation of a kinetic barrier that prevents oxygen and water from diffusing into the semiconductor film.

Zhao et al. reported the design and synthesis of an air-stable and high-performance n-type regioregular “acceptor1–donor–acceptor2–donor” configuration polymer semiconductor named PNB0, which means polymer including NDI and benzo[c]-[1,2,5]-oxidazole (BOZ) acceptor units (Figure 8c).[63] Because of the strong electron-withdrawing property of the BOZ unit, which was induced by the high electronegativity of the oxygen atom, PNB0 exhibited a low LUMO level (~3.98 eV) and a low HOMO level (~5.90 eV), which enhanced the electron injection and the blocking of hole injection. A solution-processed PNB0-based top-gate bottom-contact field-effect transistor (FET) was fabricated on an octadecyltrichlorosilane-modified SiO₂ substrate with a poly(methyl methacrylate) (PMMA) dielectric layer. The device showed a high electron mobility of 2.43 cm² V⁻¹ s⁻¹, and a negligible decay in mobility was observed (2.42 cm² V⁻¹ s⁻¹) after storage for 70 d under ambient conditions because of the encapsulation effect of the PMMA dielectric layer reducing the negative influences of water and oxygen (Figure 8d).

The ambipolar copolymer semiconductor PNDI-mT(BZ)mT (m = 1, 2), which consists of NDI units covalently connected to benzothiadiazole (BZ) units via thiophene (T) linkers, was developed by Gu et al. (Figure 8e).[64] Because PNDI-2T(BZ)2T exhibited a dihedral angle of 12° between two thiophene rings, PNDI-T(BZ)T exhibited better planarity than PNDI-2T(BZ)2T; consequently, the delocalization of the LUMO and HOMO through the PNDI-T(BZ)T chain was enhanced. In the case of the OFET performance, whereas PNDI-2T(BZ)2T-based OFET devices showed unipolar p-type characteristics, with an average hole mobility of 0.07 ± 0.02 cm² V⁻¹ s⁻¹, PNDI-T(BZ)T-based OFET devices exhibited balanced ambipolar semiconducting characteristics, with average hole and electron mobilities of 0.1 ± 0.03 and 0.05 ± 0.02 cm² V⁻¹ s⁻¹, respectively. The polymers showed low LUMO levels of ~4.17 and ~4.05 eV for PNDI-T(BZ)T and PNDI-2T(BZ)2T, respectively, which resulted in high air stability of the fabricated OFET devices; these devices did not exhibit severe degradation in charge mobility after storage under ambient conditions for 3 months (Figure 8f,g).

2.2. Approaches to Water Robustness

Despite the potential for organic electronics to be used in the healthcare industry and in environmental monitoring, they...
have a high entry barrier to being commercialized because of the degradation and delamination problems that occur when exposed to a humid environment.\[114\] For example, when p-type OFETs are exposed to water, their $V_{th}$ tends to shift toward positive values, and both the on- and off-currents often increase. These phenomena are related to water penetration through the film, which results in the accumulation of hydronium ions at the interface between the semiconductor and the dielectric. Additionally, the sides of a fabricated device have been shown to not be a major entrance channel for the diffusion of water molecules under ambient conditions.\[12,115\] Beyond these issues, low-voltage operation (below 1.23 V) should be achieved to avoid the electrolysis of water and a high ionic current through aqueous media.\[116\] To address these problems, researchers have been developing and adopting new organic materials that are stable under exposure to water. Figure 9 shows some representative chemical structures of water-robust organic electronic materials.

Fluorine–thiophene oligomers have emerged as highly stable semiconducting materials with good mobility—greater than 0.1 cm$^2$ V$^{-1}$ s$^{-1}$—and a relatively high on-off ratio. Among the various fluorine–thiophene oligomeric semiconductors, 5,5′-bis-(7-dodecyl-9H-fluoren-2-yl)-2,2′-bithiophene (DDFTTF) has been widely used to fabricate water-stable organic electronics, including chemical sensors\[65,66,117\] and biosensors,\[46,65,118,119\] because of its long dodecyl-substituted and hydrophobic alkyl side chains, which can effectively shield the main backbone where the actual charge transport occurs by closely packing to reduce degradation.\[120\]

Roberts et al. reported the first demonstration of intrinsically aqueous-stable organic electronics taking advantage of a DDFTTF semiconducting layer in 2008.\[65\] They incorporated a crosslinkable polymer dielectric, poly(4-vinylphenol) (PVP), to fabricate OFETs, not only because of its high air and moisture stability but also because of its simplicity in formulation, undergoing low-temperature crosslinking at 100 °C (Figure 10a).\[121,122\] After exposure to water, unencapsulated devices functioned well, showing only slight changes in $V_{th}$ and current levels because of doping effects (Figure 10b).\[123\] On the basis of these results, they successfully investigated the effects of water on the properties of organic semiconductor films, including the effects on their molecular structure, alkyl chain length, and thin-film morphology.\[66\] They found that the effect of water on the semiconductor properties could be reduced by increasing the thickness of the 2D films. Additionally, in the case of thermally deposited semiconductor films, the substrate temperature was found to be a major factor in delaying water propagation through the films, along with the grain size and grain boundary extension of the grown organic semiconductor films.

Previous reports considered solution-processed organic semiconductors unsuitable for aqueous applications because residual solvent causes performance deterioration and delamination of the semiconductors.\[65\] Nonetheless, the demand for water-stable and solution-processable organic semiconductors compatible with large-area, low-temperature, and low-cost processing has increased. To this end, several groups have

---

Figure 9. Chemical structures of representative water-robust organic semiconductors, electrode-surface modifiers, and protection/encapsulation materials.
successfully introduced water-robust and solution-processable organic semiconductors.[47,49,67,125] One example is the use of siloxane-terminated side chains in a conjugated polymer, which was inspired by the wide use of siloxane for crosslinking.[59,126] An isoindigo-based conjugated polymer with a siloxane terminal side chain (PII2T-Si) was successfully synthesized and used in OFETs operating in direct contact with an aqueous medium (Figure 10c). [47] The fabricated device exhibited excellent stability upon exposure to ambient conditions for months, and the aqueous stability was tested by mounting a polydimethylsiloxane flow cell and using an high-performance liquid chromatography (HPLC) pump to deliver aqueous solutions. After exposure to water, the device showed only slight increases in off-current and hysteresis. Its long-term stability was tested by storing the OFET device in deionized water (DI water) and seawater for 17 d; only a slight degradation in performance was observed in the on/off ratio and hysteresis, demonstrating the excellent water robustness of PII2T-Si (Figure 10d). Furthermore, the change in source–drain current under continuously flowing DI water and seawater exhibited a proportional relationship between current level and salt concentration because of the electrochemical doping. The PII2T-Si-based devices exhibited reproducible and stable operation (Figure 10e).

The benefits of introducing siloxane-terminated side chains were also demonstrated by Han et al.[49] They investigated how siloxane termini of the side chains, compared with alkyl-terminated groups, affect the various inherent device performance characteristics, including the electrical characteristics and environmental stability. In the case of a siloxane-terminated polymer, PDPPTT-Si[30] exhibited a comparably high performance and a remarkably high water stability over a long period of exposure to a saturated humidity atmosphere (≈100% RH).
and with in situ water droplets on the channel. The high aqueous stability of the siloxane-terminated polymer films has been suggested to be caused primarily by hydrophobic surfaces preventing water permeation. This investigation provided a new approach to solving stability issues of organic electronics while maintaining their excellent electrical properties.

The functionalization of the polymer backbone with chlorine substituents may be another solution for developing water-robust organic semiconductors. One example was demonstrated by Rye et al., who described the design, synthesis and characterization of two chlorinated NDI-based polymeric semiconductors, P(NDI2HD-T2Cl2) and P(NDI2OD-T2Cl2).[67] The chlorine substitution affected the electrochemical properties of the new polymers, resulting in a larger band gap and lower HOMO and LUMO energy levels. P(NDI2HD-T2), the unsubstituted original polymer, showed an optical band gap of 1.45 eV, and HOMO and LUMO values of −5.34 and −3.89 eV, respectively; whereas the chlorine-substituted polymer P(NDI2HD-T2Cl2) had an optical band gap of 1.69 eV and HOMO/LUMO values of −5.73/−4.04 eV, respectively. Whereas the chlorinated polymers exhibited reduced electron mobility values because of backbone distortions and greater band gaps compared with nonchlorinated derivatives, their stability was improved because their LUMO energy level was lower than −4.0 eV. Only an ≈20% electron mobility degradation after storage in humid air and nearly no change in mobility after storage in aqueous media were observed after 20 d.

Organic–inorganic hybrid perovskite solar cells fabricated with the high-performance hole-transporting material (HTM) 2,2′,7,7′-tetrakis[N,N-di-p-methoxyphenylamine]-9,9′-spirobifluorene (spiro-MeOTAD) readily undergo degradation because they require highly hygroscopic additives, such as lithium salts, to adjust the properties of the materials; these salts can lead to the decomposition of the perovskite.[127] Researchers have addressed this stability problem using water-stable organic semiconductors instead of spiro-MeOTAD as HTMs to protect the organic–inorganic hybrid perovskite from degradation.[128–130] Kwon et al. reported a stable hybrid solar cell with the π-extended diketopyrrolopyrrole (DPP)-based polymer poly[2,5-his-(2-decyl-dodecyl)-pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione-(f)-1,2-di(2′-bithiophen-5-yl)-ethene] (PDPDBTE) as the HTM.[68] They selected PDPDBTE because of its excellent charge-carrier mobility (μ = 0.32 cm2 V−1 s−1), and its appropriate oxidation potential of −5.4 eV versus the vacuum level (Figure 10f). The fabricated devices exhibited a high power conversion efficiency (PCE) of 9.2% and maintained their initial performance for over 1000 h in a humid atmosphere because of the hydrophobicity of the polymer (water contact angle as high as ≈105°), which prevented water penetration into the porous perovskite heterojunction (Figure 10g). Similarly, small molecular organic semiconductors such as the benzodithiophene (BDT)-based oligothiophene derivative DR3TBDTT[128] which has an ethylhydrodane end group, and a tetraflauvalene derivative (TTF-1)[129] have been used as HTMs to fabricate water-robust perovskite solar cells.

In OFETs, an examination of the gate dielectric is important to realize intrinsically stable organic electronic devices because the characteristics of a device can be influenced by the gate dielectric controlling the charge accumulation and transport, which primarily occurs at the interface between the gate dielectric and the semiconductor.[131,112] The commonly used gate dielectric silicon dioxide (SiO2) itself is not adequate for application in a water-robust device because it readily undergoes an electrochemical reaction after exposure to water, disturbing the charge transport; a large bias stress and a threshold shifts occur, degrading its operating performance.[133–135] Thus, the use of an intrinsically water-stable gate dielectric or passivation of the gate dielectric surface by applying a hydrophobic material is recommended. Because of the high stability of PVP, Halik et al. successfully demonstrated fully patterned OFETs with the successive patterning of a poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) gate electrode, a crosslinked PVP dielectric, a pentacene semiconductor, and gold source–drain electrodes.[121] Roberts et al. determined the influence of crosslinker type, concentration, surface treatment, and processing conditions on the physical and electrical characteristics of the PVP dielectric layers and OFETs based on them.[114] In this report, they successfully demonstrated low-voltage operation because the thin insulating PVP films were crosslinked with diianhydrides, which exhibited a capacitance of up to 400 nF cm−2 with a low leakage current, below 10−8 A cm−2, enabling water-stable operation.

Water can permeate through the interlayer of OPV devices between the PEDOT:PSS buffer layer and metal electrodes.[116] In this case, water can act as an oxidizing agent that damages metal electrodes with a low work function (WF).[22] After exposure to water, Al electrodes were found to exhibit pinholes,[137,138] which led to the penetration of more water.[119] Second, an insulating metal-oxide layer can form at the active-layer/electrode interface as a result of water penetration, resulting in a reduction of the effective active interface area and in inefficient charge extraction.[140] Finally, the position of the fullerenic acceptor in the well-studied polymer solar cell blend system P3HT:[6,6]-phenyl-C61-butyric acid methyl ester (PCBM) is rearranged by the introduction of water into the active layer, inducing further aggregation of the fullerene. The large-scale phase separation reduces the donor/acceptor interfacial area, which is detrimental to exciton dissociation and greatly reduces device performance.[141]

Furthermore, OPVs require at least one low-WF electrode to effectively collect electrons from the LUMO. However, widely used low-WF electrodes are reactive and tend to oxidize readily upon exposure to water. Several strategies to improve stability have been demonstrated; using bilayer electrodes stacked with high- and low-WF electrodes in sequence[142,143] and introducing a surface modifier can control the vacuum level and modify the electrode WF.[124,144–146] For example, Zhou et al. fabricated water-stable low-WF electrodes by introducing polymers with a high content of aliphatic amine groups, including polyethylenimine ethoxylate (PEIE) and branched polyethylenimine (PEI), onto conductive metal oxides, graphene, and conducting polymers.[124] They showed that the surface modifications could be processed under ambient conditions and observed physisorption of the added surface modifier. Additionally, the strength of the binding between the surface modifier and an electrode in aqueous media was investigated by monitoring the WF change in PEIE-coated indium tin oxide (ITO) over time to confirm water stability (Figure 10h). The PEIE-coated film...
not show a severe change in WF (<0.34 eV) with mild washing (flowing water) for 50 min, suggesting the universal suitability of aliphatic-amine-group-containing polymers for water-robust electrodes and their use as electron-selective electrodes for OPVs and OLEDs. Someya et al. used a hydrophobic fluoropolymer layer to protect source/drain electrodes from direct contact with water.\cite{147} They fabricated OFETs based on some representative organic semiconductors; the fabricated OFETs could operate stably with in situ contacts with both stationary and flowing water. Someya et al. investigated the suitability of their OFETs in other applications by checking their response to several analytes in dilute aqueous solutions (at concentrations as low as 1 ppm); they observed significant signal responses and some solute specificity. Additionally, Khan et al. fabricated high-performance OFETs with water-robust operation by introducing a thin copper phthalocyanine (CuPc) film;\cite{169} such films have been widely used to enhance charge-carrier injection from electrodes by reducing hole injection barriers.\cite{148,149} The microstructural and morphological characterization of the CuPc films revealed that the CuPc formed a highly compact and oriented face-on arrangement on pentacene, and that this arrangement prevented the penetration of water/aqueous solutions into the operating films. As a result, the fabricated OTFT devices with a CuPc passivation layer exhibited stable operation, with a hole mobility as high as 0.5 ± 0.08 cm² V⁻¹ s⁻¹ after immersion in aqueous media for 30 min. Simplifying the formation process of the encapsulating layer, Kopaniti et al. fabricated barrier films with self-assembled dense organic layers;\cite{190} PEI and stearic acid (SA) with a hydrophobic nature were chosen and crosslinked in the presence of N,N-dicyclohexyl-carbodiimide (DCC), which resulted in a reduction in water permeability to 2 × 10⁻⁸ g m⁻² d⁻¹, which is three orders of magnitude lower than that of the widely used neat Surlyn films. These results suggest the hydrophobic, covalently self-assembled films have potential applications as water-vapor barriers.

2.3. Approaches to Chemical Robustness

The robustness of organic semiconductors toward chemical species such as vaporized organic solvents, liquid-phase organic solvents, and acidic/basic solutions is more difficult to achieve than robustness toward an aqueous atmosphere because such chemical species can penetrate the film layers more easily than water.\cite{133} The chemical resistance of organic semiconductors in electronics is critical for their advanced applications in chemical/biological sensors that can detect chemical/biological species via direct contact as well as for mass production using wet fabrication processes (e.g., photolithography and wet etching).\cite{8,49,50,153} Several approaches to enhancing the chemical stability of organic semiconductors have been reported. Unlike inorganic materials, organic materials, including organic semiconductors, can be crosslinked by chemical or physical methods. The development of chemically robust organic semiconductors would open various applications such as reusable liquid-phase organic chemical/biological sensors, photolithographic organic electronics, and organic electronics suitable for harsh operating conditions, such as in wearable devices, manufacturing industries, and aerospace applications.

One approach to enhancing the solvent resistance of organic semiconductors is chemical crosslinking. Kim et al. reported on P3HT with azide groups attached to the end of the alkyl chain (P3HT–azide).\cite{153} The chemical crosslinking of azide functional groups at the end of the alkyl side chain facilitated both the maintenance of the electrical properties, without degradation of the charge transport characteristics, and excellent resistance toward liquid-phase organic solvents through simple UV irradiation (Figure 11a). An OFET fabricated with crosslinked P3HT–azide showed excellent solvent resistance toward chlorobenzene (CB). Compared with pristine P3HT films, the crosslinked P3HT–azide films were not washed out after immersion in CB (Figure 11b). The transfer characteristics of the OFETs based on crosslinked P3HT–azide were maintained, as shown before and after exposure to liquid-phase CB (Figure 11c). Generally, crosslinking of the semiconducting layer often disturbs charge transport because crosslinking with bulky functional groups tends to change the packing structure of semiconductors or to act as traps.\cite{154} However, the electrical performance of the crosslinked P3HT–azide was not degraded compared to that of pristine P3HT OFETs because the crosslinkable azide functional groups were sufficiently small, functionalized at the end of the alkyl side chains, and did not act as trap sites, thereby facilitating the charge transport that occurred primarily in the backbone of the semiconducting molecules (Figure 11d).

Park et al.\cite{52} prepared solvent-resistant HTMs for OLEDs via a chemical crosslinking method with azide groups. The crosslinkable poly(azido-styrene) and hole-transporting poly(triphenylamine) (X-PTPA-5) were copolymerized with various mole fractions of PS-N₃ (3–10 mol%) to enhance the chemical resistance of the hole-transporting layers (HTLs) (Figure 11e). The crosslinked copolymer with 5 mol% of PS-N₃ (X-PTPA-5), after 5 min of irradiation with UV light, showed high solvent resistance when the films were washed with CB; the UV–vis absorption spectra of the films rinsed with CB showed nearly the same absorption intensity as the spectra of the films subjected to 3 or 4 min of UV irradiation (Figure 11f). Brightness, power efficiency, and luminous efficiency as functions of the current density of the control device (i.e., OLEDs without an HTL) and X-PTPA-3/5/10 were compared (Figure 11g,h). Improved device performance was demonstrated with crosslinked X-PTTA-5 in terms of the external quantum efficiency (EQE) (11.8%), power efficiency (10.4 lm W⁻¹), and luminous efficiency (43.7 cd A⁻¹) versus the control device (6.2%, 5.2 lm W⁻¹, and 22.3 cd A⁻¹, respectively). The photo-crosslinkable azide platform was successfully applied to another HTM (poly(vinylbenzyl carbazole)) with 5% PS-N₃ (X-PBC-5), showing similar electrochemical and optical properties and enhanced optoelectrical performance compared with the control device.

The solvent resistance of organic semiconductors can also be enhanced through side-chain engineering with siloxane groups. Siloxane-terminated polymer semiconductors have shown high electrical performance with balanced ambipolar charge-carrier transport characteristics.\cite{47,59,126,152,155} The chemical robustness of siloxane-terminated polymers was investigated by Han et al.\cite{49} OFETs with siloxane side chains (PDPPTT-SiMe₃) showed superior operational stability in a saturated humidity atmosphere (20.6% mobility degradation after a 12 h exposure)
versus those with alkyl side chains (39.1% mobility degradation, Figure 12a). Furthermore, a solvent resistance test of OFETs with siloxane side chains was also carried out with water, toluene, and chloroform, which revealed that the OFETs exhibited high stability toward liquid-phase organic solvents (Figure 12b,c). Lee et al. investigated the solvent resistance of the siloxane-terminated polymer semiconductor (PTDPPSe-SiC₄) with four organic solvents (DI water, ethanol, acetone, and CB), as shown in Figure 12d.[50] The UV–vis spectra of thin PTDPPSe-SiC₄ and P3HT films were compared before and after they were soaked for 24 h. Nearly identical UV–vis spectra were obtained for the solvent-soaked PTDPPSe-SiC₄ films, whereas the spectra of the acetone- and CB-soaked P3HT showed distinct absorption peaks; these results indicated the excellent solvent resistance of PTDPPSe-SiC₄ upon direct exposure to organic solvents (Figure 12e,f). To demonstrate solvent-resistant OFETs for possible applications in chemical sensors, the authors investigated the sensing response of the device to vaporized acetone. The sensing demonstration of the PTDPPSe-SiC₄-based OFETs was carried out with repeated sensing responses to acetone exposure, revealing a negative response to acetone because of the electron-donating characteristics of acetone molecules.

2.4. Approaches to Thermal Robustness

Most organic semiconducting materials are vulnerable to high-temperature conditions because of thermally induced degradation such as thermal oxidation, deformation of the crystal structure, and mechanical stresses caused by the thermal expansion of the material.[74] Although the low stability of organic electronics under high temperatures has been highlighted less than other environmental vulnerabilities, heat resistance is a key factor for the commercialization of organic electronics, which may require various high-temperature processes during device fabrication. Such processes would cause severe degradation of organic electronic materials without heat resistance and reduce the electrical performance of the final devices. Additionally, when in use, most electronic devices are frequently exposed to heat from various sources, such as sunlight or simple Joule heating of the internal circuits, which may induce further morphological degradation in the organic electronic layers.[156] Thus, organic electronic materials with low thermal stability cannot be developed into commercial electronic devices because of their poor processability and inadequate long-term operational instability. To achieve thermally stable organic electronics, various approaches have been reported, including the development of thermally stable semiconducting and conducting materials, and the adoption of an encapsulation layer to protect the devices from high-temperature-induced degradation.[70–74,100,156–177]

Some groups have reported thermally stable organic electronic devices based on semiconducting conjugated polymers and single molecules with thermal robustness. For example, Cho et al. reported the fabrication of thermally stable OFETs using a thermally stable semiconducting polymer, poly[N-N-hepta-decanyl-2,7-carbazole-alt-5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzothiadiazole)] (PCDТBT; Figure 13a).[71] Structurally, a fully amorphous PCDТBT film showed greater thermal stability than other typical semicrystalline conjugated polymers that undergo crystallinity changes when heated above their glass-transition temperature (Tᵥ), which usually changes their electronic properties. Additionally, because of its relatively low HOMO...
Figure 12. a) Molecular structure of PDPPTT-SiTG (top) device configuration of solvent-resistant OFETs (bottom). b,c) Comparison of transfer characteristics (b) and optical microscopy images (c) of PDPPTT-R_{TG} and PDPPTT-SiTG OFETs after exposure to toluene and chloroform consecutively. Scale bar = 200 μm. Reproduced with permission.© Copyright 2016, American Chemical Society. d) Molecular structure of PTDPPSe-SiC4 (top) and device structure of flexible solvent-resistant OFETs (bottom). e) Photographic images P3HT and PTDPPSe-SiC4 films soaked in CB for 24 h. f) UV–vis spectra of the solvents which have soaked P3HT and PTDPPSe-SiC4 for 24 h and pure CB. Reproduced with permission.© Copyright 2017, Wiley-VCH.

Figure 13. a) Molecular structure of PCDTBT and hole mobility of PCDTBT (red) as a function of annealing temperature up to 400 °C. The results obtained from a P3HT device are shown for comparison (black). Reproduced with permission.© Copyright 2010, Wiley-VCH. b) Molecular structure of PCDTPT and mobility of FETs after exposure to various temperatures. Reproduced with permission.© Copyright 2016, American Chemical Society. c) Molecular structure of in situ compatibilizer for thermally stable OPVs and efficiencies of the OPVs with 0%, 10%, or 15% of P3HT–azide10 copolymer during 150 °C of thermal annealing with PCBM electron acceptor. Reproduced with permission.© Copyright 2012, American Chemical Society.
level (∼5.5 eV), the PCDTBT film showed remarkable stability against oxidation in air even at relatively high temperatures, which otherwise results in the degradation of the electronic structure and semiconducting properties. Because of these advantages, the PCDTBT film maintained its chemical bonding and electronic properties after high-temperature annealing. The PCDTBT-based FET devices showed stable operation, with only small changes in mobility, after being heated to temperatures as high as 350 °C under nitrogen; under ambient conditions, the film was stable at temperatures up to 150 °C (Figure 13a).

The fabrication of a high-mobility and thermally robust polymer FET that can withstand medical sterilization processes has been reported.[73] The semiconducting polymer poly[4-(4,4-di­hexadecyl-4H-cyclo­penta[1,2-b:5,4-b′]dithio­phone-2-yl]alt[1,2,5]-thiadiazolo [3,4-c] pyri­dine] (PCDTPT) (Figure 13b) was analyzed using UV–vis–near infrared absorption spectroscopy and X-ray photoelectron spectroscopy (XPS) to confirm its high thermal stability, and the investigators concluded that the electronic structure of a PCDTPT film was stable after exposure to temperatures as high as 350 °C in N2 and 200 °C in air. The remarkable thermal stability of PCDTPT was attributed to its relatively high HOMO level (−5.2 eV) and rigid backbone structure with fused aromatic rings. A PCDTPT-based FET device showed high hole mobility (≈1.6 cm2 V−1 s−1) with outstanding thermal stability in air. After exposure to a temperature of 200 °C in air, the FET mobility decreased by only 25% and the variation in the Vth was maintained to within ±2.5 V (Figure 13b). On the basis of the thermally stable PCDTPT device, an FET integrated with a protective packaging using a heat-sealable composite film was fabricated to endure a medical sterilization process. After steam sterilization (heating to 121 °C for 30 min in a pressurized autoclave at 15 psi), the encapsulated FET device showed a mobility of 1.2 cm2 V−1 s−1, a decrease of only 15% versus the as-fabricated FET (1.4 cm2 V−1 s−1), with low hysteresis and similar operating conditions. As a further demonstration, an FET was fabricated using the biocompatible SU-8 dielectric; the SU-8-based device maintained its high mobility before (1.3 cm2 V−1 s−1) and after sterilization (1.1 cm2 V−1 s−1).

Kim and co-workers synthesized a crosslinkable conjugated polymer with thermal stability for the development of thermally stable OPVs.[153] When an azide crosslinkable group is introduced into P3HT, a photo-crosslinkable P3HT–azide copolymer was obtained (Figure 13c). The fabricated OPVs based on a (P3HT + P3HT–azide10)/PCBM blend with 15% P3HT–azide exhibited high thermal stability and a constant PCE greater than 3.3% after annealing at 150 °C for 40 h (Figure 13c). The enhanced stability was due to the high-temperature-annealing-induced formation of in situ fullerene-attached P3HT–azide graft copolymers at the interface of P3HT/PCBM, which served as an in situ compatibilizer that reduced interfacial tension with a suppressed macrophase separation; these factors usually cause degradation of OPV device performance.

In addition to conjugated polymeric semiconductors, research on other ways to enhance the thermal stability of small-molecule organic semiconductors has been carried out. Park et al. reported the synthesis of a four-thiophene-fused heteroacene semiconducting material, dibenzothiopheno[6,5-b′:6′,5′-f′-f′-thieno[3,2-b]thiophene (DBTTT), by modifying the structure of the well-known high-performance organic semiconductor DNTT (Figure 14a).[19] Because of the introduced strong sulfur–sulfur van der Waals interaction, DBTTT has a substantially closer intermolecular distance along the π-stacking direction (5.91 Å) than the reported intermolecular distance of DNTT molecules (6.19 Å), which results in the enhanced molecular packing density of DBTTT (1.622 g cm−3).

Figure 14. a) Molecular structure of DBTTT and transfer characteristics at different temperature. Reproduced with permission.[19] Copyright 2015, American Chemical Society. b) Molecular structure of DPh-BBTNDT and transfer curves of OFET devices based on DPh-BBTNDT (upon pristine condition and annealed conditions from 100 to 300 °C under ambient conditions). Reproduced with permission.[151] Copyright 2015, American Chemical Society. c) Molecular structure of FL-DPP(TBFu)2 and average field-effect mobility as functions of thin-film annealing temperatures. Reproduced with permission.[165] Copyright 2015, Wiley-VCH.
for DBTTT vs 1.473 g cm\(^{-3}\) for DNTT). On the basis of the stiffness of the packing structure of DBTTT, which was caused by the strong \(\pi-\pi\) interactions and intermolecular networking through sulfur–sulfur van der Waals contacts, DBTTT-based FETs exhibited superior electrical properties, with a high mobility of 19.3 cm\(^2\) V\(^{-1}\) s\(^{-1}\). They also exhibited high thermal stability, maintaining their initial electrical characteristics at temperatures as high as 140 °C (Figure 14a).

Thermally stable organic small-molecule semiconductors with a high electrical performance were developed by Abe et al.\(^{[72]}\). They synthesized the high-performance semiconductor \(\text{bis[1]benzothieno[2,3-d;2',3'-d']-naphtho[2,3-b:6-b']dithiophene (BBTNDT)}\) and its derivatives, DPh-BBTNDT (Figure 14b) and C6-BBTNDT, with different alkyl substituents. By fabricating FET devices, the authors compared the electrical properties and thermal stability of BBTNDT and the derivatives. Among them, the DPh-BBTNDT-based devices showed the highest hole mobility (7.0 cm\(^2\) V\(^{-1}\) s\(^{-1}\)) and excellent thermal stability, with only a small \(V_{th}\) shift after annealing at 300 °C for 30 min (Figure 14b). The higher thermal stability of DPh-BBTNDT was attributed to its relatively large ionization potential (5.3 eV) compared with those of C6-BBTNDT (5.0 eV) and BBTNDT (5.1 eV). Additionally, thermal stability also arises from the denser packing structure caused by the intermolecular interaction between phenyl groups of adjacent molecules through \(\mathrm{CH}-\pi\) hydrogen-bond-like interactions.

Gasperini et al. reported a new approach for enhancing the thermal stability of organic semiconducting small-molecule thin films.\(^{[65]}\). They suggested the concept of a flexible linker (FL) approach, where molecular semiconductor segments are linked with polymeric materials via flexible aliphatic chains. The flexibly linked derivative of the molecular semiconductor 3,6-bis(5-(benzofuran-2-yl)thiophen-2-yl)-2,5-bis(2-ethylhexyl)-pyrrolo[3,4-c]pyrrole-1,4(2\(H\),5\(H\))-dione (DPP(TBu)\(_2\)) was synthesized and blended with neat DPP(TBu)\(_2\) (Figure 14c). FET devices fabricated using a blend of DPP(TBu)\(_2\) and 1 wt% of FL containing DPP(TBu)\(_2\) (FL-DPP(TBu)\(_2\)) showed higher thermal stability than an FET based on neat DPP(TBu)\(_2\) with maintained mobility during long-term annealing. By contrast, neat DPP(TBu)\(_2\) FETs showed a rapid decrease in mobility (Figure 14c), which was attributed to changes in crystal domain formation induced by the FL additive and to the bridging between adjacent crystal domains; this bridging originated from the polymeric structure and the properties of the FL. In addition, bulk heterojunction (BHJ) OPV devices were fabricated with DPP(TBu)\(_2\) as the donor, PC\(_{60}\)BM as the acceptor, and a small amount of FL-DPP(TBu)\(_2\) as the additive. Similar to the FETs, the FL-blended (0.5 wt%) BHJ OPVs exhibited high thermal stability with maintained PCE after annealing at 100 °C for 22 h, whereas OPVs without the FL blending exhibited a large decrease in PCE after thermal annealing at 100 °C for 3 h.

Jones et al. reported the strong effect of an anchor group on the thermal stability of organic semiconductor self-assembled monolayers (SAMs).\(^{[166]}\) Perylene bisimide (PBI) monolayers with a phospohane anchor group (PBI–PA) maintained molecular ordering up to a temperature of 250 °C, whereas PBI monolayers with no anchor group (PBI–alkyl) maintained monolayer ordering only up to a temperature of 100 °C on aluminum oxide deposited onto a silicon wafer. The greater thermal stability of PBI–PA was due to the stable covalent anchoring of the phosphonic acid anchoring group in the PBI–PA SAM compared with that in the physisorbed PBI–alkyl monolayer.

The development of new, thermally stable organic electronic materials is not the only viable approach to achieving thermal stability of organic electronic devices. By adopting appropriate encapsulation layers to protect the devices from oxygen and humidity, researchers have also demonstrated enhanced thermal stability of organic electronic devices based on conventional organic semiconductors. For example, Kuribara et al. reported a thermally stable organic transistor for medical applications, with DNTT as the organic semiconductor layer.\(^{[74]}\) For medical use, organic electronic devices should withstand sterilization processes, which usually include heating at temperatures above 100 °C. Although DNTT is a well-known and highly stable organic semiconductor, in the absence of an encapsulation layer, the electrical performance of DNTT transistors gradually degrades at temperatures above 100 °C. To protect devices from harsh sterilization conditions, researchers have encapsulated them by sequential deposition of polychloro-p-xylene, also called parylene, followed by a gold layer and another parylene layer. The organic transistors were subjected to various sterilization processes, including immersion in boiling water (100 °C) for 30 min, exposure to saturated steam (120 °C) for 20 min, and annealing at 150 °C for 20 s in air, together with yeast cells to quantify the effect of the sterilization. Most of the yeast cells were killed; however, the encapsulated transistors maintained their previous electrical performance because of their enhanced thermal stability.

To realize thermally stable organic electronics, in addition to thermally stable organic semiconductor, the development of electrodes based on organic conductors with thermal robustness is also necessary. Recently, Chu et al.\(^{[178]}\) developed an environmentally stable and transparent graphene-laminated polymer-based conductor. The stable organic conducting layer based on PEDOT:PSS film containing dimethylsulfoxide (DMSO) and Zonyl fluorosurfactant, named as PDZ film was manufactured. A graphene film grown on Cu foil using CVD was laminated on top of the PDZ-based conductive layer. Graphene-laminated transparent electrodes showed a low sheet resistance of 120 ± 14.9 Ω\(^{-1}\) and outstanding stability against various environmental factors, including mechanical strain (=23%), UV irradiation (\(\lambda = 254\) nm, a power of 6 W), relative humidity (80%), and high temperature (150 °C), because of the laminated graphene top layer, which functioned as a barrier layer that protected the PDZ layer.

The ability of nanocomposite interlayers at the surface of an anode to enhance of thermal stability of OLEDs was systematically investigated by Grozea et al.\(^{[175]}\). The large surface energy difference at the interface of a hydrophilic ITO anode and a hydrophobic HTL, such as \(N,N\)-bis(1-naphthyl)-\(N,N\)’-diphenyl-1,1’-biphenyl-4,4’-diamine (NPB), induced interfacial instability and strong dewetting of the HTL on ITO, which caused decohesion and local crystallization in films when the films were thermally annealed at a temperature near the glass-transition temperature, \(T_g\). To overcome the problems induced by the large surface energy difference and to solve the wetting problem at the anode–HTL interface, a graded interface
with doped or nanocomposite organic buffer layers was introduced. When an LiF-doped NPB buffer layer was positioned at the interface of ITO and NPB, the OLED driving voltage was increased; however, the current efficiency was higher than in a device with an undoped layer. Additionally, an LiF-doped NPB-based sample (ITO/NPB:LiF (5 wt%) (10 nm)/NPB (50 nm)) suppressed dewetting and crystallization of the film after it was annealed at 120 °C, whereas samples with no buffer layer showed clear dewetting before annealing and a considerable area of crystallization after annealing. As another option, the thermal stability and dewetting characteristics of a CuPc:C_{60} nanocomposite with the structure of anode/CuPc:C_{60} (25 nm)/NPB (45 nm) were analyzed using the same method. The nanocomposite-inserted sample showed no decohesion or crystallization of the ITO and Au anode after annealing at 120 °C. The doping-induced enhancement of adhesion may be due to the physical inhibition of crosslinking between molecules via electrostatic interactions of low-surface-energy spherical clusters with organic molecules.

2.5. Approaches to Photo-oxidation Robustness

The photoreactivity of acenes typically originates from photo-oxidation by oxygen molecules and dimerization under light illumination.[178–182] Rubrene, one of the p-type small molecular organic semiconductors, has been intensively investigated as both thin films and crystals because of its superior charge transport properties. The charge transport of rubrene crystals strongly depends on their degree of crystallinity. However, the electrical properties of rubrene are severely decreased by photo-oxidation under illumination. Various scanning probe techniques, such as atomic force microscopy (AFM) and Kelvin probe, have been used to study the oxidation mechanisms of rubrene crystalline films grown by organic molecular beam epitaxy under ambient conditions. The results revealed that a native crystalline rubrene peroxide layer is formed on top of crystalline domains of pristine rubrene.[183] One strategy to enhance the stability of rubrene is a chemical modification of the rubrene core via fluorination.[184–188] Anger et al. demonstrated that modification of rubrene with fluorine atoms could enhance the stability of rubrene against photo-oxidation both in solution and in the solid state because of the increased oxidation potential.[185]

6,13-Bis(triisopropylsilylethynyl)pentacene (TIPS-pentacene), a functionalized pentacene that is soluble in common organic solvents, showed high hole mobility (>0.1 cm² V⁻¹ s⁻¹) in FET devices (Figure 15a).[189] TIPS-pentacene was more stable than unsubstituted pentacene with regard to degradation in tetrahydrofuran solution by a factor of ~50. Compared with pentacene, TIPS-pentacene exhibited enhanced photostability in solution, as shown in Figure 15b. This enhancement was attributed to the low triplet energy and low LUMO energy for TIPS-pentacene. However, solid-state thin films of pentacene were more stable than those of TIPS-pentacene in terms of photo-oxidation. The different photostabilities between solvated and solid-state TIPS-pentacene and pentacene imply that interactions in the solid state affect lifetimes of the excited state and/or the permeability of oxygen.[190] These results reveal that to achieve long-term photostability of p-type organic semiconductors, careful attention should be focused on the design stage to not only the HOMO energy levels but also to the triplet and LUMO energy levels related to photoexcitation.

The cyano group is among the strongest electron-withdrawing functional groups because of its inductive (permanent state of polarization) and mesomeric (delocalization of electrons) effects; it is also thermally very stable. Cyanation substantially reduces the LUMO level of PAHs, whereas the impact on the HOMO level is negligible. In addition, hydrogen bonding and dipole interactions arising from cyanation impart aromatic molecules with a densely crystallized structure. For example, 6,13-dicyanopentacene and 5,7,12,14-tetraycanopentacene were stable under continuous light exposure (Figure 15c).[191]

Moreover, n-type N,N'-1H,1H-perfluorobutyldicyanoperylene-carboxydi-imide (PDIF-CN₂, chemical structure in Figure 16a) OFETs operated at a high temperature of ~100 °C and were photostable.[175] The electron mobility of solution-processed PDIF-CN₂ was independent of temperature variations, making it applicable to practical organic electronics. Typically, the energy transfer from photoexcited molecules to oxygen molecules in

Figure 15. a) The chemical structures of 6,13-bis(tri-isopropylsilylethynyl)pentacene (TIPS-pentacene). b) Stability of air-saturated solutions of TIPS-pentacene and pentacene stored in the dark. Optical densities are monitored at 640 nm for TIPS-pentacene (open squares) and 575 nm for pentacene (closed squares). Reproduced with permission.[190] Copyright 2004, Royal Society of Chemistry. c) The chemical structures of cyanate pentacene derivatives, 5,7,12,14-tetraycanopentacene (TCP) and 6,13-dicyanopentacene (DCP) that are photostable.
air is related to the photo-oxidation of many p-type organic semiconductors. Highly reactive singlet oxygen molecules \((O_2 \rightarrow O_2^*)\) arising from the energy transfer oxidize organic molecules quickly.\(^{[192]}\) A hermetic chamber was prepared to test the photo-oxidation of unencapsulated PDIF-CN\(_2\) OFETs under an oxygen gas condition. These OFETs were exposed to white light (light power density = 85 mW cm\(^{-2}\)) for 10 min, where the UV component was removed by a thick glass filter. Figure 16b clearly shows that p-type rubrene OFETs exhibited substantial reductions in hole mobility (by more than 50%) when illuminated in an O\(_2\) atmosphere for 10 min. By contrast, the electron mobility of n-type PDIF-CN\(_2\) OFETs was retained for 40 min. The absence of photo-oxidation in PDIF-CN\(_2\) is closely related to the low LUMO (−4.5 eV) that decreases the rate of energy transfer to oxygen molecules.\(^{[75]}\)

In the case of polymer semiconductors, the mechanisms of photo-oxidation have not been studied extensively in OFETs. Poly(p-phenylene vinylene) (PPV), which exhibits photoluminescence in the green-visible range (notable photoluminescence peak 1: 505 nm and peak 2: 545 nm), is widely used as an active component in the application of OLEDs.\(^{[193,194]}\) The color of PPV can be modified through the manipulation of its main chain and side groups. Poly[2-methoxy,5-(2′-ethylhexoxy)1,4-phenylene vinylene] (MEH-PPV; its chemical structure is shown in Figure 17a), which is a soluble PPV derivative that emits red–orange light, was degraded when exposed to light and an O\(_2\) atmosphere. Sutherland et al. demonstrated that MEH-PPV was oxidized upon light exposure in an O\(_2\) atmosphere. Specifically, the vinyl group (the double bond between carbon atoms 7 and 8) of MEH-PPV was destroyed under illumination; thus, the conjugation in MEH-PPV was lost.\(^{[195]}\)

Additionally, the photophysics with respect to oxygen and photochemistry of poly[2,5-bis(5,6-dihydrocholestanoxy)-1,4-phenylevinylene] (BCHA-PPV) was examined.

---

**Figure 16.** a) The chemical structure of \(N,N′-1H,1H\)-perfluorobutylcyanoperylene-carboxydi-imide (PDIF-CN\(_2\)). b) The mobility changes of PDIF-CN\(_2\) for the electron transport and rubrene for the hole transport as a function of photo-oxidation time \((t_{\text{PO}})\). Light with 85 mW cm\(^{-2}\) generated by a xenon lamp was illuminated to the samples under the oxygen atmosphere (the distance between light source and samples was 10 in.). Reproduced with permission.\(^{[75]}\) Copyright 2015, Wiley-VCH.

**Figure 17.** a) The chemical structure of MEH-PPV. b) The oxygen-dependent photophysics and photochemistry of BCHA-PPV. The photoinduced reaction by singlet oxygen resulted in extensive chain scission of BCHA-PPV. Reproduced with permission.\(^{[196]}\) Copyright 1995, American Chemical Society. c) The photodegradation mechanism of diCN-PPVs. At first, two oxo-acetonitrile groups are generated by attacks of singlet O\(_2\) to the C=C through a 2 + 2 cycloaddition. The generated oxo-acetonitrile group can easily react with H\(_2\)O in the ambient atmosphere, resulting in the carboxylic acid groups. Thus, vinylene groups of the polymer reaction are fragmented. Reproduced with permission.\(^{[197]}\) Copyright 2015, Wiley-VCH.
Scurlock et al. reported that the photo-oxidative decomposition in both liquid solutions and solid films of BCHA-PPV was induced mainly by singlet oxygen. The photoinduced singlet oxygen promoted extensive scissions of BCHA-PPV chains in both liquid solutions and solid films. In addition, the energy transfer from the BCHA-PPV triplet state to ground-state oxygen resulted in singlet oxygen in the solution phase.

Sanow et al. studied the photodegradation mechanism of poly(2,5-dioctyl-1,4-phenylene-1,2-dicyanovinylene) (C8-diCN-PPV) and poly[2,5-bis(decyloxy)-1,4-phenylene-1,2-dicyanovinylene] (ROdiCN-PPV). C8-diCN-PPV, which has a lower LUMO than ROdiCN-PPV, exhibited faster photodegradation than ROdiCN-PPV. Both C8-diCN-PPV and ROdiCN-PPV were not susceptible to the radical superoxide anion mechanism because of the diCN substitution. IR analyses revealed that singlet oxygen was the main reason for the photodegradation of both polymers because it breaks the C=C bonds into carboxylic acids. They reported that the intersystem crossing of C8-diCN-PPV promotes the generation of singlet oxygen upon photoexcitation, resulting in faster photodegradation (Figure 17c). Photoscavengers were transferred from the polymer backbone to the phenol-type radical scavengers to stabilize resonance in the rings of the scavengers.

Madogni et al. summarized the photodegradation process of BHJ OPVs. The studied BHJ OPV was composed of glass/ITO/PEDOT:PSS/P3HT:PCBM/Yb/Al. A blend of P3HT:PCBM was subjected to photodegradation under the influence of oxygen molecules and water molecules in the presence of light. Both P3HT and PCBM were fragmented upon light illumination, leading to degradation of the active layer (Figure 18a). The oxygen and water molecules, upon light exposure, caused the photo-oxidation of the active layer, which subsequently interrupted the electrochemical processes involved in the photovoltaic performance. In the case of degradation at the interface between the organic active layer and the metal electrode, both water and oxygen molecules diffused through the metal electrode. Oxygen molecules reached the interface between the organic active layer and the metal electrode through microscopic pinholes in the Al layer; by contrast, water molecules reached the interface through the Al grains. Thus, the homogeneous photo-oxidation of the interface caused by water molecules was observed over the entire interface between the organic active layer and the metal electrode. By contrast, partial surficial protrusions due to inhomogeneous photo-oxidation caused by oxygen molecules were centered at the microscopic pinholes in the Al layer, as shown in Figure 18b.

In organic optoelectronic devices such as OPVs and OLEDs, the photostability can be greatly enhanced by introducing metal nanoparticles (NPs) into the active layer. Sygletou et al. reported that active materials mixed with surfactant-free Al NPs can enhance the stability of BHJ OPV devices. The improvement of the lifetime of the BHJ OPV devices was attributed to two different reasons: first, triplet excitons induced by oxygen molecules prevented the photo-oxidation of the donor polymer because of the overlap of excitonic levels with the plasmonic resonance of the mixed Al NPs; second, PCBM hydrolysis was suppressed by the corrosive reaction with Al NPs and water under illumination, leading to Al₂O₃ formation.

The degradation of the active layer in OPVs can be induced by a PEDOT:PSS conductive layer. The degradation brings about a reduction in absorbance and the formation of micrometer-scale aggregates. Manceau et al. reported "induced" and "direct" degradation pathways of the active layer. The "induced" degradation was related to the PEDOT:PSS layer. Increasing the annealing temperature to 180 °C in the PEDOT:PSS layer retarded the induced degradation. P3HT is chemically instable under illumination. The degradation process of P3HT under light illumination was regarded as "direct" degradation. The direct degradation of P3HT could be suppressed by increasing the amount of PCBM in the active layer.
layer. Additionally, the P3HT:PCBM layer was morphologically unstable because of the low $T_g$. Either a low-temperature annealing of the PEDOT:PSS layer or a low content ratio of PCBM with respect to P3HT could result in absorbance reduction, adversely affecting device performance. The light illumination of the BHJ OPV induced a phase segregation and formed PCBM domains, regardless of the annealing temperature of the PEDOT:PSS. Over a long period of light exposure, the size of the PCBM domains could reach 500 nm. They also confirmed that control of the PCBM ratio could enhance the chemical stability of the P3HT:PCBM active layer. PCBM performed as an effective stabilizer in the active layer under light exposure. However, an unreasonably increased PCBM ratio in the active layer decreased the device performance; thus, optimization of the ratio of PCBM and P3HT was required to achieve good device performance and long-term stability of the OPVs.\cite{200}

3. Applications of Environmentally Robust OrganicSemiconductors

3.1. Water-Stable Chem/Biosensors

An isoindigo-based semiconducting polymer with siloxaneterminated side chains (PII2T-Si) was recently synthesized and used for OFETs that can operate in aqueous media with nearly no degradation for 17 d (Figure 20a).\cite{47} Based on a water-stable PII2T-Si, OFET-based chemical sensors for detecting heavy-metal ions in seawater were fabricated by Knopfmacher et al. The high selectivity of chemical sensors toward mercury ions (Hg$^{2+}$) was achieved by functionalizing the surface of the PII2T-Si layer with deoxyribonucleic acid (DNA)-functionalized Au NPs, which selectively bind with Hg$^{2+}$. The developed chemical sensors showed sensitive Hg$^{2+}$ detection in seawater at a lower detection limit of $10 \times 10^{-6}$ M and selective Hg$^{2+}$ sensing behaviors than other seawater contaminants (i.e., Zn$^{2+}$ and Pb$^{2+}$) (Figure 20b,c).

Jang et al. demonstrated OFET-based neurotransmitter acetylcholine (ACh$^+$) sensors that operated well with exposure to ACh$^+$ in an aqueous medium (Figure 20d).\cite{46} To enable selective sensing, they formed an additional layer of the synthetic receptor cucurbit[6]uril (insoluble in water but soluble in methanol) via solution-deposition onto the DDFTTF surface. The fabricated sensors exhibited a detection limit of $1 \times 10^{-12}$ M, which is substantially lower than that of ion-selective electrode-based sensors ($=1 \times 10^{-6}$ M) and acetylcholine-esterase-based biosensors ($=100 \times 10^{-12}$ M), respectively (Figure 20e). The selective sensing of ACh$^+$ in mixtures of ACh$^+$ and Ch$^+$ was also demonstrated (Figure 20f).

Biosensor applications based on water-stable organic semiconductors have also been demonstrated for the detection of biological species in an aqueous medium.\cite{201–203} Mulia and co-workers reported water-gated organic field-effect transistors based on odorant binding proteins that showed different interactions with chiral carvones (i.e., (S)-(−)- and (R)-(−)-carvone). PBTTT-C14 was utilized as the organic semiconducting layer, and the surface of the gate electrode was functionalized with a SAM of porcine OBPs (pOBPs), which could detect (S)-(−)- and (R)-(−)-carvone enantiomers. The sensitive sensing response was observed by the small capacitance change of pOBPs’ SAM as a ligand–protein complex formed. Biodegradable and water-stable OFETs with DDFTTF semiconductors were also constructed with biocompatible polymers.\cite{204} Poly(vinyl alcohol) (PVA), poly(lactide-co-glycolide) (PLGA) were used as the dielectric layer and the substrate, respectively. PVA and PLGA have great potential for applications in biomedical devices because of their biocompatibilities. In particular, PVA can be crosslinked by exposure to 254 nm wavelength light in the presence of ammonium dichromate. After exposure to water, these OFETs maintained functionality and exhibited a resorbable response toward water. The devices maintained their mass for 30 d; afterward, a loss of mass and hydrolysis in the devices were observed. The demonstration of resorbable organic electronics has expedited the development of biodegradable dielectrics and biocompatible organic semiconductors.

Water-stable organic electrochemical transistors to detect DNA strands were fabricated using poly[3-(5-carboxypentyl) thiophene-2,5-diy] (P3PT-COOH) as the organic semiconductor and a phosphate buffer solution or pure water as the dielectric.\cite{205} Because of the effect of an electric double layer in the electrolytes, a high electric field was generated at the interface between the semiconductor and electrolyte, allowing for a low gate voltage ranging from −0.5 to +0.5 V. The P3PT-COOH-containing carboxylic acid moieties formed covalent oligonucleotides (ODNs) grafting hybridized with DNA, resulting in conformational changes (formation of a rigid double helix). Electrical changes in source-drain current were observed after immobilization of DNA on the P3PT-COOH layer.
3.2. Chemical Sensors for Liquid-Phase Analytes

The fabrication of chemically robust organic semiconductors can lead to the development of electronic devices such as chemical sensors with the ability to detect liquid-phase organic solvents through direct exposure. Lee et al. reported solvent-resistant OFET-based chemical sensors that could detect liquid-phase organic solvents; they used a crosslinked P3HT–azide and calixarene derivatives (calix[8]arene, C[8] A) as the solvent-resistant active layer and selective binding layer, respectively (Figure 20g).[48] These sensors detected liquid-phase organic solvents (e.g., methanol, ethanol, toluene, n-hexane, and DI water) as well as aqueous solutions of various pH levels (Figure 20h). A 1 vol% detection limit for the fabricated OFET-based sensors was demonstrated from experiments using mixed solutions of methanol, ethanol, and n-hexane, with toluene as the base medium (Figure 20i). Repeated sensing tests with single sensors were demonstrated to confirm the reusability of the sensors, which is an important issue for practical applications. Crosslinked P3HT–azide-based sensors showed excellent solvent stability, up to three sensing cycles, whereas non-crosslinked sensors exhibited poor stability from the second sensing cycle on. A sensing demonstration using flexible chemical sensors was also carried out, and the results agreed well with sensors prepared on a silicon wafer.
A siloxane-terminated polymer semiconductor with excellent solvent resistance was also used as the sensing layer for chemical sensors that could detect organic solvents. The stable sensing behaviors of PDPPTT-SiC4 OFETs upon exposure to liquid-phase DI water, toluene, and chloroform clearly demonstrated the potential of siloxane-terminated semiconducting polymers for use in highly stable chemical sensors for detecting liquid-phase chemicals. For practical applications in sensors, further developments to enhance chemical robustness are still necessary.

3.3. Photolithographic Patterning of Organic Semiconductors

Conventional microelectronic processes of electronic devices with integrated circuits usually involve multiple manufacturing steps, including photolithography and wet etching. Generally, organic electronic devices do not endure such wet-based manufacturing steps because of poor solvent resistance. Various approaches have been reported to pattern organic semiconducting layers, i.e., inkjet printing, soft lithography, and solvent orthogonality properties. Inkjet printing can facilitate selective deposition of the organic semiconducting layer for the fabrication of electronic device arrays. However, this approach usually encounters limitations in the feature size of patterns. In comparison with the typical sub-micrometer feature size of photolithography, the feature size of inkjet printing methods is generally greater than 10 μm. The patterning of organic semiconductors using the photolithography technique was demonstrated by introducing a passivation layer on top of the organic semiconductor. DeFranco et al. demonstrated the patterning of pentacene and PEDOT:PSS using parylene as the passivation layer. They further demonstrated its applicability to additive and subtractive patterning. The pentacene transistor, with a 2 μm channel length, and the PEDOT:PSS electrodes were fabricated. However, the introduction of passivation layers to the organic semiconducting layer and polymer electrodes often increases the cost of device fabrication and reduces the degree of freedom of the device fabrication. Thus, the development of chemically robust organic semiconductors that can endure wet-based photolithography processes is of great importance.

Recently, several demonstrations of the application of chemical-resistant organic semiconductors to wet-based patterning processes have been reported. Park et al. demonstrated patternable HTMs for OLEDs. The micrometer-scale pixelation of the HTLs using X-PTPA-5 was successfully demonstrated via selective UV irradiation (λ = 254 nm, intensity = 2 mW cm⁻²) based on photolithography technology (Figure 21a). X-PTPA-5 dissolved in CB was spin-coated onto a PEDOT:PSS/Si substrate. After the selective UV irradiation of the X-PTPA-5 films, several washing processes were carried out with CB to remove non-crosslinked X-PTPA-5. As a result, a distinct brightness difference was observed in the micrometer-size pixelized OLED arrays (Figure 21b). Lee et al. fabricated flexible 10 × 10 arrays of OFETs using a patterned semiconducting layer with a chemically robust siloxane-terminated polymer semiconductor, DPP−selenophene copolymers with siloxane-terminated side chains (PTDPPSe−Si) (Figure 21c). PTDPPSe-SiC4 with butyl spacers was used because of its optimized chemical resistance. The graphene source/drain electrodes fabricated using CVD facilitated electron transport between electrodes and semiconductors, leading to balanced hole and electron mobilities of the ambipolar OFETs. The fabricated PTDPPSe-SiC4-based chemically robust OFETs showed stable electrical characteristics after immersion for 1 d in various liquid-phase solvents (DI water, ethanol, acetone, and CB). The flexible 10 × 10 chemical sensor arrays were fabricated using patterned PTDPPSe-SiC4 thin films as the semiconductor, SU-8 as the dielectric, and transparent polyimide as the substrate (Figure 21d). The feature sizes of the photolithographic pattern of PTDPPSe-SiC4 films were 2–20 μm, demonstrating the high processability of the chemically robust organic semiconductor PTDPPSe-SiC4.

4. Conclusion and Perspectives

The field of organic electronics has undergone rapid development, and most research efforts have been devoted to enhancing charge transport and electrical performance. To date, the stability issues of organic electronic devices have received relatively less attention; however, they are critical for realizing device commercialization. Remarkable progress toward environmental robust organic electronics has been made in recent years, as described in Section 1. Most organic electronic devices consist of complex multilayered structures, in which each layer would be degraded by itself for different reasons, and the interaction between layers may deteriorate physically and chemically in various ways. Currently, our understanding of the degradation of organic electronic devices is far from complete. However, some key factors of the degradation mechanisms and the solutions to circumvent them and to enhance the stability of organic electronics have been identified.

Here, we have described and discussed the current development status of organic semiconductors and devices that are stable with respect to the given degradation factors in devices, such as oxygen, water, chemicals, heat, and light irradiation. The optimization of materials syntheses and thin-film preparation, and the tailoring of their functional properties and their morphology play important roles in the efficiency, performance, and long-term stability of the final devices. In addition, an overview of the applications of environmentally stable organic electronic materials in advanced architectures or systems was presented in Section 3 to describe the status of the progress in this field; water-stable chem/bio-organic sensors, liquid-type chemical sensors with enhanced durability and repeatability, and photolithographical patterning of organic semiconductors were covered as examples.

Most of the degradation mechanisms discussed in this review are common to many organic materials. The degradation mechanisms can be elucidated through diverse organic chemistry, irrespective of the specifics of the materials. In some cases, the different degradation mechanisms can be observed depending on the surrounding conditions. The degradation in I−V characteristics during the operation of devices and during storage under ambient conditions can also be related to various mechanisms and the combined effects of environmental factors including oxygen, water, chemicals, heat, and light. Consequently, both discriminating a dominant factor among...
the potential factors in a specific degradation and precisely estimating the lifetime of a specific organic electronic device are difficult. Nonetheless, the long-term stability of organic electronic materials and devices has improved gradually in recent years, and further progress in this research field will accelerate the commercialization of various organic electronic devices and extend the range of practical applications.

Acknowledgements

E.K.L. and M.Y.L. contributed equally to this work. This work was supported by the Center for Advanced Soft Electronics under the Global Frontier Research Program (Grant No: 2013M3A6A5073175) of the Ministry of Science, ICT and Future Planning, Korea. This work was also supported by the display research center program of Samsung Display Co., Ltd.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

environmental stability, organic electronics, organic field-effect transistors, organic light-emitting diodes, organic photovoltaics

Figure 21. a) Optical microscope image of X-PTPA-5 pixels patterned by photolithography. (37 × 37 μm squares with 5 μm of spacing; inset: schematic illustration of the process for photolithography). b) Photographic image of operating micropixel-patterned OLED (2 mA) based on photolithography Reproduced with permission.[52] Copyright 2014, Wiley-VCH. c) Optical microscopy image of patterned OFET arrays based on PTDDPPSe-SiC4 by photolithography. d) Hole mobility mapping of 10 × 10 flexible OFET arrays in ambient atmosphere. Reproduced with permission.[50] Copyright 2017, Wiley-VCH.

Received: June 30, 2017
Revised: August 7, 2017
Published online: