

Chapter 2

Electrical Properties of Organic Semiconductor Heterojunctions

2.1 Current–Voltage Characteristics

The current–voltage (I - V) characteristics can be able to explain the electrical conduction mechanism of heterojunctions, also be generally used to determine the built-in junction potential and energy discontinuities in band edges at the interface of heterojunctions. The various heterojunction models for the I - V characteristics of heterojunctions based on inorganic semiconductors have been developed [1]. The I - V characteristics of organic semiconductor heterojunctions are often similar to those of inorganic heterojunctions. As a consequence, the theoretical models based on inorganic heterojunctions have been extended to organic heterojunctions [2]. However, the models derived for inorganic heterojunctions are based on energy band structure where thermal and optical excitation results in delocalized free charge carriers. In contrast, organic semiconductors are generally characterized by hopping transport and tightly bound, localized exciton states that require significant energy to dissociate into free charge carriers. Therefore, these descriptions do not rigorously apply to the physics of organic heterojunctions.

Forrest et al. derived the ideal diode equation specifically for the case of organic heterojunctions [3]. Explicitly treating polaron pair generation, recombination, and dissociation at the heterojunctions, they developed a current density–voltage (J - V) characteristic similar in form to the Shockley but differing in several key aspects. In this polaron pair (PP) model, it is assumed that the recombination and generation (if excitons are considered) govern the currents in the system. As shown in Fig. 2.1a, the average polaron pair separation, a_0 , thus defines the “volume” of the heterojunction region, the current outside of this region is unipolar with pure hole and electron currents flowing in the P and N bulk, respectively. Figure 2.1b shows the processes that occur within the organic heterojunction volume. The recombination of polaron pairs is described via

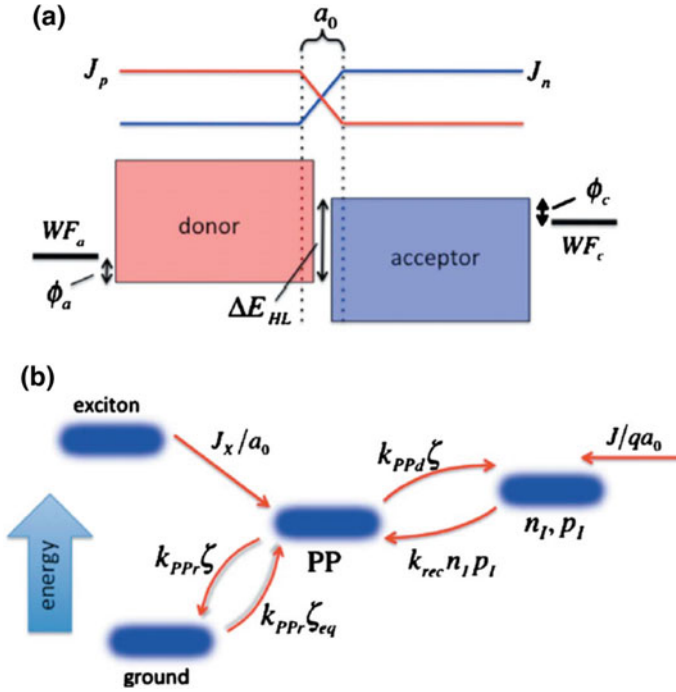


Fig. 2.1 **a** Energy level diagram showing the anode and cathode work functions, WF_a and WF_c , and their associated injection barriers ϕ_a and ϕ_c , respectively. The interfacial gap, ΔE_{HL} , is the energy difference between the highest occupied molecular orbital energy of the donor and the lowest unoccupied molecular orbital energy of the acceptor. Current is unipolar in the donor (J_p) and acceptor (J_n) layers and is determined from generation/recombination in the heterojunction region, roughly defined by the spatial extent, a_0 , of the polaron pair distribution at the interface. **b** Processes occurring within the heterojunction region. Excitons diffuse, with current density, J_x , to the heterojunction and undergo charge transfer to form polaron pairs. These may recombine, at rate k_{PPr} , or dissociate with rate, k_{PPd} , as determined by the Onsager–Braun model (C. L. Braun, *J. Chem. Phys.*, **80**, 4157 (1984)). The current density, J , contributes to the interfacial free electron (n_I) and hole (p_I) densities, which bimolecularly recombine to form polaron pairs at rate k_{rec} . Reprinted from [3]

$$\frac{J_x}{a_0} - k_{PPr}(\xi - \xi_{eq}) - k_{PPd}\xi + k_{rec}n_I p_I = 0 \quad (2.1)$$

and for free carriers:

$$k_{PPd}\xi - k_{rec}n_I p_I + \frac{J_x}{qa_0} = 0 \quad (2.2)$$

where steady-state conditions are assumed. Here, ξ is the PP density, J_x is the exciton current density diffusing to the interface, J is the charge current density flowing through the device, q is the electron charge, and n_I and p_I are the interfacial free electron and hole densities, respectively.

Solving Eq. (2.1) for the PP density and substituting the result into Eq. (2.2) give

$$J = qa_0 k_{\text{rec}} \left(\frac{k_{\text{PP}r}}{k_{\text{PP}d} + k_{\text{PP}r}} \right) \left(n_I p_I - \frac{k_{\text{PP}d}}{k_{\text{PP}d, \text{eq}}} n_{I, \text{eq}} p_{I, \text{eq}} \right) - q J_X \left(\frac{k_{\text{PP}d}}{k_{\text{PP}d} + k_{\text{PP}r}} \right) \quad (2.3)$$

where $\xi_{\text{eq}} = k_{\text{rec}} n_{I, \text{eq}} p_{I, \text{eq}} / k_{\text{PP}d, \text{eq}}$ is used from Eq. (2.2). The subscript *eq* indicates the thermal equilibrium value in the absence of bias or illumination. Similar to the Shockley equation, quasi-equilibrium is assumed. Hence, the carrier densities at the interface (n_I , p_I) and contacts (n_C , p_C) are related via

$$n_I = n_C \exp \left[\frac{\delta_A q (V_a - V_{bi})}{k_b T} \right] \quad (2.4a)$$

and

$$p_I = p_C \exp \left[\frac{\delta_D q (V_a - V_{bi})}{k_b T} \right] \quad (2.4b)$$

where $\delta_D + \delta_A = 1$ are the fractions of the potential dropped across the donor (D) and acceptor (A) layers, respectively. Here, V_a is the applied bias, k_b is Boltzmann's constant, and T is the temperature. These relations are strictly valid only when $J = 0$, but are a good approximation at low current when J is much smaller than either of its drift or diffusion components.

Use of Eq. (2.4a, b) in Eq. (2.3) yields

$$J = qa_0 k_{\text{rec}} n_C p_C (1 - \eta_{\text{PP}d}) \exp \left(-\frac{q V_{bi}}{k_b T} \right) \times \left\{ \exp \left(\frac{q V_a}{k_b T} \right) - \frac{k_{\text{PP}d}}{k_{\text{PP}d, \text{eq}}} \right\} - q \eta_{\text{PP}d} J_X \quad (2.5)$$

where $\eta_{\text{PP}d} = k_{\text{PP}d} / (k_{\text{PP}d} + k_{\text{PP}r})$ is the PP dissociation probability. Assuming detailed balance of the charge density adjacent to an injecting contact, then

$$n_C = f(F_c, T) N_{\text{LUMO}} \exp(-\phi_c / k_b T) \quad (2.6)$$

where N_{LUMO} is the density of states (DOS) at the acceptor LUMO, and F_c is the electric field at the cathode contact. The analogous relation involving the injection barrier, ϕ_a , (see Fig. 2.1a) exists for holes at the anode with N_{HOMO} as the DOS at the donor HOMO. The term $f(F_c, T)$ is dominated by Schottky barrier lowering, which can be neglected since it is near unity except for the case of high field and/or low temperature here. Thus, the ideal diode equation for an organic heterojunction in the absence of traps can be obtained

$$\begin{aligned}
J &= qa_0 k_{\text{rec}} n_C p_C N_{\text{HOMO}} N_{\text{LUMO}} (1 - \eta_{\text{PPd}}) \exp\left(-\frac{E_{\text{HL}}}{k_b T}\right) \\
&\times \left\{ \exp\left(\frac{qV_a}{k_b T}\right) - \frac{k_{\text{PPd}}}{k_{\text{PPd,eq}}} \right\} - q\eta_{\text{PPd}} J_X \\
&= J_{s0} \left\{ \exp\left(\frac{qV_a}{k_b T}\right) - \frac{k_{\text{PPd}}}{k_{\text{PPd,eq}}} \right\} - q\eta_{\text{PPd}} J_X
\end{aligned} \tag{2.7}$$

where $\Delta E_{\text{HL}} = \phi_a + \phi_c + qV_{bi}$ from Fig. 2.1a.

Under forward bias, k_{PPd} is similar to or less than $k_{\text{PPd,eq}}$, and the current density increases exponentially with an ideality factor $n = 1$. In this case, Eq. (2.7) reduces to the familiar

$$J = J_{s0} \left\{ \exp\left(\frac{qV_a}{k_b T}\right) - 1 \right\} - q\eta_{\text{PPd}} J_X \tag{2.8}$$

which is frequently used to model organic heterojunction solar cells. As expected, the photocurrent is directly proportional to the PP dissociation efficiency, which diminishes with increasing forward bias.

It is well-known that the significant molecular disorder of organic semiconductors leads to a broad density of states with an approximately Gaussian energetic distribution at the HOMO and LUMO levels [4]. Evidence also suggests that ground-state interactions between the donor and acceptor further broaden this distribution near the heterojunction interface [5]. The low-energy tail of the DOS can be modeled as an exponential distribution of traps [6]. This changes the kinetics of recombination at the interface and introduces an ideality factor $n > 1$ in the diode equation.

Assuming an exponential trap distribution with characteristic trap temperature, $T_{t,A}$, in the acceptor, the trapped (n_t) and free (n) electron densities are related approximately via

$$n_t \approx H_A \exp\left(\frac{E_{Fn} - E_{\text{LUMO}}}{k_b T_{t,A}}\right) \approx H_A \left(\frac{n}{N_{\text{LUMO}}}\right)^{1/l_A} \tag{2.9}$$

where H_A is the density of trap states at the acceptor LUMO, E_{Fn} is its electron quasi-Fermi energy, E_{LUMO} is the LUMO energy of the acceptor, and $l_A = T_{t,A}/T$. A similar relationship holds for the trapped hole density, p_t , in the donor. Assuming that the trapped carrier density significantly exceeds the free carrier density, Eq. (2.3) becomes

$$\begin{aligned}
J &= qa_0 \left(\frac{k_{\text{PPr}}}{k_{\text{PPd}} + k_{\text{PPr}}} \right) \left\{ k_{\text{rec},n} \left(n_I p_I - \frac{k_{\text{PPd}}}{k_{\text{PPd,eq}}} n_{I,\text{eq}} p_{I,\text{eq}} \right) \right. \\
&\quad \left. + k_{\text{rec},p} \left(p_I n_{II} - \frac{k_{\text{PPd}}}{k_{\text{PPd,eq}}} p_{I,\text{eq}} p_{II,\text{eq}} \right) \right\} - qJ_X \left(\frac{k_{\text{PPd}}}{k_{\text{PPd}} + k_{\text{PPr}}} \right)
\end{aligned} \tag{2.10}$$

where recombination now occurs primarily at trap states, and $k_{\text{rec},n}$ and $k_{\text{rec},p}$ are the rate constants describing recombination at the heterojunction between a free electron in the acceptor (n_I) with a trapped hole in the donor (p_H), and vice versa.

Using Eqs. (2.4a, b), (2.9), and (2.10) gives

$$\begin{aligned} J = & qa_0(1 - \eta_{\text{PPd}}) \left\{ k_{\text{rec},n} N_{\text{LUMO}} H_D \exp(-\alpha_D/k_b T) \right. \\ & \times \left[\exp(qV_a/n_D k_b T) - \frac{k_{\text{PPd}}}{k_{\text{PPd,eq}}} \right] + k_{\text{rec},n} N_{\text{LUMO}} H_A \\ & \times \exp(-\alpha_D/k_b T) \left[\exp(qV_a/n_A k_b T) - \frac{k_{\text{PPd}}}{k_{\text{PPd,eq}}} \right] \left. \right\} - q\eta_{\text{PPd}} J_X \end{aligned} \quad (2.11a)$$

where

$$\alpha_D = \frac{\Delta E_{\text{HL}}}{n_D} + \frac{l_D - 1}{l_D} (\delta_D \phi_c - \delta_A \phi_a) \quad (2.11b)$$

and

$$\alpha_A = \frac{\Delta E_{\text{HL}}}{n_A} + \frac{l_A - 1}{l_A} (\delta_A \phi_a - \delta_D \phi_c) \quad (2.11c)$$

The ideality factors n_A and n_D are given by

$$n_A = \frac{l_A}{\delta_D(l_A - 1) + 1} \quad (2.12a)$$

and

$$n_D = \frac{l_D}{\delta_A(l_D - 1) + 1} \quad (2.12b)$$

More compactly, Eq. (2.11a–c) becomes the ideal diode equation in the presence of traps

$$\begin{aligned} J = & J_{sD} \left[\exp(qV_a/n_D k_b T) - \frac{k_{\text{PPd}}}{k_{\text{PPd,eq}}} \right] \\ & + J_{sA} \left[\exp(qV_a/n_A k_b T) - \frac{k_{\text{PPd}}}{k_{\text{PPd,eq}}} \right] - q\eta_{\text{PPd}} J_X \end{aligned} \quad (2.13a)$$

which simplifies to

$$J = J_{sD} [\exp(qV_a/n_D k_b T) - 1] + J_{sA} [\exp(qV_a/n_A k_b T) - 1] - q\eta_{\text{PPd}} J_X \quad (2.13b)$$

when $k_{PPd} \leq k_{PPd,eq}$ under forward bias (cf. Eq. (2.8)). Here J_{sD} and J_{sA} are the dark saturation currents given by the prefactors in Eq. (2.11a–c).

The ideal diode equation (2.13a, b) is modified to include the effect of series resistance, and R_s can be written as

$$J = J_{sD}[\exp(q(V_a - JR_s)/n_D k_b T) - 1] + J_{sA}[\exp(q(V_a - JR_s)/n_A k_b T) - 1] - q\eta_{PPd}J_X \quad (2.14)$$

Figure 2.2a shows a set of dark J - V characteristics calculated using Eq. (2.11a–c) over the temperature range from 120 to 296 K. The used parameters are listed in Table 2.1 for organic semiconductors. The series resistance of $R_s = 1 \Omega \text{ cm}^2$ (in which case, V_a is replaced by $V_a - JR_s$) and assumed that most of the potential is dropped across the donor layer, resulting in different ideality factors according to Eq. (2.12a–c). Figure 2.2b gives the ideality factors and their associated dark saturation currents. It can be seen that both ideality factors increase with temperature decrease, and the quantity $n \ln(J_s)$, where the argument in the logarithm is implicitly normalized to 1 A/cm^2 , is nonlinear when plotted versus $1/k_b T$. This contrasts with previous analyses based on the Shockley equation [2], which predict a linear relationship for this quantity with a slope equal to $-\Delta E_{HL}/2$.

Figure 2.3a, b shows the forward bias J - V characteristics of both ITO/CuPc/C₆₀/BPhen/Al and ITO/SubPc/C₆₀/BPhen/Al devices taken over a range of temperatures from 114 to 296 K. The fitting curves by Eq. (2.14) are also given. It can be seen

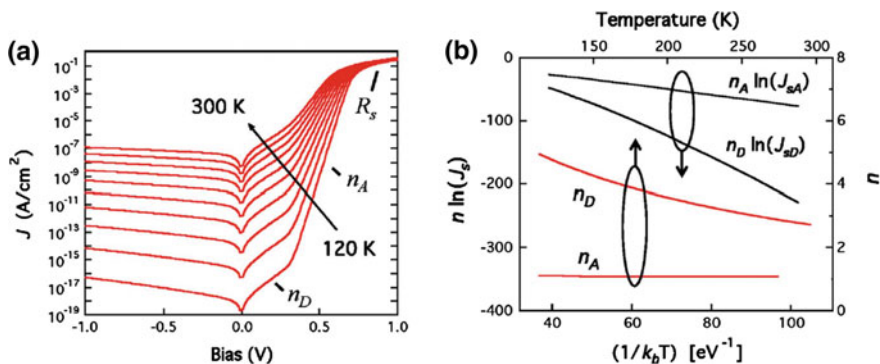


Fig. 2.2 **a** Calculated dark J - V characteristics over the temperature range from 120 to 300 K in 20 K increments using Eq. (2.11a–c). The slope in reverse bias is due to the field-dependent dissociation of thermally generated polaron pairs. In forward bias, three regions are apparent. At $V_a < 0.3 \text{ V}$, trap-limited recombination involving free acceptor electrons and trapped donor holes dominates, and the slope is proportional to the donor ideality factor, n_D . At higher bias, the inverse process dominates (i.e., free donor holes recombine with trapped acceptor electrons) and the slope is proportional to the acceptor ideality factor, n_A . Series resistance (R_s) limits the current at $V_a > 0.8 \text{ V}$. **b** Diode parameters n and $n \ln(J_s)$ corresponding to the dark currents in (a). Both ideality factors increase with decreasing temperature, though n_A does so only slightly. Reprinted from [3]

Table 2.1 Model parameter values for calculation here. Reprinted from [3]

Parameter	Value
Donor thickness = acceptor thickness	40 nm
ΔE_{HL}	1.2 eV
v_{bi}	0.5 V
$T_{t,a} = T_{t,D}$	1000 K
$H_A = H_D$	$10^{18}/\text{cm}^3$
$N_{\text{HOMO}} = N_{\text{LUMO}}$	$10^{21}/\text{cm}^3$
δ_A	0.1
a_0	1.5 nm
k_{ppr}	1 / μs
$k_{\text{rec},n} = k_{\text{rec},p} = q\mu/\varepsilon$	$\varepsilon/\varepsilon_0 = 3, \mu = 10^{-3} \text{ cm}^2/\text{V s}$
R_s	1 $\Omega \text{ cm}^2$

that Eq. (2.14) fits the experimental data over the entire temperature range well, demonstrating the validity of Eq. (2.14) to accurately describe the J - V characteristics of organic heterojunction-based devices.

As we know, a notable feature of inorganic heterojunctions is the rectifying characteristics, i.e., the current is very small at reverse voltage, until reverse breakdown. This is the basic property of a depletion-type heterojunction. As shown in Figs. 2.2a and 2.3, organic heterojunctions with depletion space charge region also show the same rectifying characteristics and can be explained well by the modified Shockley Eq. (2.14). However, the heterojunctions formed by two organic semiconductors become accumulation-type junction, and the J - V characteristics cannot be modeled well by thermionic emission processes. For the case of accumulation junctions, the electrons accumulate at the N -type semiconductor, and the holes accumulate at the P -type semiconductor; therefore, a large number of free

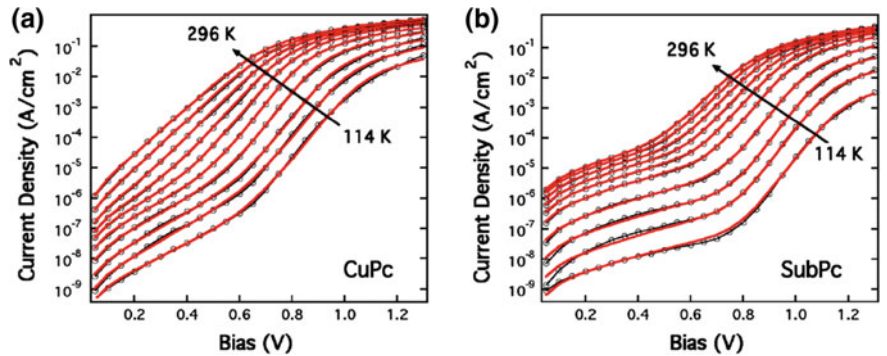


Fig. 2.3 Dark current density versus forward voltage for **a** CuPc/C₆₀ and **b** SubPc/C₆₀ devices recorded for $T = 296, 275, 247, 218, 193, 171, 155, 145, 128$, and 114 K. **Bold red lines** indicate fits to Eq. (2.14) in the text. *Thin black lines* connect the data points. Reprinted from [3]

charge carriers exist in the space charge region [7], and besides the large current property at forward bias, it is experimentally shown [8] that the reverse bias also produces large current. Figure 2.4 shows the J - V characteristics of ITO/MoO₃ (3 nm)/20 wt% MoO₃:TAPC (50 nm)/m-MTDATA (15 nm)/HAT-CN (15 nm)/3 wt% Cs₂CO₃:BPhen (50 nm)/Cs₂CO₃ (1 nm)/Al heterojunction device 1 and ITO/MoO₃ (3 nm)/20 wt% MoO₃:TAPC (50 nm)/m-MTDATA (15 nm)/3 wt% Cs₂CO₃:BPhen (50 nm)/Cs₂CO₃ (1 nm)/Al non-heterojunction device 2. It can be seen that m-MTDATA/HAT-CN heterojunction device 1 produces a highly symmetric current property at forward and reverse bias, and the current is much larger than that of non-heterojunction device 2. As shown, the J - V characteristic of non-heterojunction device 2 can be well described by Shockley equation, where the slope of the linear region corresponds to the ideality factor $n = 2$, typical Shockley diode property. However, heterojunction device 1 does show a clear linear straight region in J - V characteristic, indicating that the electrical property cannot be explained only by using thermionic emission. To elucidate this, the reverse bias J - V characteristics of heterojunction device 1 under different temperatures were tested. As shown in Fig. 2.5, a relation of $\ln(J) \sim T$ is obtained well, a typical tunneling process [9]. This also indicates that the charge generation of m-MTDATA/HAT-CN heterojunction is a tunneling process.

The tunneling equation for heterojunctions under reverse bias was proposed by Riben et al. as follows [10]

$$J_r = G_0 V_a \exp \left[-U(V_d + V_a)^{-1/2} \right] \quad (2.15)$$

where J_r is the reverse current density, G_0 is a constant determined by the nature of the material, U is a linear variable of temperature, V_d is the built-in potential, and V_a is the applied reverse voltage (written as a positive value). Initially, the Zener tunneling equation well described the electron tunneling from the valence band of the P -type semiconductor to the conduct band of the N -type semiconductor in staggered gap-type heterojunctions. Figure 2.6 gives the double logarithm J - V plot of m-MTDATA/HAT-CN heterojunction device 1 under various temperatures. The curves are well fitted by Eq. (2.15) at high voltage region, further demonstrating

Fig. 2.4 J - V characteristics of heterojunction device 1 and non-heterojunction device 2. The fitting curves by tunnel (red solid line) and thermionic emission (black solid line) models are given. Reprinted from [8]

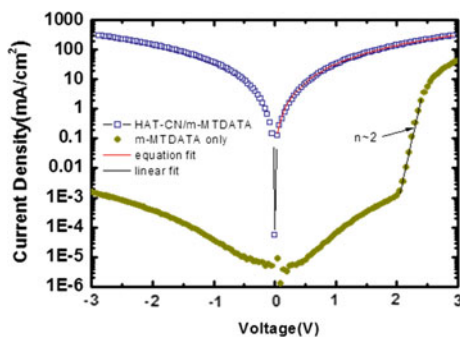


Fig. 2.5 Temperature–current density dependence of heterojunction device 1 under fixed voltages of 0.5 and 1 V. Reprinted from [8]

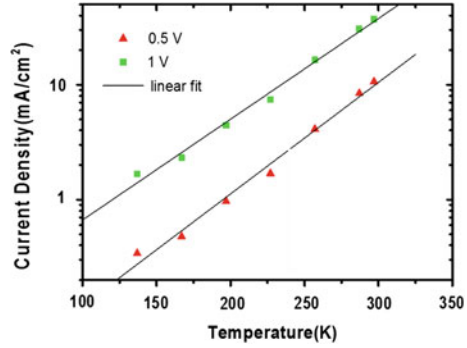
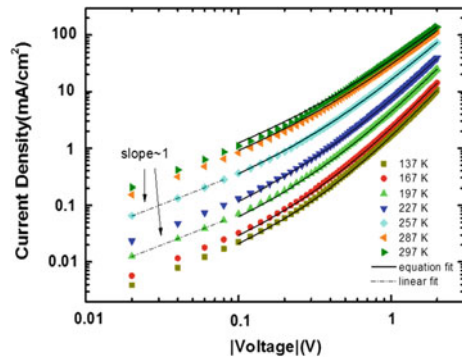


Fig. 2.6 J - V characteristics of m-MTDATA/HAT-CN heterojunction device 1 at different temperatures. The fitting curves by Eq. (2.15) are given by *solid lines*. The reverse voltages are absolute values. Reprinted from [8]



that the current process of m-MTDATA/HAT-CN organic heterojunction is Zener tunneling.

It can be seen that the current at high voltage region agrees with the tunneling model, but deviates at low bias region. The deviation has been attributed the contribution of thermionic emission, and the fact that the Fermi–Dirac distribution is not a step function at temperatures higher than absolute zero [11, 12]. Therefore, a modified Fowler–Nordheim (F-N) tunneling model is described by [12]

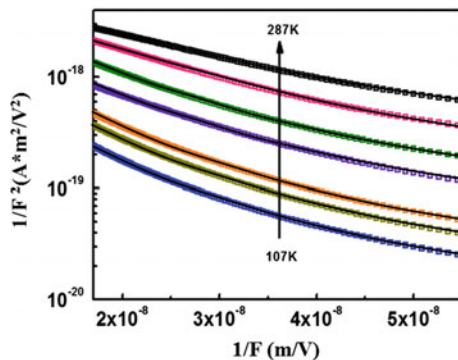
$$\ln(I/F^2) = -\frac{P_1}{F} + \ln\left(\frac{P_2}{F}\right) - \ln\left(\sin\left(\frac{P_3}{F}\right)\right) \quad (2.16)$$

where P_1 , P_2 , and P_3 are constant parameters in a constant temperature measurement. If the thickness cannot be determined, then the Eq. (2.16) can be written as

$$\ln(I/V^2) = -\frac{\tilde{P}_1}{V} + \ln\left(\frac{\tilde{P}_2}{V}\right) - \ln\left(\sin\left(\frac{\tilde{P}_3}{V}\right)\right) \quad (2.17)$$

Equation (2.16) has well suited for fitting the current characteristics of pentacene/C₇₀organic heterojunction-based devices at different temperatures [13].

Fig. 2.7 Tunneling current characteristics of ITO/MoO₃ (3 nm)/TAPC: MoO₃ (30%, 50 nm)/pentacene (30 nm)/C₇₀ (30 nm)/Li₂CO₃ (1 nm)/Bphen: Li₂CO₃ (3%, 45 nm)/Li₂CO₃ (1 nm)/Al at different temperatures. The black solid lines are the fitting curves by Eq. 2.16. Reprinted from [13]



As shown in Fig. 2.7, the modified F-N tunneling model of Eq. (2.16) fits quite well with the experimental data at all temperatures, indicating that the charge generation processes in pentacene/C₇₀ organic heterojunction are also tunneling.

2.2 Capacitance–Voltage Characteristics

The capacitance–voltage (*C-V*) characteristics are also an important means to characterize the electrical properties of a heterojunction. The measurement of the junction capacitance ($C = dQ/dV$) as a function of reverse bias is often used as a powerful experimental method for the analysis of the space charge region potential and the charge distribution in a heterojunction.

When two semiconductors with opposite conductivity contact, there occurs charge transfer between two semiconductors until the Fermi levels are equalized. This causes the formation of a space charge layer on both sides of the interface. If no considering interface states, the expression of junction capacitance per unit area of an abrupt anisotype heterojunction can be written as [14]

$$C = \left[\frac{q\epsilon_n\epsilon_p N_n P_p}{2(\epsilon_n N_n + \epsilon_p P_p)} \right]^{1/2} (V_D - V)^{-1/2} \quad (2.18)$$

where N_n and N_p are the donor and acceptor concentrations in, and ϵ_n and ϵ_p are the dielectric constants of, *N*- and *P*-type semiconductors, respectively, V_D is the built-in junction potential, V is the applied voltage and q is the electronic charges. It is clear that a plot of C^{-2} against applied reverse voltage V is linear and its extrapolated intercept on the voltage axis gives the built-in junction potential V_D .

If considering interface states and electric dipole, then the junction capacitance per unit area of an abrupt anisotype heterojunction can be expressed as [15]

$$C = B_1 \left[1 + f(V) \frac{qQ_{Is}}{dV} + \frac{q\phi_m}{dV} \right] (V_D - V - \phi_m - B_2 Q_{Is}^2)^{-1/2} \quad (2.19a)$$

where

$$f(V) = 2B_2 Q_{Is} + 2(B_2 \epsilon_n N_n / \epsilon_p P_p)^{1/2} (V_D - V - \phi_m - B_2 Q_{Is}^2)^{-1/2} \quad (2.19b)$$

$$B_1 = \left[\frac{q\epsilon_n \epsilon_p N_n P_p}{2(\epsilon_n N_n + \epsilon_p P_p)} \right]^{1/2} \quad (2.19c)$$

$$B_2 = [2q(\epsilon_n N_n + \epsilon_p P_p)]^{-1} \quad (2.19d)$$

and Q_{Is} and ϕ_m are the net charge on the interface states and the electric dipole, respectively.

If the net charge on the interface states is independent on the applied voltage and the electric dipole is absent, then the expression (2.19) reduces to

$$C = \left[\frac{q\epsilon_n \epsilon_p N_n P_p}{2(\epsilon_n N_n + \epsilon_p P_p)} \right]^{1/2} (V_D - V - B_2 Q_{Is}^2)^{-1/2} \quad (2.20)$$

It can be seen that this expression also has a linear relation of C^{-2} versus V similar to Eq. (2.18), but the extrapolated intercept of this plot on the voltage axis gives rise to an apparent built-in junction voltage ($V_D - B_2 Q_{Is}^2$) instead of V_D .

Ma et al. studied the capacitance characteristics of pentacene/C₇₀ organic heterojunction [13]. The current–capacitance–voltage characteristics of pentacene/C₇₀ organic heterojunction-based device are shown in Fig. 2.8. It can be seen that in the forward direction, the capacitance begins to drop drastically at about 0.5 V because of the significant injection and recombination of carriers, which just corresponds to the exponential increase of the current. Similarly, the breakdown of current and the severe drop of capacitance both happen at the reverse voltage of

Fig. 2.8 Current–capacitance–voltage characteristics of ITO/MoO₃ (3 nm)/TAPC: MoO₃ (30%, 50 nm)/pentacene (30 nm)/C₇₀ (30 nm)/Li₂CO₃ (1 nm)/Bphen: Li₂CO₃ (3%, 45 nm)/Li₂CO₃ (1 nm)/Al device at 287 K. Reprinted from [13]

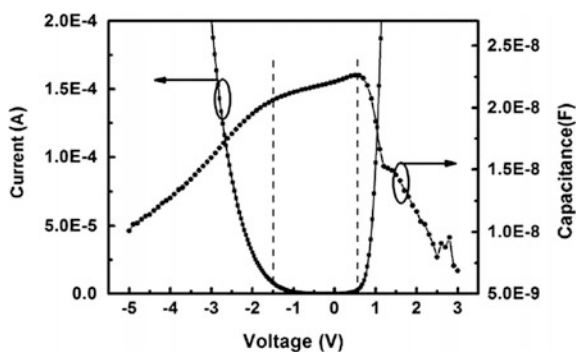
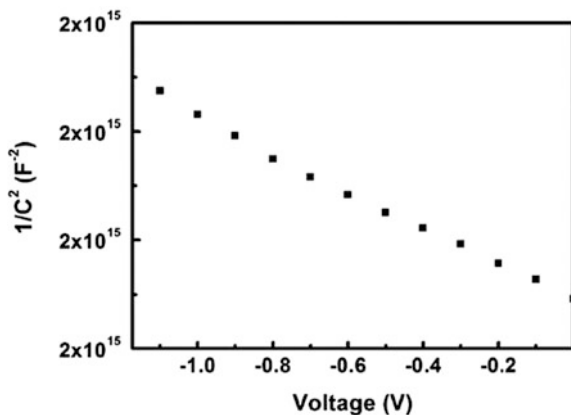


Fig. 2.9 $1/C^2$ against V relation of ITO/MoO₃ (3 nm)/TAPC: MoO₃ (30%, 50 nm)/pentacene (30 nm)/C₇₀ (30 nm)/Li₂CO₃ (1 nm)/Bphen: Li₂CO₃ (3%, 45 nm)/Li₂CO₃ (1 nm)/Al device at 1 kHz. Reprinted from [13]



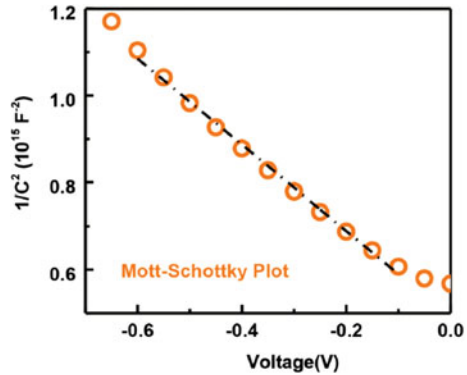
about 1.5 V, which should be caused by the large amount of generated charges in the pentacene/C₇₀ heterojunction. It should be noticed that the large reverse current should mainly come from the charge generation instead of the injection from the electrode under reverse voltage, because the doped hole and electron transport layer could effectively block the injection of electrons and holes, respectively. Figure 2.9 gives $1/C^2$ against V relation of pentacene/C₇₀ organic heterojunction-based device. A linear relation of the inverse capacitance square versus the reverse voltage is clearly seen, which corresponds well with the Mott–Schottky relation [16]. Similar to Eq. (2.18), Mott–Schottky relation is generally written as

$$\frac{1}{C^2} = \frac{2(V_b - V)}{eN_A \epsilon_r \epsilon_0 A^2} \quad (2.21)$$

where V_b is the built-in voltage, N is the density of free charge carriers, ϵ_0 is the permittivity of free space, ϵ_r is the relative dielectric constant, and A is the active area. Therefore, the density of free charge carriers N in space charge region could be calculated from the slope, in the range of $10^{19}/\text{cm}^3$, which is quite high for organic heterojunctions [17]. The high free carrier density guarantees the large tunneling current density and thus the possibility of efficient charge generation in pentacene/C₇₀ organic heterojunction.

It has been proven experimentally that organic bulk heterojunctions possess the property of high conductivity [18], not only as a highly efficient charge generation layer (CGL) to fabricate high-efficiency tandem OLEDs, but also as excellent hole-transporting layer to realize the large injection of holes in OLEDs [19]. It can be seen that the high conductivity of organic bulk heterojunctions may be well studied by C - V measurement. Figure 2.10 shows $1/C^2$ against V relation of HAT-CN/HAT-CN:TAPC/TAPC organic heterojunction-based device. According to the classical Mott–Schottky theory, the relation of C versus V for HAT-CN/HAT-CN:TAPC/TAPC structure device can be written as

Fig. 2.10 Mott–Schottky plot of ITO/HAT-CN (10 nm)/HAT-CN:TAPC (30 wt%) (100 nm)/TAPC (10 nm)/Al device at 5 kHz. Reprinted from [19]

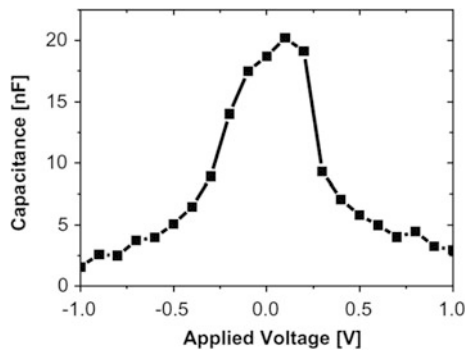


$$\frac{1}{C^2} = \frac{2(V_b - V)}{eN_A\epsilon_r\epsilon_0 A^2} + \frac{d_i^2}{(\epsilon_r\epsilon_0 A)^2} \quad (2.22)$$

where e is the charge of one electron, d_i is the thickness of intrinsic layer, N_A is the density of ionized free charges. Thus, N_A is estimated to be in the range of $10^{19}/\text{cm}^3$ by Eq. (2.22), which is several orders higher than a typical intrinsic organic semiconductor (usually less than $10^{15}/\text{cm}^3$) [20]. This high free charge density does confirm that HAT-CN/HAT-CN:TAPC/TAPC organic heterojunction efficiently generates the more free charges, thus making it highly conductive and preferable for hole transporting.

The C - V measurement can also be used to well determine the electronic structures and energy level alignment at the interface of organic heterojunctions by the extracted data of space charge width, built-in potentials, and vacuum-level shift information [21]. Kim et al. studied the interface energy level alignment of a doped organic heterojunction using this method [22]. Figure 2.11 gives the C - V characteristic of ITO/15 mol% Cs_2CO_3 -doped BPhen (20 nm)/HAT-CN (20 nm)/Al device. The large capacitance implies that the depletion width in the junction is very

Fig. 2.11 C - V characteristic of ITO/ Cs_2CO_3 -doped BPhen/HAT-CN/Al device (measured at 1 kHz, and an applied AC bias voltage of 10 mV). Reprinted from [22]



narrow. The device may be simply assumed as a planar capacitor. Therefore, the depletion width (W) is written as

$$W = \varepsilon_r \varepsilon_0 \frac{A}{C_0} \quad (2.23)$$

where ε_r is the relative dielectric constant of the Cs_2CO_3 -doped BPhen layer (3.5 for organic), ε_r is the permittivity of free space, C_0 is the capacitance at 0 V, and A is the area of the device. Thus, the depletion width W of 6.6 nm in Cs_2CO_3 -doped BPhen layer is obtained by correlating the capacitance at 0 V.

The built-in potential in Cs_2CO_3 -doped BPhen side at 0 V is estimated using the Mott–Schottky equation

$$\psi_2 = \frac{qn_2}{2\varepsilon_r\varepsilon_0} W_2^2 \quad (2.24)$$

where ψ_2 is the built-in potential, q is the electric charge, n_2 is the carrier density. Here n_2 is $6.36 \times 10^{18}/\text{cm}^3$ [23]. Then, the built-in potential ψ_2 is calculated to be 0.71 eV. The built-in potential in HAT-CN side at 0 V can be given by [24]

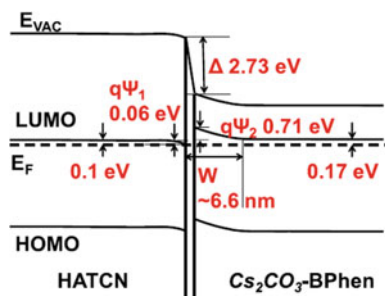
$$\psi_1 < \left[\frac{2kt}{q} \frac{\varepsilon_r n_2}{\varepsilon_r n_1} \psi_2 \right]^{1/2} \quad (2.25)$$

where k is the Boltzmann constant and T is the temperature. Here, the free carrier density n_1 of HAT-CN is $6.39 \times 10^{19}/\text{cm}^3$, then the upper limit of the built-in potential ψ_1 on HAT-CN is then estimated from Eq. 2.25 as 0.06 V. Finally, the vacuum-level shift (Δ) at the HAT-CN/ Cs_2CO_3 -doped BPhen junction can then be estimated from the LUMO levels of HAT-CN and Cs_2CO_3 -doped BPhen using Eq. (2.26)

$$\Delta = \text{LUMO}_{\text{HAT-CN}} - \text{LUMO}_{\text{Cs}_2\text{CO}_3:\text{BPhen}} - \sum_{i=1,2} q\psi_i \quad (2.26)$$

By calculation, Δ is 2.73 eV. Figure 2.12 gives the energy level alignment at thermal equilibrium based on the information for HAT-CN/ Cs_2CO_3 -doped BPhen interface.

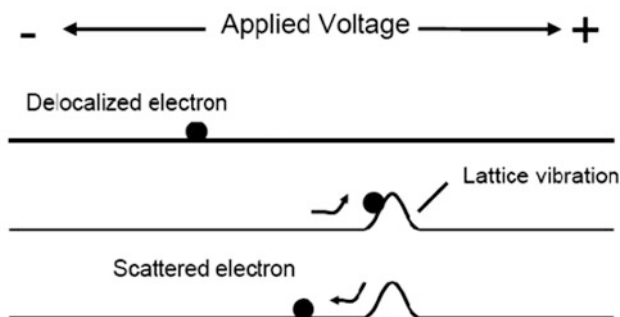
Fig. 2.12 Energy level diagram of the HAT-CN/ Cs_2CO_3 -doped BPhen interface determined by the C - V method. Reprinted from [22]



2.3 Charge Transport Properties

The transport of charges in semiconductors is the fundamental process of any optoelectronic devices. The correct description and understanding on the transport are the basis for the optimization of optoelectronic devices. In inorganic semiconductors, strong covalent bonds hold atoms together with well ordered configurations. The energy band in this case extends continuously in the bulk, and therefore, the delocalized charges can freely move along the band with a relative high mobility, as depicted in Fig. 2.13a. However, for most organic semiconductors, the weak intermolecular forces between molecules are predominant. In this case, discrete energy band structure is dominant in the bulk. The freely propagation wave of charges as usually seen in inorganic semiconductor no longer exists. In organics, the molecular orientation and energetic profile are intrinsically disordered. As a result, the charge transport in organic semiconductors becomes a hopping process that involves thermionic emission and tunneling of carriers between

(a) Band-type conduction



(b) Hopping conduction

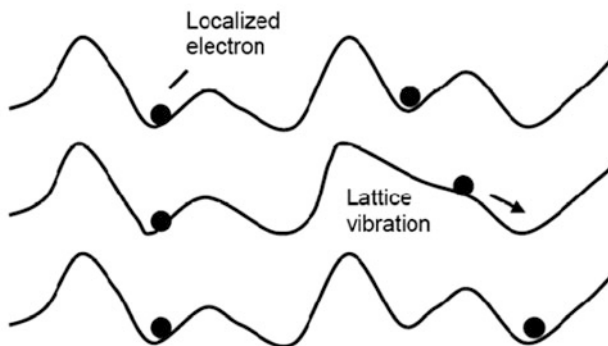


Fig. 2.13 **a** Band and **b** hopping transport mechanism in different type of semiconductors

localized sites, as shown in Fig. 2.13b. This is an activated process; the mobility increases with increasing temperature and is a field dependent. It can be readily predicted that the carrier mobility in most organic semiconductors is much smaller than that in their inorganic counterparts.

There are several proposed models, mainly including the empirical Poole–Frenkel formula [25], the Gaussian disorder model (GDM) [26], and correlated disorder model (CDM) [27], to describe the temperature- and field-dependent charge transport in disordered organic semiconductors.

The empirical Poole–Frenkel is simply written as

$$\mu(F, T) = \mu_0 \exp\left(-\frac{E_0 - \beta\sqrt{F}}{kT_{\text{eff}}}\right) \quad (2.27)$$

with $\beta = \sqrt{\frac{e^3}{\pi\epsilon\epsilon_0}}$ and $T_{\text{eff}}^{-1} = T^{-1} - T_0^{-1}$

where F is the electric field, E_0 is the thermal activation energy at $F = 0$, k is the Boltzmann constant, T_0 is the temperature at which Arrhenius plots of μ at various F intersect, and μ_0 is the mobility at T_0 . β is called the Poole–Frenkel coefficient, and it is in some cases reported to be temperature-dependent [28].

A reasonable assumption for the disorder based on the central limit theorem is a Gaussian distribution. This has led to the development of GDM. The general behavior of the mobility as a function of both temperature and electric field in the presence of diagonal and off-diagonal disorder is given as

$$\mu(F, T) = \mu_0 \exp\left[\left(-\frac{2\sigma}{3kT}\right)^2\right] \times \begin{cases} \exp[C(\sigma'^2 - \Sigma^2)\sqrt{F}] & \text{if } \Sigma \geq 1.5 \\ \exp[C(\sigma'^2 - 2.25)\sqrt{F}] & \text{if } \Sigma \leq 1.5 \end{cases} \quad (2.28)$$

where C is a numerical constant and $\sigma' = \sigma/kT$. σ is the standard deviation of the dispersion in energy levels. Σ is the standard deviation associated with the positional disorder. At high fields, μ saturates, because the gain in electrostatic energy compensates the disorder. Using the GDM, it was shown that the experimentally observed Poole–Frenkel field dependence is a sign for charge carrier hopping in a disordered system. Still, at low fields $\leq \approx 10^5$ V/m the predicted GDM produces a different field dependence than the experimentally observed Poole–Frenkel behavior.

CDM introduced site correlations, that is, neighboring sites influence each others' energy rather than being independent of each other, which reproduces the Poole–Frenkel-type field dependence at low electric fields and matches the GDM at high fields. CDM has the following formation [29]

$$\mu(F, T) = \mu_0 \exp\left[-\left(\frac{3\sigma'_d}{5}\right)^2 + C_0\left(\sigma_d'^{3/2} - \Gamma\right)\sqrt{\frac{eaF}{\sigma_d}}\right] \quad (2.29)$$

where $\sigma_d' = \sigma_d/kT$, $\sigma_d = 2.35ep/\epsilon a^2$. a is the minimal charge–dipole separation. p is the independently and randomly oriented dipole of moment. The model describes a non-dispersive mobility in correlated (e.g., dipolar) media, where $C_0 = 0.78$, and $\Gamma = 2$. The parameter μ_0 may have additional temperature dependence due to other less correlated sources of energy disorder or polaron effects.

The result of hopping transport caused by disorder generally leads the charge transport in organic semiconductors to be space charge limited. The space charge limited current (SCLC) obeys Child's law [30]

$$J = \frac{9}{8} \epsilon \epsilon_0 \mu(F, T) \frac{V^2}{d^3} \quad (2.30)$$

where ϵ is the dielectric constant, ϵ_0 is the vacuum permittivity, V the bias voltage, and d the thickness of organic layer.

Figure 2.14 shows the J - V characteristics of ITO/HAT-CN(10 nm)/HAT-CN:TAPC (30 wt%) (X nm)/TAPC(Y nm)/Al (device A: $X = 50$ nm, $Y = 10$ nm; device B: $X = 100$ nm, $Y = 10$ nm, and device C: $X = 150$ nm, $Y = 10$ nm) [19]. It can be seen that there are two regions in this $\log(J)$ - $\log(V)$ plot: ohmic conduction region with slope of 1 at low voltage and SCLC region with slope of about 2 at high voltage. This indicates that the charge transport in HAT-CN/HAT-CN:TAPC/TAPC organic heterojunction is bulk-limited. Importantly, it is found that increasing the thickness of HAT-CN:TAPC does not reduce the current in devices, indicating that HAT-CN:TAPC bulk heterojunction is highly conductive. This also further demonstrates that HAT-CN/HAT-CN:TAPC/TAPC organic heterojunction possesses excellent charge transport properties.

Figure 2.15 shows the J - V characteristics of Device 1: ITO/MoO₃ (0.75 nm)/NPB (20 nm)/HAT-CN (60 nm)/NPB (20 nm)/MoO₃ (5 nm)/Al and Device 2: ITO/MoO₃ (0.75 nm)/NPB (100 nm)/MoO₃ (5 nm)/Al [31]. They showed excellent SCLC property at high voltage region. However, it is clear that by insertion of the HAT-CN layer between NPB layers, the hole carrier mobility was remarkably increased for more than one order of magnitude, which has been attributed to the

Fig. 2.14 J - V characteristics of ITO/HAT-CN/HAT-CN:TAPC/TAPC/Al devices with different thicknesses of HAT-CN:TAPC layer. Reprinted from [19]

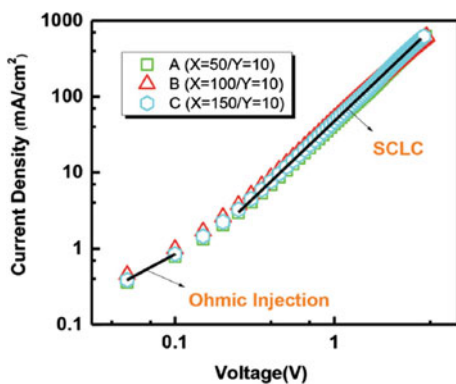
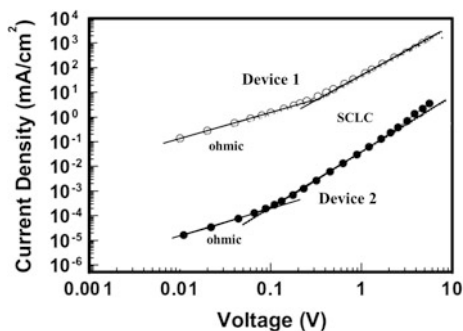


Fig. 2.15 J - V characteristics of ITO/MoO₃/NPB/HAT-CN/NPB/MoO₃/Al Device 1 and ITO/MoO₃/NPB/MoO₃/Al Device 2. Reprinted from [31]



carrier recombination at NPB/HAT-CN/NPB interfaces through coulombic interaction.

2.4 Charge Generation Properties

In inorganic semiconductor heterojunctions, the space charge region at the heterojunction interface is formed by charge diffusion due to the high mobility and free charge carrier density of inorganic semiconductors. In this case, the formed space charge region is generally depleted, where the holes are presented on the side of N -type semiconductor and the electrons are on the side of P -type semiconductor, and the charges are immobile. Therefore, the space charge region is highly resistant. However, the formation of the space charge region is a charge transfer process in organic semiconductor heterojunctions due to the low mobility and free charge carrier density in organic semiconductors. In addition to the formation of depletion-type heterojunctions like inorganic semiconductors, an accumulation-type heterojunction can also be formed [7]. When the Fermi level of P -type organic semiconductors is higher than that of N -type organic semiconductors, the electrons will be transferred from P -type semiconductors to N -type semiconductors, thus the side of N -type semiconductors accumulates electrons and the side of P -type semiconductors accumulates holes. The accumulation-type organic heterojunctions form a highly conductive space charge region due to the existence of a large number of free charge carriers. As shown in Fig. 2.16, the charge transfer pins the Fermi level at the heterojunction interface, which is dominated by the gap states tailed from the HOMO onset of P -type organic semiconductors, resulting in that the charges fill the band gap, therefore the conductivity is greatly enhanced. The experimental results have shown that a large transfer of charges between two organic semiconductors is a promising way to obtain high mobility and highly conductive organic films, which are interesting not only for practical applications but also for understanding the operation mechanisms in organic optoelectronic devices [32–35].

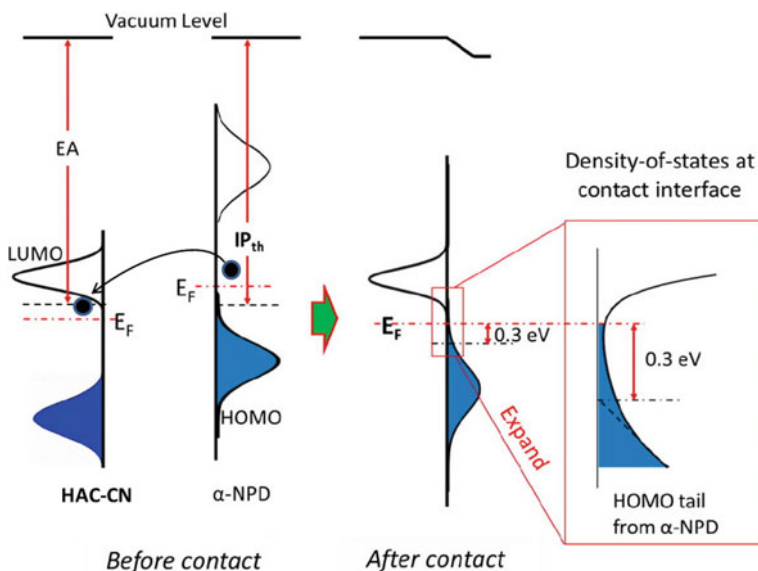


Fig. 2.16 Schematic diagram of charge transfer states in HAT-CN/α-NPD organic heterojunction before contact and after contact. The density of states are assumed to be Gaussian

The important applications of organic semiconductor heterojunctions are charge injectors and CGLs in OLEDs [36, 37]. It is clearly demonstrated that the charge generation behavior is independent of the work function of the contact electrodes but was strongly dependent on the energy level alignment between the HOMO of *P*-type organic semiconductors and the LUMO of *N*-type organic semiconductors. Therefore, by controlling the energy level, we can realize the accumulation-type organic

heterojunction with high conductance. It can be seen that using the accumulation-type organic heterojunction as charge injectors can realize high-efficiency OLEDs independent on the work function of used metal electrodes, as CGLs can realize high power efficiency tandem OLEDs. The achievement of the good performance in OLEDs has been attributed to the larger free charge generation and the high conductivity. Adachi et al. have verified this point [38]. Figure 2.17 is the energy level diagram of F₁₆CuPc/m-MTDATA organic heterojunction-based devices that is used to study. Obviously, in forward bias, both electrons and holes cannot be injected into the organic layers because the work function of Al is not aligned to the energy levels of both the m-MTDATA LUMO and the F₁₆CuPc HOMO. However, as shown in Fig. 2.18, a very large current is observed, clearly indicating the large charge generation from the interface between m-MTDATA and F₁₆CuPc heterojunction. It can be seen that the device current is greatly reduced as using α-NPD instead of m-MTDATA. This behavior has been ascribed to the difference in the HOMO levels of α-NPD (5.6 eV) and m-MTDATA (5.0 eV). This leads to the number of transferred charges from α-NPD to F₁₆CuPc negligible. This

Fig. 2.17 Energy level diagram of $F_{16}CuPc/m$ -MTDATA organic heterojunction-based devices. Reprinted from [38]

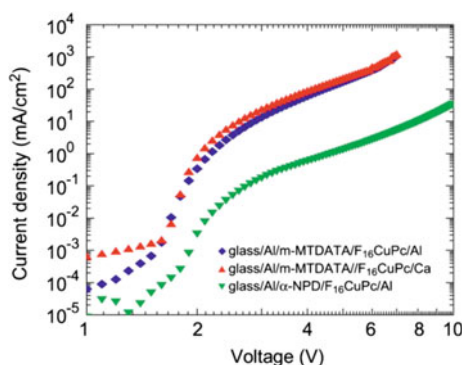
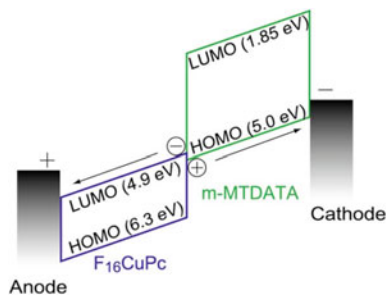
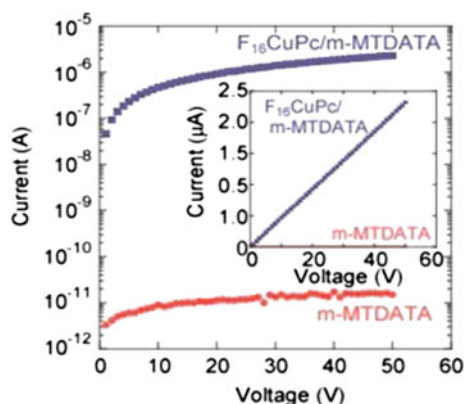


Fig. 2.18 J - V characteristics of devices composed of Al/m -MTDATA/ $F_{16}CuPc/Al$, Al/m -MTDATA/ $F_{16}CuPc/Ca/Al$ and Al/α -NPD/ $F_{16}CuPc/Al$. Reprinted from [38]

also implies that the charge separation at the $F_{16}CuPc/\alpha$ -NPD interface is mainly induced by the external electric field. With respect to the energy level alignment, the work function of the contacts is unimportant, even when very low work function metals such as calcium (2.9 eV) are used as the anode, the current is almost the same as that for the aluminum anode.

Figure 2.19 shows the I - V characteristics of $F_{16}CuPc$ (20 nm)/ m -MTDATA (20 nm) heterojunction and m -MTDATA (30 nm) single-layer devices. Clearly, the single-layer m -MTDATA film shows a current as low as 2×10^{-11} A even at 50 V, and its conductivity is calculated to be of the order of 10^{-10} S/cm, which is a typical value for organic semiconductors that have few charge carriers. On the other hand, the $F_{16}CuPc/m$ -MTDATA heterojunction film shows a current five orders of magnitude higher. As shown in the inset of Fig. 2.19, an ohmic behavior is observed, implying that the carrier density at the $F_{16}CuPc/m$ -MTDATA heterojunction interface is very high. By calculation, the carrier density at the $F_{16}CuPc/m$ -MTDATA heterojunction interface is as high as about $1 \times 10^{18}/cm^3$,

Fig. 2.19 I - V characteristics of m-MTDATA single layer and F_{16} CuPc/m-MTDATA heterojunction on a semilogarithmic scale. The inset shows the I - V characteristics on a linear scale for the same data. Reprinted from [38]



whereas that for a single layer of F_{16} CuPc is about $1 \times 10^{12}/\text{cm}^3$, and the conductivity also reaches 0.001 S/cm.

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