Organic heterostructures in organic field-effect transistors

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A heterojunction is an interface between two semiconductor materials of differing energy gap, and inorganic heterojunctions have been studied as the basis of electronic devices for over half a century. Organic heterojunctions have also been successfully applied in organic electronic devices over the past two decades. However, a theoretical understanding comparable to that of inorganic heterojunctions has yet to be developed for organic heterojunctions. Organic heterojunctions have been drawing increasing attention following the discovery of high conductivity in organic heterojunction transistors constructed with active layers of p-type and n-type thin crystalline films. In contrast with the depletion layers that form in inorganic heterojunctions, electron- and hole-accumulation layers have been observed on both sides of organic heterojunction interfaces. Heterojunction films with high conductivity have been used as charge injection buffer layers and as a connecting unit for tandem diodes. Ambipolar transistors and light-emitting transistors have also been realized using organic heterojunction films as active layers. This review highlights the organic heterojunction effect and the application of organic heterostructures in organic field-effect transistors. The category of heterojunction, including organic and inorganic semiconductor heterojunctions, is given on the basis of the work function of the constituent materials, and it is shown that a rich variety of organic heterojunctions are possible based on the formation of molecular pairs.

Considerable effort has been devoted to the development of low-cost, flexible, large-area organic electronics for consumer products over the past two decades [1–3]. Organic field-effect transistors (OFETs), important organic electronic devices, are of considerable interest due to their wide range of potential applications, including use as display drivers and in identification tags and sensors. Many methods have been developed to improve OFET performance by increasing mobility and the on/off ratio, and by reducing the threshold voltage. These improvements have been achieved through the synthesis of new organic semiconductor materials, improving the device structure, controlling the deposition of crystalline organic films and adopting various organic heterostructures. Recently, OFETs exhibiting mobility of the same order of magnitude as that of amorphous silicon FETs have been successfully demonstrated.

Organic heterostructures have been used in organic light-emitting diodes (OLEDs) and organic photovoltaic (OPV) cells to improve device performance. In a typical double-layer OLED structure [4], the organic heterojunction reduces the onset voltage and improves the illumination efficiency. Organic heterojunctions have also been used to improve the power conversion efficiency of OPV cells by an order of magnitude over single-layer cells [5]. Ambipolar OFETs, which require that both electrons and holes be accumulated and transported in the device channel depending on the applied voltage, were first realized by introducing organic heterostructures as active layers [6]. It is therefore clear that organic heterostructures have an important role in the continued development of organic electronic devices. The introduction of organic heterostructures has significantly improved device performance and allowed new functions in many applications, and so understanding the effects of the organic heterostructure is desirable and necessary.

There has been considerable focus on understanding the interfacial electronic structures of organic heterostructure consisting of amorphous

or semi-crystalline organic semiconductors [7–9]. Various models have been proposed to predict the alignment of the vacuum level and the interface dipole in certain organic heterojunctions [8,9], and a dependence of the interface dipole on the molecular orientation has been reported [10]. In crystalline organic semiconductors, the phenomenon of band bending [11,12] has been observed at organic/inorganic and organic/organic interfaces, and band transport, in which orbital-derived electronic bands are produced due to the overlap of the π -orbitals of adjacent molecules, has also been argued [13].

The recent discovery of high conductivity in heterojunction transistors constructed using thin crystalline films of p-type copper phthalocyanine (CuPc) and n-type copper-hexadecafluoro-phthalocyanine (F_{16} CuPc) as active layers has stimulated interest in organic heterojunctions [14–16]. Electron- and hole-accumulation layers have been observed in these devices on both sides of the organic heterojunction interface, which could give rise to interactions that lead to carrier redistribution and band bending. In this article, we review the organic heterojunction effect and the application of organic heterojunctions in OFETs. We show the dependence of the ambipolar transport on film morphology and device performance in organic heterojunction transistors, and discuss the application of bulk heterostructures in OFETs. The ambipolar transport behavior of organic heterojunctions presents the possibility of fabricating OLED FETs with high quantum efficiency, and a transistor structure for such applications is proposed. The application of organic heterostructures as a buffer layer to improve the contact between organic layers and metal electrodes is also discussed. Charge transport in organic semiconductors is influenced by many factors—the present review emphasizes the use of intentionally doped n- and p-type organic semiconductors, and primarily considers organic heterojunctions composed of crystalline organic films displaying band transport behavior.

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Figure 1. Device structures and current-voltage characteristics of CuPc/F₁₆CuPc heterojunction transistors and diodes. (a) Output characteristics of a CuPc/F₁₆CuPc heterojunction transistor and a single-component CuPc transistor. The heterojunction transistor operates in hole normally-on mode, which originates from the heterojunction effect of CuPc and F₁₆CuPc. Inset shows a schematic of the heterojunction transistor, with mobile free electrons and holes shown in the n- and p-type semiconductors, respectively. Modified after Ref. 14, reproduced with permission (© 2005 AIP). (b) Device configuration for planar heterojunction diodes and corresponding current-voltage curves: (i) single-CuPc device, (ii) CuPc/F₁₆CuPc diode with top-contact configuration, (iii) CuPc/F₁₆CuPc diode with sandwich-contact configuration and (iv) device with a layer of blended CuPc and F₁₆CuPc. Inset shows a schematic of the predicted interfacial electronic structure. Modified after Ref. 14, reproduced with permission (© 2005 AIP). (c) Current-voltage characteristic for a CuPc/F₁₆CuPc heterojunction diode. The device shows a reverse-rectifying property, which is opposite to that of conventional inorganic p-n junction diodes. Inset shows the corresponding device configuration. Modified after Ref. 15, reproduced with permission (© 2006 Elsevier).

The organic heterojunction effect

The charge accumulation effect of heterojunctions between organic semiconductors was discovered in an investigation of the high conductivity of CuPc/F₁₆CuPc transistors [14–16]. Experiments and ultraviolet photoemission spectroscopy (UPS) measurements confirmed that the high conductivity in this organic transistor is due to the accumulation of free charge at the heterojunction interfaces.

Normally-on OFETs with a CuPc/F₁₆CuPc heterojunction

In general, OFETs operate in accumulation mode. In hole-accumulation mode OFETs, for example, when a negative voltage is applied to the gate relative to the source electrode (which is grounded), the formation of positive charges (holes) is induced in the organic layer near the insulator layer. When the applied gate voltage exceeds the threshold voltage (V_T), the induced holes form a conducting channel and allow current to flow from the drain to the source under a potential bias (V_{DS}) applied to the drain electrode relative to the source electrode. The channel in OFETs contains mobile free holes, and the threshold voltage is the minimum gate voltage required to induce formation of the conducting channel. Therefore, OFETs operate in accumulation mode, or as a ‘normally-off’ device. However, in some case, OFETs can have an open channel under zero gate voltage, meaning that an opposite gate voltage is required to turn the device off. These devices are therefore called ‘normally-on’ or ‘depletion-mode’ transistors.

Normally-on characteristics have been observed in OFETs having a CuPc/F₁₆CuPc heterojunction [14,15]. As shown in Figure 1(a), the single-CuPc transistor and the CuPc/F₁₆CuPc transistor operate in the hole-accumulation mode and hole normally-on mode, respectively. The

Figure 2. Transfer characteristics of F₁₆CuPc/CuPc heterojunction transistors of various thicknesses. These devices show similar electron mobility, and an estimated hole-accumulation thickness of about 10 nm. Right panel is a schematic of the device showing the charge distribution in the double-layer heterojunction film. Modified after Ref. 15, reproduced with permission (© 2006 Elsevier).

source-drain current of the CuPc/F₁₆CuPc transistor is three orders of magnitude higher than that of the single-CuPc device under zero gate voltage, indicating that a conducting channel exists in the heterojunction transistor. Furthermore, the threshold voltage is –17 V in the single-CuPc device and +19 V in the heterojunction device, which also implies a change in the mode of device operation.

The charge-carrier type in the conducting channel for the normally-on CuPc/F₁₆CuPc heterojunction transistor is dependent on the bottom-layer semiconductor (organic layer near the insulator). When the bottom-layer semiconductor is p-type CuPc, CuPc/F₁₆CuPc heterojunction transistors operate in hole normally-on mode, whereas electron normally-on operation mode is obtained when the bottom-layer semiconductor is an n-type F₁₆CuPc semiconductor. These results demonstrate the abundance of mobile free electrons and holes in the F₁₆CuPc and CuPc layers, which is the origin of the normally-on characteristic (Figure 1(a), inset). Charge accumulation can lead to upward band bending in p-type CuPc and downward band bending in n-type F₁₆CuPc from the bulk to the interface (Figure 1(b), inset), which is different to the case for a conventional inorganic p–n junction. Similar band bending has also been observed by UPS in a ZnPc/F₁₆ZnPc system [12]. As free electrons and holes co-exist in CuPc/F₁₆CuPc heterojunction films, it is plausible that the films can transport either electrons or holes, depending on the gate voltage. In fact, after optimizing the film thickness and device configuration, ambipolar transport behavior has been observed [14,17].

Planar and vertical heterojunction diodes

Figure 1(b) shows the configuration of planar heterojunction diodes and the current-voltage curves for these devices. Carrier transport is parallel to the heterojunction interface, similar to the case for OFETs and directly reflecting the conductivity of the heterojunction film. The conductivity of diodes with a double-layer structure is about one order of magnitude higher than that for single-CuPc devices. According to the results for the normally-on transistors, the induced electrons and holes form a conducting channel in the films, leading to high conductivity. The mixed film of CuPc and F₁₆CuPc does not show high conductivity, possibly originating from the higher roughness of the interface, which could make it difficult to form a continuous channel for charge transport.

The induced electrons and holes in n- and p-type semiconductors form a space-charge region at the heterojunction interface, which can result in a built-in electric field from the p- to the n-type semiconductor. Such a build up is revealed in the electronic properties of diodes with this vertical structure [15]. Figure 1(c) shows the configuration of a CuPc/F₁₆CuPc heterojunction diode and the device’s current-voltage characteristic. The diode produces a small current under a positive potential bias and a large current under a negative bias. In contrast with an inorganic p–n diode, the CuPc/F₁₆CuPc heterojunction diode shows a reverse-rectifying characteristic. The positive bias strengthens band bending and restricts carrier flow, whereas under negative bias, the

Figure 3. Energy level diagrams for CuPc/ F_{16} CuPc heterojunctions. (a) Energy level diagram of CuPc/ F_{16} CuPc heterojunctions, obtained by UPS measurements. Modified after Ref. 16, reproduced with permission (© 2006 AIP). (b) Schematic diagram illustrating charge exchange and the distribution of charges in CuPc/ F_{16} CuPc heterojunction films. Energy levels are given before contact (prior to charge exchange).

applied electric field opposes the built-in field, resulting in a lowering of the potential barrier. Band bending is therefore weakened under negative bias, and current flow through the junction is assisted.

Charge accumulation thickness and shift of threshold voltage

As charge carriers accumulate on both sides of the CuPc/ F_{16} CuPc interface, the thickness of the accumulation layer is of interest. The existence of a built-in field at the heterojunction interface, which acts as a self-bias, allows the threshold voltage in OFETs to be modified by exploiting this effect [15]. In n-channel CuPc/ F_{16} CuPc heterojunction transistors (for example, Figure 2), the threshold voltage is correlated with the trap density in the F_{16} CuPc layer. The induced electrons can fill the traps; therefore, under the conditions of constant F_{16} CuPc thickness, the threshold voltage decreases with increasing electron density. Under neutral conditions, the number of induced holes in the CuPc layer is equal to that in the F_{16} CuPc layer, and increases with CuPc thickness tending toward saturation. Therefore, the threshold voltage of CuPc/ F_{16} CuPc heterojunction transistors can be reduced by increasing the thickness of the CuPc layer. The charge accumulation thickness can be estimated from the point at which the threshold voltage no longer changes with increasing CuPc thickness.

Figure 2 shows the transfer characteristics of F_{16} CuPc/CuPc heterojunction transistors with various layer thicknesses. For transistors with the same thickness of F_{16} CuPc, the threshold voltage decreases with increasing CuPc thickness, reaching saturation at a CuPc thickness of 10 nm. The hole-accumulation thickness in CuPc is thus estimated to be about 10 nm. The electron-accumulation thickness in F_{16} CuPc may also be around 10 nm due to the similarity of molecular packing in these crystalline films. The mobilities of these heterojunction transistors are approximately the same due to the similar slopes of the $I_{DS}^{1/2} \sim V_{GS}$ (I_{DS} , drain current; V_{GS} , gate voltage) curves, which indicates that the drain current is dominated by induced electrons in the F_{16} CuPc layer.

For a thinner F_{16} CuPc layer, such as in a F_{16} CuPc(3 nm)/CuPc(10 nm) device, the number of free electrons generated by the heterojunction effect exceeds the number of traps in the F_{16} CuPc layer, causing the free electrons to appear in the semiconductor layer and the device to operate in electron normally-on mode with a negative threshold voltage.

Interfacial electronic structure of CuPc/ F_{16} CuPc heterojunctions

As shown in Figure 3(a), UPS measurements [16] confirm exactly the experimental results, including the appearance of band bending, charge accumulation and the thickness of the space-charge region. The charge density is estimated to be $8.5 \times 10^{17} \text{ cm}^{-3}$ assuming a uniform distribution of charge in a thin layer near the heterojunction interface at a density six orders of magnitude higher than that in single-component films. The excessive carrier density results in the high conductivity of

Figure 4. Four types of semiconductor heterojunctions, classified by work function and conductivity type.

CuPc/ F_{16} CuPc heterojunction films. Recently, CuPc/ F_{16} CuPc heterojunction films fabricated by weak epitaxial growth were reported to show a Hall effect with high carrier mobility and a charge-accumulation layer thickness of 40 nm [18,19].

Formation of organic accumulation heterojunctions

The diffusion model proposed by Shockley for the silicon p–n junction has been widely used in inorganic semiconductor physics [20]. Electrons in n-type semiconductors and holes in p-type semiconductors are driven by the density gradient, inter-diffusing and recombining to produce a depletion junction between the n- and p-type semiconductors. The formation of an accumulation heterojunction is difficult to understand based on the diffusion model, because the electrons in the low-density region of CuPc must move to the high-density region of F_{16} CuPc.

The work function can be used to understand charge transfer at heterojunction interfaces. The work function represents the energy required to remove an electron from the semiconductor to the vacuum level and is the difference between the vacuum level and the Fermi level (E_F). According to UPS studies [16], the work function of CuPc is smaller than that of F_{16} CuPc; that is, the electron energy in the F_{16} CuPc layer is greater than in the CuPc layer. The electrostatic potential is therefore greater in the CuPc layer than in the F_{16} CuPc layer, and when the two semiconductors are brought into contact, electrons transfer

Figure 5. Three organic semiconductor heterojunctions. (a) Transfer characteristics of a ZnPc(9 nm)/C₆₀(40 nm) heterojunction transistor and the plot of $I_{DS}^{1/2} \sim V_{GS}$ for varying ZnPc thickness and constant C₆₀ thickness. ZnPc as the bottom layer semiconductor. The low off-current indicates that the heterojunction film has high resistance parallel to the heterojunction. Inset shows the device configuration. The threshold voltage increases with decreasing ZnPc thickness, which reveals the depletion heterojunction between ZnPc and C₆₀. (b) Energy band profile of the ZnPc/C₆₀ heterojunction. (c) Interfacial electronic structures of F₁₆CuPc and SnCl₂Pc heterojunctions from Kelvin probe force microscopy. Insets show the corresponding sample configuration, with the down and up triangles indicating the bulk potential of F₁₆CuPc and SnCl₂Pc, respectively. (d) Transfer characteristics of heterojunction OFETs with a constant 10 nm F₁₆CuPc layer and SnCl₂Pc layers of various thicknesses. Inset gives the device configuration and the molecular structure of SnCl₂Pc. (e) Typical capacitance–voltage curves of metal-oxide-semiconductor diodes with VOPc(10 nm)/Ph3(7 nm) layers (solid circle) and VOPc(10 nm)/Ph3(24 nm) layers (solid square) acting as active layers. (f) Electronic structure at the interface of Ph3 and VOPc. Arrow indicates the direction of the built-in field (E_{bi}). Modified after Refs 26 (c,d) and 27 (e,f), reproduced with permission (© 2008 AIP).

from CuPc to F₁₆CuPc, while holes migrate in the opposite direction. At equilibrium, the Fermi levels are aligned, which leads to electron accumulation in F₁₆CuPc and hole accumulation in CuPc (Figure 3(b)). Therefore, the work function plays an important role in the formation of a semiconductor heterojunction.

Types of semiconductor heterojunctions

The difference between the work functions of the two semiconductors constituting a heterojunction leads to various electron states in the space-charge region. The semiconductor heterojunction is also classified by the conductivity type of the two semiconductors forming the heterojunction. If the two semiconductors have the same type of conductivity, then the junction is called an isotype heterojunction; otherwise it is known as anisotype heterojunction. Therefore, according to the relative position of the work functions and the types of conductivity, the heterojunction can be classified into four categories, as shown in Figure 4.

Anisotype heterojunctions

Electrons and holes can be simultaneously accumulated and depleted on both sides of anisotype heterojunctions, due to the difference in the Fermi levels of the two components.

Depletion heterojunction. If the work function of the p-type semiconductor is greater than that of the n-type semiconductor ($\varphi_p > \varphi_n$), depletion layers of electrons and holes are present on either side of the

heterojunction, and the space-charge region is composed of immobile negative and positive ions (Figure 4(a)). This type of heterojunction is known as a depletion heterojunction, and most inorganic heterojunctions belong to this class of heterojunction, including the conventional p–n homojunction.

The material pair of ZnPc and C₆₀ is a typical photovoltaic system with well-known rectifying characteristics. Experiments on heterojunction transistors indicate that ZnPc and C₆₀ form a depletion heterojunction similar to inorganic p–n homojunctions. The device configuration and transfer characteristics of ZnPc/C₆₀ heterojunction transistors are shown in Figure 5(a). The heterojunction transistor has a low off-current, which indicates that mobile electrons and holes do not appear at the heterojunction interface. The heterojunction transistor operates in hole accumulation mode under a negative gate bias, with a hole mobility of $0.025 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The ZnPc/C₆₀ heterojunction is therefore not an accumulation heterojunction. The threshold voltage increases with decreasing ZnPc layer thickness (with respect to fixed C₆₀ thickness). These phenomena can be explained by the formation of a depletion heterojunction between ZnPc and C₆₀. Holes in the ZnPc layer are depleted, and the direction of the built-in electric field is opposite to that of the gate bias field in hole-accumulation mode. A larger gate bias $|V_{GS}|$ is therefore needed to overcome the built-in electric field in the ZnPc layer, which results in a high threshold voltage. The energy band profile of the ZnPc/C₆₀ heterojunction is shown in Figure 5(b). The space-charge region in the ZnPc layer near the heterojunction interface consists of negative ions and features a downward bend in its energy band, whereas the space-charge region in the C₆₀ layer near the

heterojunction interface consists of positive ions and has an upward bend in its energy band. The built-in field is directed from the n-type to the p-type semiconductor. The heterojunction film exhibits high resistance parallel to the interface due to the depletion of charges, and thus ZnPc/C₆₀ heterojunction transistors express normally-off characteristics.

Accumulation heterojunction. If the work function of the p-type semiconductor is smaller than that of the n-type semiconductor ($\varphi_p < \varphi_n$), the space-charge region consists of the induced free charges on either side of the heterojunction. This is referred to as an accumulation heterojunction, and is shown in Figure 4(b). Examples of this type of heterojunction include the CuPc/F₁₆CuPc and 2,5-bis(4-biphenyl)bithiophene (BP2T)/F₁₆CuPc heterojunctions [21–23]. Fewer cases are observed in inorganic heterojunctions.

Electron affinity is defined as the energy required to remove an electron from the bottom of a semiconductor's conduction band to the vacuum level. Electron affinity and the band gap (E_g) are intrinsic properties of semiconductor materials and are independent of doping, whereas the work function is dependent on doping. When two semiconductors with different electron affinities, band gaps and work functions are brought together to form a heterojunction, discontinuities form in the energy bands, thought to be due to the Fermi level alignment. In an ideal case of free interface states and vacuum level alignment (*i.e.* without an interface dipole), the discontinuities in the conduction band (ΔE_c) are equal to the difference in the electron affinities (χ) of the two semiconductors, *i.e.*,

$$\Delta E_c = \chi_1 - \chi_2 \quad (1)$$

This is known as the Anderson affinity rule [24]. The discontinuities in the valence band (ΔE_v) are given by $\Delta E_g - \Delta E_c$, where ΔE_g is the difference in band gap between the two semiconductors. The energy band profiles can be constructed according to this rule.

The work functions of n- and p-type semiconductors can be written as

$$\varphi_n = \chi_n + \delta_n \quad (2)$$

$$\varphi_p = \chi_p + E_{g,p} - \delta_p \quad (3)$$

where the n and p subscripts denote the n- and p-type semiconductors, respectively, and δ is the distance between the Fermi level and the valence (conduction) band for p-type (n-type) semiconductors. The formation of an accumulation heterojunction must satisfy the condition $\varphi_p < \varphi_n$ based on the Anderson affinity rule, such that

$$\chi_n - \chi_p > E_{g,p} - (\delta_n + \delta_p) \quad (4)$$

The energy levels of CuPc and F₁₆CuPc satisfy the above condition, and thus an accumulation heterojunction is formed in this system. For a homojunction between n- and p-type semiconductor layers in a single material with different doping densities, it is impossible to meet the conditions of equation (4) because the electron affinities are identical ($\chi_n = \chi_p$). Homojunctions therefore cannot exhibit the accumulation of free carriers. However, homojunctions always satisfy the relation $\varphi_p > \varphi_n$, and can thus form a depletion junction—the crystalline silicon p–n junction is a representative example. Additionally, homojunction characteristics have also been observed in organic semiconductors by doping ZnPc [25]. The characteristics of accumulation heterojunctions (CuPc/F₁₆CuPc) are compared with those for silicon p–n homojunctions in Table 1.

Isotype heterojunctions

Electron accumulation/depletion heterojunction. For n–n isotype heterojunctions comprising two n-type semiconductors with different work functions, assuming $\varphi_{n1} < \varphi_{n2}$, the semiconductor layer with φ_{n1} is

the electron depletion region (near the interface), and the semiconductor layer with φ_{n2} is the electron accumulation region. This heterojunction is known as an electron accumulation/depletion heterojunction, and is shown in Figure 4(c).

The effect of the n–n isotype organic heterojunction has been observed in a system composed of F₁₆CuPc and phthalocyanine tin(IV) dichloride (SnCl₂Pc) [26]. Kelvin probe force microscopy (Figure 5(c)) reveals that the energy band of SnCl₂Pc shows an upward bending of around 0.35 eV from the bulk to the interface, which indicates the presence of an electron-depletion region. In the F₁₆CuPc layer, there is a downward band bending of around 0.26 eV from the bulk to the interface, which indicates the presence of an electron-accumulation region. The F₁₆CuPc/SnCl₂Pc heterojunction is therefore an electron-accumulation/depletion heterojunction. For heterojunction transistors with fixed F₁₆CuPc thicknesses (bottom layer) and various SnCl₂Pc thicknesses, the threshold voltage decreases from 21.5 V (as in single-F₁₆CuPc transistors) to –30.1 V (Figure 5(d)) as the SnCl₂Pc thickness increases, because the trap states are filled by the accumulated electrons in the F₁₆CuPc layer. In the same way, the operational mode of the device also changes from accumulation mode to normally-on mode. The high electron field-effect mobility of 0.056 cm² V^{–1} s^{–1} is achieved in heterojunction transistors—twice that of single-F₁₆CuPc transistors.

Hole accumulation/depletion heterojunction. For p–p isotype heterojunctions ($\varphi_{p1} < \varphi_{p2}$), holes are depleted on the side containing the semiconductor with φ_{p2} , and are accumulated on the side containing the semiconductor with φ_{p1} . This is referred to as a hole-accumulation/depletion heterojunction (Figure 4(d)).

The characteristics of organic p–p isotype heterojunctions have been observed between two p-type semiconductors: 2,2';7',2''-terphenanthrenyl (Ph3) and vanadyl-phthalocyanine (VOPc) [27]. Capacitance–voltage measurements of metal-oxide-semiconductor diodes show that the holes and the electrons are accumulated and transported in the Ph3 and VOPc layers, respectively (Figure 5(e)). The space-charge region in the VOPc layer consists of mobile electron charges, and the band is bent downwards from the bulk to the interface. In the Ph3 layer, the band is bent upwards, which causes an accumulation of holes near the interface. An energy diagram for this situation is given in Figure 5(f).

Generally, VOPc is considered to be a hole-transport material. However, in the Ph3/VOPc heterojunction, not only are hole carriers in the VOPc layer depleted, but the VOPc layer may also exhibit strong band bending, which generates an inversion layer—an accumulation of electrons—near the heterojunction interface. As a result, electrons can be transported in the VOPc layer, making Ph3/VOPc p–p isotype

Table 1. Comparison of CuPc/F₁₆CuPc heterojunctions with silicon p–n homojunctions

	p-Type CuPc and n-type F ₁₆ CuPc heterojunction	Typical silicon p–n homojunction
Space-charge region	Mobile electrons in n-type layer; mobile holes in p-type layer	Immobile negative ions in p-type semiconductors; positive ions in n-type
Build-in potential	From p-type CuPc to n-type F ₁₆ CuPc	From n-type to p-type
Band bending	Upward in p-type layer; downward in n-type layer	Upward in n-type layer; downward in p-type layer
Conductivity ^a	High conductivity, due to mobile carriers in space-charge region	High resistance, due to immobile ions
Current–voltage characteristic ^b	Reverse-rectifying	Rectifying

^a Parallel to the heterojunction interface. The high conductivity of the organic heterojunction overcomes the limitations of single-semiconductor material devices, allowing better utilization in organic electronic devices.

^b Perpendicular to the heterojunction interface.

Figure 6. Dependence of performance of BP2T/F₁₆CuPc heterojunction OFETs on film morphology and heterojunction effect. (a) Dependence of electron and hole mobility on the thickness of BP2T films in organic heterojunction transistors. The thickness of F₁₆CuPc films was held constant (20 nm). These heterojunction devices operate at three modes: n-channel, ambipolar and p-channel. Solid lines are lines of best fit. Field-effect mobilities of the single-component transistors BP2T and F₁₆CuPc are also shown in the graph. (b–e) Atomic force microscopy topographical images of BP2T films of thickness 1 nm (b), 3 nm (c), 5 nm (d) and 20 nm (e). Areas are all 4 μm × 4 μm. Modified after Ref. 22, reproduced with permission (© 2008 Wiley-VCH Verlag GmbH & Co. KGaA).

heterojunctions into hole-accumulation/depletion (hole-accumulation/electron-accumulation) heterojunctions. Furthermore, heterojunction transistors with Ph3/VOPc heterojunction films as active layers show ambipolar transport behavior and a threshold voltage that is dependent on film thickness.

Double-layer heterostructure and ambipolar transport in OFETs

Ambipolar OFETs have been a research focus due to their possible applications in organic integrated circuits. Such circuits have many advantages, including better immunity, lower power dissipation, and simpler fabrication and circuit design. Dodabapular *et al.* achieved the first demonstration of ambipolar transport in OFETs using a bi-layer heterostructure of α-hexathienylene (α-6T) and C₆₀ as the active

layer [6]. The suitability of ambipolar organic transistors for organic integrated circuits was demonstrated for use in complementary metal-oxide-semiconductor (CMOS)-like inverters [21,28]. Ambipolar charge transport has also been realized in single-component OFETs [2,3,29,30], and is generally observed under a rigorous operation environment (*e.g.* measurements under high vacuum). An efficient and convenient method for achieving this is to combine high mobility n- and p-type organic semiconductors and use them as the active layer in the device [6,17,21,22,31]. However, in most materials tested so far, the mobility of electrons and/or holes in ambipolar OFETs is much lower than that of unipolar OFETs. Ambipolar transport is influenced by many factors, including the effective carrier injection from electrodes into organic layers and the transport of electrons and holes in the device channel.

Carrier injection in ambipolar OFETs

Ambipolar behavior indicates that electrons and holes are both being transported between the source and drain electrodes, which requires electrons and holes to be efficiently injected into the active layers of the ambipolar transistor; that is, for heterostructure FETs, electrons injected into the lowest occupied molecular orbital of n-type semiconductors, and holes injected into the highest occupied molecular orbital of p-type semiconductors. However, this will result in an injection barrier for at least one of the carriers. One way of solving this problem is to use asymmetrical source and drain contacts. Rost *et al.* reported a device with magnesium top and gold bottom contacts, which served to inject electrons into the n-type material N,N'-ditridecylperylene-3,4,9,10-tetracarboxylic diimide (PTCDI-C₁₃H₂₇, P13) and holes into the p-type material pentacene, respectively [32]. Gold and magnesium have high and low work functions, respectively, and were therefore expected to have low injection barriers for achieving efficient hole and electron injection. The device was shown to exhibit electron and hole mobilities of 3×10^{-3} and 1×10^{-4} cm² V⁻¹ s⁻¹, respectively.

An ambipolar pentacene transistor with both gold and calcium top contacts was realized by using a parallactic shadow mask effect during vapor deposition [33]. Devices with asymmetrical source and drain contacts have also been used to achieve electron and hole injection in light-emitting OFETs [34–36].

Film morphology and heterojunction effect in ambipolar OFETs

The morphology of organic films may strongly influence the characteristics of OFETs, and this is also true for organic ambipolar FETs, particularly double-layer heterojunction transistors. The morphology of the bottom layer determines the quality of the heterojunction interface and the carrier transport in these devices. The heterojunction effect will influence the characteristics of an ambipolar transistor when the film thickness is similar to the accumulated thickness of the charge carriers.

BP2T/F₁₆CuPc heterojunction OFETs illustrate the effect of film morphology and the heterojunction effect on device performance [22], as shown in Figure 6. The heterojunction transistors show three different operational modes—n-channel, ambipolar and p-channel regions—with varying BP2T film thickness. The evolution of the operational mode and the variation in carrier mobility with thickness of the organic film demonstrate the combined effects of film morphology and the heterojunction effect, and either of these may be the main contributing factor to device performance. Flat and continuous films in the first semiconductor layer can produce to a smooth heterojunction interface, and the charge carriers accumulated due to the heterojunction effect can fill the trap states in the organic layer and thereby improve carrier transport. The highest hole mobility for organic heterojunction transistors (0.12 cm² V⁻¹ s⁻¹), three times higher than that for single-component transistors, is achieved at a layer thickness of around 5 nm, where the BP2T film shows a layered structure with lamellar crystals. Hole transport in a continuous BP2T film is enhanced by the organic heterojunction effect, and thus high device performance can be obtained. The dependence of device performance on film morphology and the

Figure 7. Solution-processed bulk heterostructures. (a) Transfer characteristics of complementary-like inverters based on two identical ambipolar OC₁C₁₀-PPV/PCBM field-effect transistors. Depending on the polarity of the supply voltage V_{DD} , the inverter works in the first or third quadrant. A schematic of the inverter and the chemical structures of OC₁C₁₀-PPV and PCBM are given in the insets. Modified after Ref. 50, reproduced with permission (© 2003 E. J. Meijer). (b) The tapping mode atomic force microscopy picture of MDMO-PPV:PF:PCBM (1:1:2) blend on PVA, BCB and PVP, indicating large phase-separated film on PVA (around 200 nm) and less phase-separated film on BCB and PVP. Modified after Ref. 51, reproduced with permission (© 2005 AIP). (c) Chemical structures of diF-TESADT and TIPS-pentacene and a schematic of a top-gate structure device. PFBT, pentapentafluorobenzene thiol. Modified after Ref. 58, reproduced with permission (© 2009 Wiley-VCH Verlag GmbH & Co. KGaA).

heterojunction effect has been further demonstrated through the observation of ambipolar transport in organic heterojunction transistors with metal phthalocyanine or a phenanthrene-based conjugated oligomer as the first semiconductor and copper-hexadecafluoro-phthalocyanine as the second [37].

BP2T/F₁₆CuPc heterojunction transistors also show good air stability, high mobility and balanced ambipolar transport under optimized conditions [34]. The electron and hole field-effect mobilities are about $0.04 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, which is higher than the mobilities of the corresponding single-layer devices. CMOS-like inverters comprising two identical ambipolar OFETs show high gain, a good noise margin and good dynamic response.

Ambipolar transport has been demonstrated in many other bi-layer heterostructures, including C₆₀/pentacene [38–40], C₆₀/BP2T [41], C₆₀/2,6-diphenylbenzo[1,2-b:4,5-b'] diselenophene (DPh-BDS) [42], C₆₀/2,2',7,7'-tetra-(m-tolyl-phenylamino)-9,9'-spirobifluorene (spiro-TPD) [43], P13- α/ω -dihexyl-quaterthiophene (DH4T) [44, 45], P13- α/ω -dihexylsexithiophene (DH6T) [46], F₁₆CuPc- α/α' -dihexylsexithiophene (DH- α 6T) [47] and pentacene/perfluoropentacene [48].

Bulk heterostructures in OFETs

A bulk heterostructure consists of an intimate mixture of two different materials that are usually fabricated through solution-processing techniques, either from a single solution containing two organic soluble semiconductors, or from the co-evaporation of two organic small-molecular materials. Recently, organic bulk heterostructures have been widely used in OPV cells due to the expanded interface available for charge separation, which can overcome the limits of short exciton diffusion length in organic semiconductors. However, because the transport in OFETs is parallel to the substrate, many interfaces in bulk heterostructures may interrupt the carrier transport channel and thus enhance the scattering of carriers.

Solution-processed bulk heterostructures

Tada *et al.* suggested that spin-coating could be used to fabricate ambipolar OFETs with interpenetrating networks of p- and n-type semiconductors [49]. These ambipolar transistors were fabricated on an Si/SiO₂ substrate with finger-shaped, bottom-contact tin/gold electrodes, and

the effective electron and hole mobilities were very low—estimated to be 10^{-9} and $10^{-7} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively.

In 2003, Meijer *et al.* realized ambipolar transport in an interpenetrating network of n-type [6,6]-phenyl C₆₁-butyric acid methyl ester (PCBM) and p-type poly[2-methoxy-5-(3,7-dimethyloctyloxy)]-p-phenylene vinylene (OC₁C₁₀-PPV) [50]. Mixed solutions of PCBM and OC₁C₁₀-PPV were spin-coated on a hexamethyldisilazane modified Si/SiO₂ substrate with a ring-type bottom contact to eliminate parasitic leakage currents, and the completed devices were then annealed under vacuum. The interpenetrating networks were similar to those used in OPV cells, and exhibited field-effect mobilities of $7 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for holes and $3 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for electrons (Figure 7(a)). The authors also proposed the use of low-band-gap semiconductors for reducing the carrier injection barriers.

Singh *et al.* fabricated polymer ambipolar transistors with a blend film of three organic semiconductors [51]: poly[2-methoxy-5-(3,7-dimethyloctyloxy)]-1,4-phenylenevinylene (MDMO-PPV), poly(9,9-dioctyl-fluorenyl-2,7-diyl) end-capped with N,N-bis(4-methylphenyl)-4-aniline (PF), and PCBM (1:1:2 by weight) as active layers on different polymer dielectric layers. The results suggest a strong correlation between thin-film nanomorphology and ambipolar transport in field-effect devices (Figure 7(b)). Blended films on divinyltetramethyldisiloxanebis (benzocyclobutane) (BCB) and poly(4-vinyl phenol) (PVP) films without large phase-separated domains exhibit ambipolar transport, whereas films on polyvinyl alcohol (PVA) exhibit a phase-separated domain structure of around 200 nm with a nanocrystal-like film, which gives rise to unipolar transport properties.

Many other bulk heterostructures have shown ambipolar transport behavior, including blends of poly(2-methoxy-5-(2'-ethylhexyloxy))-1,4-phenylenevinylene (MEH-PPV) and C₆₀ [52], poly[2-methoxy-5-(3,7'-dimethyloctyloxy)]-1,4-phenylenevinylene (MDMO-PPV) and PCBM [53], CuPc and poly(benzobisimidazo-benzophenanthro-line) [54], P3HT and PCBM [55, 56], and thieno[2,3-b]-thiophene terthiophene polymer and PCBM [57].

Recently, Hamilton *et al.* fabricated high-hole-mobility transistors by spin coating a blend solution containing a small molecule p-type and an inert polymer (Figure 7(c)) [58]. A maximum hole mobility of $2.4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ was achieved in organic thin-film transistors from soluble blends of the fluorinated acene 5,11-bis(triethylsilyl)ethynyl anthradithiophene (diF-TESADT) and polytriarylamine (PTAA) with

Figure 8. Organic light-emitting field-effect transistors. (a) Molecular structure of α -5T and P13 and device structure of an OLET consisting of a co-evaporated thin film of α -5T and P13. Modified after Ref. 59, reproduced with permission (© 2004 AIP). (b) Schematic of an OLET device based on a DH4T–P13 bilayer. Modified after Ref. 44, reproduced with permission (© 2006 Wiley-VCH Verlag GmbH & Co. KGaA). (c) Fabricating an overlapping p–n heterostructure (P13/O-octyl-OPV5) inside the transistor channel by changing the tilt angle of the substrate during the sequential deposition process (schematic of n-type semiconductor deposition). Modified after Ref. 69, reproduced with permission (© 2006 AIP). (d) OLET device structure combined with organic SIT and OLED. Modified after Ref. 70, reproduced with permission (© 2003 Elsevier).

a top-gate device configuration. The two components show vertical phase separation, and the small molecule diF-TESADT migrates to the exposed interface, allowing large crystals to form within the channel region of the device. This provides efficient charge transport pathways, while the amorphous polymer PTAA acts as a matrix and aids uniformity and processing.

Co-evaporated bulk heterostructures

Bulk heterostructure thin films based on co-evaporated small organic molecules have also been explored in FETs. An ambipolar light-emitting transistor was realized using a co-evaporated thin film with p-type α -quinoxithiophene (α -5T) and n-type P13 as the active materials [59], with hole and electron mobility of $10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively. The hole mobility in α -5T was two orders of magnitude smaller than that in single-layer devices, whereas electron mobility in P13 was similar to that in single-layer devices. A co-evaporated film of pentacene and P13 also showed ambipolar operation on an organic dielectric, with a field-effect hole mobility of $0.09 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and a field-effect electron mobility of $9.3 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, close to those obtained for unipolar devices [60].

Furthermore, the bulk heterostructure of $\text{CuPc}/\text{F}_{16}\text{CuPc}$ [61], which has an interpenetrating network structure, can be controlled through the film morphology of each material. This can be achieved by varying the substrate temperatures, and the resulting heterojunction transistors have shown ambipolar transport with low mobility. Other co-evaporated bulk-heterostructure n- and p-type semiconductors include pentacene/perfluoropentacene [62], $\text{CuPc}/\text{F}_{16}\text{CuPc}$ [63], $\text{BP2T}/\text{C}_{60}$ [41] and $\text{CuPc}/\text{C}_{60}$ [64].

Bulk p–p heterostructures have also been prepared by co-evaporating either two metal phthalocyanine molecules or two sexithiophene derivatives. The blend films of CuPc/CoPc and CuPc/NiPc have been shown to be more efficient field-effect transistors than their single-component counterparts [65], which may be attributable to charge transfer between the materials and uniform film morphology due to their similar crystal structures. For blend films of DH6T and α -6T [66], the field-effect mobility and threshold voltage are located between those of the individual materials, and can be tuned by changing the constituent ratio. Single-component DH6T transistors exhibit high mobility and a large positive threshold voltage, whereas α -6T transistors exhibit low mobility and a negative threshold voltage.

Organic light-emitting field-effect transistors

In ambipolar transistors, electrons and holes are simultaneously accumulated and transported in the channel, resulting in an interface similar to that of a p–n junction. Light emission may be observed due to the recombination of electrons and holes in the joint region. As the location of the joint region in the channel is dependent on the gate and drain voltages, the emission region can be tuned.

The organic light-emitting transistor (OLET) was developed by Hepp *et al.* in 2003 [67]. The device operates in unipolar p-type mode, and produces green electroluminescence close to the gold drain electrode (electron injection). The emission region of their device, however, could not be modulated due to the unipolar operation mode. Balanced ambipolar transport is highly desirable for improving the quantum efficiency of OLETs, and is important to both single-component and heterostructure transistors. As single-component devices are beyond the scope of this review, here, we focus on heterostructure OLETs.

Rost *et al.* reported the first ambipolar OLET based on the heterostructure of a co-evaporated thin film of α -5T as the hole-transport material and P13 as the electron-transport material (Figure 8(a)) [59]. The light intensity was controlled by both the drain–source voltage and the gate voltage. Later, Loi *et al.* found that the carrier mobility and electroluminescent properties of OLETs based on the same materials can be tuned by changing the ratio of the two components [68]. The highest electroluminescent efficiency and balanced electron/hole mobilities were obtained for samples with equal concentrations of α -5T and P13. A higher concentration of α -5T resulted in non-light-emitting ambipolar FETs, whereas a higher concentration of P13 resulted in light-emitting unipolar n-channel FETs.

OLETs based on two-component layered structures can be realized by sequentially depositing p-type α , ω -dihexyl-quaterthiophene (DH4T) and n-type P13 (Figure 8(b)) [44]. The highest mobility and most balanced transport are obtained by growing DH4T in direct contact with the dielectric. Morphological analysis indicates a continuous interface between the two organic films, which is crucial for controlling the quality of the interface and the resulting optoelectronic properties of the OLETs.

An overlapping p–n heterostructure (P13/O-octyl-OPV5) can be confined inside the transistor channel by changing the tilt angle of the substrate during the sequential deposition process (Figure 8(c)) [69].

Figure 9. Organic heterostructures used in OFETs for improving the contact between the metal and organic layers: (a) CuPc/F₁₆CuPc, (b) pentacene/BP3T, (c) CuPc/pentacene, (d) C₆₀/pentacene.

The emission region (the overlapping region) is kept away from the hole and electron source electrodes, avoiding exciton and photon quenching at the metal electrodes. OLETs have also been realized in some alternative heterostructures, including a vertical combination static induction transistor with an OLED (Figure 8(d)) [70], top-gate-type OLETs similar to a top-gate static induction transistor or triode [71], and OLETs having a laterally arranged heterojunction structure and diode/FET hybrid [72].

Organic heterostructures as buffer layers in OFETs

Organic heterostructures have also been used as buffer layers in OFETs to improve the contact between the electrodes and the organic layers. Hajlaoui *et al.* inserted a thin layer of tetracyanoquinodimethane (TCNQ) between the electrodes and the semiconducting layer, resulting in better carrier injection and improved mobility [73]. A CuPc/F₁₆CuPc heterojunction with high conductivity has also been used as a buffer layer in OFETs to improve the contact between metal and organic semiconductors (Figure 9(a)) [74], improving the electron field-effect mobility from 4.2×10^{-2} to $6.6 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Other heterostructures have also been used to improve the contact, including pentacene/BP3T (Figure 9(b)) [34], CuPc/pentacene (Figure 9(c)) [75], C₆₀/pentacene (Figure 9(d)) [76], LuPc₂/CuPc [77] and 4,4',4''-tris-(3-methylphenylphenylamino)triphenylamine (*m*-MTDATA)/pentacene [78]. Moreover, a metal–organic charge-transfer salt, (tetrathiafulvalene) (tetracyanoquinodimethane), (TTF)(TCNQ), has been used as the source and drain contacts in OFETs [79]. The contact resistance of pentacene OFETs with (TTF)(TCNQ) electrodes is almost the same for bottom-contact and top-contact geometries, and comparable to top-contact gold transistors. Organic heterostructures have also been used to improve the contact in OPV cells, and as connecting units in stacked OPV cells and OLEDs.

Concluding remarks

Organic semiconductor heterojunctions have many rich varieties compared with inorganic semiconductor heterojunctions, and this is due to the abundance of organic semiconductor materials that can be produced by chemical synthesis or modification. Charge accumulation can induce high conductivity along the interface of a heterojunction, and this effect can overcome the disadvantage of the low conductivity of organic semiconductors. Organic field-effect transistors with normally-on operational mode, charge injection buffer layers and connecting units for tandem diodes have all been realized by utilizing the high-conductivity characteristics of organic semiconductor heterojunctions.

At present, the organic heterojunction effect still has few applications in organic electronic devices, particularly for organic field-effect transistors. Further research into organic heterojunctions promises to offer the potential for improving device performance and fabricating novel organic electronic devices.

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