**Review**

**Organic Semiconductor Interfaces and Their Effects in Organic Solar Cells**

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**Abstract**

Energy levels and energy level alignment at interfaces play a decisive role in designing efficient and stable organic solar cells (OSCs). In this review two usually used technologies in organic photovoltaic communities for measuring energy levels of organic semiconductors, photoelectron spectroscopy and electrochemical methods, are introduced, and the relationships between the values obtained from the corresponding techniques are compared. The energy level and energy level alignment across the interfaces involved in solution processed organic photovoltaics are described, and the corresponding integer charge transfer model for predicting and explaining energy level alignment are presented. The effects of the interface properties in designing efficient binary and ternary OSCs were discussed. The effects of environmental factors mainly including water vapor, oxygen gas and thermal annealing on energy levels and energy level alignment involved in photoactive layers, and the subsequent effects on the corresponding OSC properties are given.

**Introduction**

Solution processed organic solar cells (OSCs) are attractive because of their light weight, potable and mechanical flexibility, and hence are promising power generators of off-the-grid devices such as wireless self-powered stretchable and wearable electronic devices[1,2]. In OSCs, the photoactive layer consisting of solution processable organic semiconductor donors and acceptors is sandwiched between an anode and a cathode. The blended donor and acceptor can be deposited as a single layer in bulk heterojunction OSCs[3-6], or the donor and acceptor can be deposited successively on top of each other in pseudo planer heterojunction OSCs[7-9]. Both in bulk and pseudo planer heterojunction OSCs, organic and metal electrode (O-M) interfaces are introduced between electrodes and organic semiconductor donor and acceptor, and organic donor and accepter (D-A) interfaces are formed in the photoactive layer. Optical excitation of the photoactive layer will result in photoinduced exciton dissociation across D-A interfaces, and subsequent charge transport through donor and acceptor phases and finally charge extraction across O-M interfaces. The energy level alignments at these interfaces control exciton dissociation, charge recombination and extraction[10-13]. Thus, understanding the energy level alignment at these interfaces is crucial for efficient and stable OSCs design. Since the emergence of the heterojunction OSCs[3,14], the efficiency has been improved to over 19% in single junction cell and over 20% in tandem cell thanks to the synthesis of new photoactive layer materials and interface materials, development of different device structure and concepts, optimization of photoactive layer morphology or combination of several strategies[6,15-22]. At present the review on new materials [23-28], device optoelectronic physics understanding[29-31], and the evolution of the photoactive layer morphology[32-35] are all providing a constructive instruction for further development of OSCs. The energy level and energy level alignment at interfaces determine charge generation and recombination[11], and subsequent the device efficiency and stability, which are the two key parameters for OSCs commercialization and application. Thus, a review from interface energetic point view is necessary for developing more efficient and stable OSCs.

In this review, we will first describe the basic concepts of the energy levels involved in OSCs and introduce two main popular used techniques for energy level measurement followed by comparing the relationships between these different values measured by different techniques. Next, the energy level alignment at the interfaces and the integer charge transfer (ICT) model for prediction and explanation of energy level alignment across the interfaces will be presented, and then the application of the ICT model in both binary and ternary OSC design will be discussed. Finally, three different parameters affecting the energy levels, energy level aliment, and the corresponding device properties will be summarized.

**Techniques of Determining Energy Levels**

In the photoactive layer of OSCs, organic semiconductor molecules or polymers acting as electron donors and acceptors are stacked into amorphous or semicrystalline films, and these molecules or polymers are weakly coupled with each other through intermolecular van der Waals forces. Thus, the energy band concept used in inorganic semiconductors usually does not hold in organic semiconductors. Instead, molecular orbitals are employed to describe the electronic structure. According to molecular orbital theory, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are defined as the frontier molecular orbitals. The frontier molecular orbitals determine the chemical and optoelectronic properties of organic semiconductors. A single molecule or polymer has distinct frontier molecular orbitals, and the ionization potential (*IP*) is defined as the energy needed when an electron is removed from HOMO, and the energy released when an electron is added to the LUMO is referred to as electron affinity (*EA*). Because of the soft property of the organic semiconductors, when a hole or an electron is added to the HOMO or the LUMO, the electronic density and nuclei of the organic semiconductor will reorganize to screen the extra added hole or electron, leading to the distortion of the geometry and electronic structures. The added extra charge together with the distorted lattice are called polaron. According to the above definition, the *IP* and *EA* is positive and negative polaron formation energy and should be smaller and larger than the neutral HOMO and LUMO energy of the molecule or polymer, but are usually considered approximately equal to neutral HOMO and LUMO energy according to Koppemans theory. Though the single molecule or polymer has well defined and discrete individual *IP* and *EA*, the *IP* and *EA* of the molecule or polymer in the solid films will become different because the nearby molecules or polymers will also reorganize and make the polaron formation energy in the film become larger or smaller further than the positive or negative polaron formation energy in a single molecule or polymer, and there will be also an *IP* and *EA* distribution in the solid films because of the different molecular or polymer environment in the condensed solid films[36-38]. The *IP* of the solid film is usually represented by the smallest individual *IP*, and the *EA* of the solid film is referred to as the individual largest *EA*. The electrical bandgap of the film is represented by the difference between the smallest individual *IP* and the largest individual *EA*, and this electrical band gap is different from the neutral optical band gap because of the quite large exciton binding energy of the neutral photoexcited excitons [30]. Exciton binding energy of the photoexcited excitons hinders exciton dissociation and free charge generation in organic solar cells. To overcome the binding energy and produce free charges in OSCs, semiconductor donors and acceptors with suitable HOMO and LUMO energy levels are needed in efficient OSCs, even for the-state-of-the-art non-fullerene acceptors such as Y6 with much smaller exciton binding energy[39,40]. The empirical rule reveals that the LUMO energy offset of 0.3 eV between donor and acceptor is essential for efficient exciton dissociation in fullerene based OSCs[41], and the HOMO energy offset is also crucial for efficient hole transfer from fullerene acceptors to polymer donors[42]. Similar with fullerene system, enough LUMO energy offset between donor and non-fullerene acceptor is necessary for efficient exciton dissociation[43]. With the development of low band gap non-fullerene acceptors, the energy transfer from donor to acceptor make the LUMO energy offset probably less important, and the HOMO energy offsets between donors and acceptors are proved to be essential for efficient exciton dissociation in OSCs[12,44,45]. However, the efficient exciton dissociation is also observed in a number of systems with the LUMO energy offsets or HOMO energy offsets minimized to near zero[46-49]. The above different experiment results about the energy offsets are either probably system dependence or probably caused by different measuring methods as demonstrated by Baran et al.[50,51]. Thus, precise determination of the energy levels is prerequirement for understanding the correlation between exciton dissociation and energy level offset between donor and acceptor. The open-circuit voltage of the OSC is original determined by the offset between HOMO energy of the donor and LUMO energy of the acceptor, and the liner dependence of the open-circuit voltage on the energy gap between HOMO of the donor and LUMO of the acceptor (usually named transport gap or photovoltaic gap) is typically revealed either in fullerene OSC or the state-of-the-art non-fullerene OSC[50,52-55]. So precise determination of the energy levels can help reveal a more accurate relationship between HOMO energy and open-circuit voltage, or between transport gap/photovoltaic gap and open-circuit voltage losses. When the semiconductor donors or acceptors contact with the electrodes in the devices, the energy differences between fermi levels or pining levels and frontier molecular orbital levels determine the charge injection and extraction[37,56,57], and hence the efficiency of the devices. In addition, trap states are easily introduced in organic semiconductor donors and acceptors with deep HOMO and shallow LUMO energy levels, so the HOMO of the donor and LUMO of the acceptor for holes and electrons transport should be inside trap free windows in which case can contribute to organic solar cell efficiency and stability[58]. Above all, the HOMO and LUMO energy levels play a critical role in efficient and stable OSC design, and precise measurement of the HOMO and LUMO energy levels and energy level alignment at interfaces are important.

Usually, the HOMO and LUMO energies can be measured by ultraviolet photoelectron spectroscopy (UPS) and invers photoemission spectroscopy (IPES) respectively and approximately equal to the measured *IP* and *EA* based onKoppemans theory[57,59,60], or the HOMO and LUMO energies can be calculated from oxidation potential and reduction potential respectively measured by electrochemical method such as cyclic voltammetry (CV) or square wave voltammetry (SWV)[61,62]. UPS is a direct and precise technique for *IP* measurement, and the precision is better than 0.1 eV. The detailed mechanisms of *IP* measurement via UPS can be found in many previous reports[11,57]. A typical UPS spectra are shown in Figure 1. The *IP* is the energy difference between the frontier orbital edge and the vacuum level, and the value can be calculated according to the equation *IP* = *E*F vb+*E*vac F= 21.2 eV – (*E*cutoff – *E*F vb). The *IP* measured by UPS is overestimated compared to the positive hole polaron formation energy because the nuclear is frozen during photoemission process and the energy of the nuclear geometric relaxation cannot be counted[11]. Different from *IP* measurement, the direct *EA* measurement by inverse photoelectron spectroscopy (IPES) is usually problematic because of several drawbacks of common IPES, such as low energy resolution of the IPES and sensitivity of the organic semiconductors to radiation damage. while the development of low energy IPES (LEIPES) affords the probability for direct precise *EA* measurement of organic semiconductors[59,63], and the resolution can be improved to be better than 0.3 eV with negligible radiation damage in organic molecule[63,64]. The *EA* are also usually calculated based on measured *IP* and the optical bandgap *E*g, but the calculated optical *EA* is larger than negative polaron formation energy because of the quite large exciton binding energy of photoexcited excitons in organic semiconductors. Thus, the combination of the UPS and optical methods could lead to inaccurate conclusions. UPS and LEIPES are accurate and direct methods for *IP* and *EA* measurement but are expensive and are still not available in many labs. Cyclic voltammetry instead is a cheaper and simpler electrochemical technique for estimating HOMO and LUMO energies through redox potential measurement and is widely used in organic photovoltaic research community. The HOMO and LUMO energies are estimated from oxidation potential (*E*ox) and reduction potential (*E*red)of the organic semiconductors relative to the fermi level of the reference electrodes based on the equation *E*HOMO/LUMO = q*E*ox/red + WFref [65,66]. During the process of oxidation and reduction, organic semiconductors experience geometric and electronic relaxation, and the doping and de-doping process are not irreversible, thus the onset potential where holes and electrons are initial injected to the HOMO and LUMO with the currents starting to rise are used to estimate oxidation potential and reduction potential (Figure 1 b). Regarding the inaccuracy of oxidation and reduction potential measuring or reading in CV methods, square wave voltammetry (SWV) was employed and now are widely used in the organic photovoltaic community, and the measurement accuracy in HOMO energy was proved to be comparable with UPS[52]. Recent years, some new or modified techniques are also developed for energy level measurement such as energy-resolved electrochemical impedance spectroscopy (ER-EIS)[67-69].

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**Figure 1. (**a) typical UPS spectra and (b) CV spectra of PFO. Data taken from Wang et al.[70].

In order to compare the values measured by photoelectron spectroscopy and electrochemical methods, researchers tried to figure out the relationships between *E*ox and *IP,* and*/*or *E*redand *EA*. All studies revealed that there should be a linear relationship between *E*ox and *IP*, and *E*red and *EA*, However, no agreement has been reached on the slope and intercept of the linear equation at present. In 2005, Thompson reported that there is a liner relationship between *IP* and *E*ox with the slope around 1.4 and the intercept around 4.6 eV[71], and in 2009, the author studied 24 small molecules and compared the LUMO energies measured by IPES and *E*red measured by CV, and found that there is also a linear relationship between *EA* and *E*red with the slope around 1.19 and the intercept around 4.8[72]. In 2016, Sworakowski collected the data from the reported literature and found an empirical linear correlations between *IP* and *E*ox, and *EA* and *E*red[73], the slops of the linear relationship are close to unity and the intercepts are around 4.8. In 2017, Sworakowski compared the oxidation potentials and *IP* of 33 polymers reported in literature and found the correlation does not obey the relationship commonly used for HOMO calculation based on CV methods, the slop of the correlation deviate from unity and is as large as 1.7[74]. In 2018, Wang et. al. studied the polymers and molecules usually used in organic photovoltaics and found that there is a linear relationship between *IP* and *E*ox, and the slop is approximation to unity. The linear relationship with a slope ≈ 1.0 is confirmed by studying the voltage losses of the corresponding OSCs[70]. The voltage losses relative to the band gaps estimated from CV based on the relationship is around 0.39 V, in accordance with previous findings[54,75]. In 2019, Janson et al. studied 19 diketopyrrolopyrrole (DPP)-based polymers and concluded that the oxidation potential obtained from SWV and ionization potential measured by UPS can be correlated with a slop close to unity and an intercept around 4.6 in the linear relationship, and the authors also demonstrated that the open-circuit voltage of the solar cell can be estimated from the oxidation potential measured by SWV based on a linear equation with the slope of 0.75[52]. However, recently Baran studied 33 semiconductors including polymers and state-of-the-art non-fullerene acceptors usually used in high power conversion efficiency OSCs and found the slope of the linear correlation between *E*ox and *IP* for the polymers is around 1.4, deviated from the unity[50], and the intercept is around 4.18. For non-fullerene acceptors, the slope of the linear correlation is around 1.32 and the intercept is around 4.60. The linear relationship with the unity slope means we can use *IP* and *E*ox interchangeably, but the larger slope values imply that with the increase of the HOMO energy, the *E*ox comparison become less meaningful. Because of lacking *EA* measured by LEIPES, accuracy comparison between *EA* and *E*ox is less studied compared to comparison between *IP* and *E*red. Baran et. al. recently studied the *EA* and *E*red of the-state-of-the-art NFA solar cell materials and get the conclusion that the slope of the fitted linear relationship between *EA* and *E*red is larger than 2.0 for polymer donors and around 0.68 for NFA, and the intercept is around 5.9 for polymer donors and around 4.5 for NFA[50].

**Energy Level Alignment at Interfaces and Their Effects in OSCs**

When the photoactive layers physically absorb on the conducting substrates, the relative position of the Fermi levels and HOMO or LUMO energy levels are not sufficient to describe the energy level alignment at interface because there is usually spontaneous integer charge transfer between organic semiconductors and the substrates to equilibrate the chemical potential, and subsequently the fermi levels usually pin to the integer charge transfer states (ICT)[37,38,57,76], introducing a large abrupt potential step at the interfaces, and the potential steps usually distribute within one to two semiconductor layers[77]. ICT states near the interface appear in the forbidden bandgap of neutral molecule or polymer (Figure 2 a), and the energy of the ICT states (*E*ICT) where the fermi level pined is referred to as positive pining energy (*E*ICT+) or negative pining energy (*E*ICT-) depending on positive polaron or negative polaron formation through integer charge transfer at interfaces. More detailed description and explanation about ICT states can be found in the papers reported by Fahlman et al.[37,38,57]. The energy level alignment at interfaces can be predicted and explained by integer charge transfer (ICT) model[57]. As shown in Figure 2 b and c, depending on the relative position of fermi energy and pining energy, the vacuum level will be aligned or shifted and three distinct regions can be observed experimentally in energy level diagram[37,38]. (i). When the work function of the substrate is smaller than the negative pining energy of the organic semiconductor donor or acceptor, spontaneous charge transfer from substrates to organic semiconductors will occur and organic semiconductors at interfaces are deoxidized, and the fermi level pins to the negative integer charge transfer states. (ii). When the fermi level is located between positive pining energy and negative pining energy, there is no charge transfer across the interface and the vacuum level is aligned. (iii). When the work function of the substrate is larger than the positive pining energy of the organic semiconductor donor or acceptor, organic donor or acceptor at the interface will be oxidized through the spontaneous integer charge transfer from organic semiconductors to the substrates. The pinning effect usually creates a hole or electron injecting barrier between pinning energy level and transport levels in organic light emitting diodes (OLEDs) or increase potential drops and voltage losses in OSCs. A strategy that can reduce these energy barriers or potential drops will potentially contribute to the organic electronic device performance. The energy difference between pinning energy level and transport energy level can be reduced by inserting a self-assembly molecule between electrodes and semiconductors as demonstrated by Lindell and coworkers[78], or it can be tuned by a thin organic semiconductor layer with a wide bandgap. When a thin layer of wide bandgap organic semiconductor with high *IP* is inserted between anode and active layer, the positive pining energy is increased to a value closer to the *IP* value and the hole injection efficiency is increased in OLEDs [79]. When the difference between the pining level and the charge transport level is decreased by inserting semiconductors with larger positive pining energy in OSCs, the voltage losses will be reduced[80,81]. Though there is debate on the accuracy of different techniques on *IP* or *EA* measurement, but only PES is an all-in-one technique that can measure work function, pining energy, charge transport levels and distribution of the transport states. The development of other electronic measurements such as ER-EIS can map the transport distribution, but pining energy cannot be obtained. Kelvin probe can detect potential steps at the interfaces, while the transport distribution cannot be obtained.

(a) (b)

(c)

**Figure 2** (a) ICT states near the interface, (b) Three regions in ICT curve and (c) the corresponding energy level alignment at interface in region (i)-(iii)[38].

In OSCs, it is usually assumed that the energy levels are aligned at D-A interfaces, and type II heterojunctions are formed between D-A interfaces, where the HOMO offsets and/or LUMO offsets between donors and acceptors afford the driving force for exciton dissociation. The empirical rule concluded based on type II heterojunction indicates that the LUMO offset should be larger than 0.3 eV in fullerene OSCs[41], and the HOMO offset between donor and acceptor should be larger than a threshold such as 0.2 eV in PBDB-TF based non-fullerene OSCs for efficient exciton dissociation[82]. However, in many cases this type II heterojunction cannot describe the true energy level alignment at D-A interfaces, and the effective transport gaps are different from the offset between HOMO energy of the donor and LUMO energy the acceptor, because there could be potential step caused by ground state charge transfer between donor and acceptor at interface or potential steps caused by other interface phenomenon, widely observed both in fullerene and non-fullerene acceptor interfaces[12,83-89]. The potential step could be larger than 1.0 eV, and should not be ignored in the OSC with the open-circuit voltage usually smaller than 1.0 eV. The ICT model can predict and explain the size and direction of the interface dipole step caused by ground state integer charge transfer between donor and acceptor. As shown in Figure 3a-b, when the positive pining energy of the donor is larger than the negative pining energy of the acceptor (*E*ICT+, D > *E*ICT-, A), the energy levels will be aligned at D-A interfaces after they are contacted with each other. When the positive pining energy of the donor is equal to or smaller than negative pining energy of the acceptor (*E*ICT+, D ≤ *E*ICT-, A), there will be ground state integer charge transfer from donor to acceptor after they are contacted with each other, and the interface dipoles are formed at D-A interfaces with the negative pole pointing to the acceptors. The scenario that the negative pining energy of the donor is larger than the positive pinging energy of the acceptor usually cannot happen in OSC (*E*ICT-, D > *E*ICT+, A), i.e. Integer charge transfer from acceptor to donor are usually not happen. In 2007, the integer charge transfer between donor and acceptor has been detected and explained by integer charge transfer model in poly(3-hexylthiophene-2,5-diyl) (P3HT): fullerene C60 system[90]. The polaron formed in the energy gap caused by integer charge transfer from donor P3HT to acceptor fullerene C60 is observed directly in the UPS spectra when the P3HT signal is subscripted from the total UPS spectra[11,90]. In 2011, Österbacka et al. predicted and proved there is also dark ground integer charge transfer between annealed polymer P3HT and fullerene PCBM because the positive pining energy of annealed P3HT becomes smaller than negative pining energy of the PCBM, and the dipole layer is formed at interface with the negative side pointing to the PCBM[91]. The dipole layer induced by integer charge transfer from donor to acceptor can assist exciton dissociate into free charge carriers and reduce charge recombination as suggested by the theoretical model[92]. The enhanced exciton dissociation has been experimentally proved by photoinduced absorption spectra in P3HT: PCBM system. In addition, the integer charge transfer between donors and acceptors occurs at the most easily oxidized and reduced molecules or segments, so the pre-occupation of these states will hinder the lower energy charge transfer states formation at D-A interfaces and the corresponding recombination will be reduced through low energy charge transfer states. Both the potential step at interfaces and pre-occupation of the most easily oxidation/reduction part can contribute to charge generation in OSCs. However, the integer charge transfer states in the gap could also act as trap states and the ICT states will probably increase the trap assisted recombination in OSCs[93-95].

In 2014, Bao et al. studied the effect of the trap states induced by integer charge transfer at interfaces on voltage losses of OSCs based on series P3HT donors and fullerene acceptors, and proved that there is a trade-off between charge generation and charge recombination caused by ICT states, and the sweet spot occurs at *E*ICT+ ≈ *E*ICT-, where the voltage losses relative to effective transport gap isminimized (Figure 3c)[96]. When *E*ICT+ of polymer donor is smaller than *E*ICT- of fullerene acceptor, trap assisted recombination will be increased and the voltage losses will become larger. When the *E*ICT+ of polymer donor is larger than *E*ICT- of fullerene acceptor, trap assisted recombination via ICT states disappears and bimolecular recombination is a dominated process in organic solar cells. Though the ICT model and rule for choosing donor and acceptor in efficient solar cell is achieved based on P3HT and fullerene solar cell, the efficient OSCs with minimal voltage losses based on other donors and fullerene acceptors reported in literature also follow this trend such as poly [[2,6′-4,8-di(5-ethylhexylthienyl)benzo[1,2-b;3,3-b]dithiophene][3-fluoro-2[(2ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl]] (PTB7-Th) and Poly[[2,3-bis(3-octyloxyphenyl)-5,8-quinoxalinediyl]-2,5-thiophenediyl] (TQ1) (Figure 3d). The positive pining energy of both PTB7-Th and TQ1 are equal to the negative pining energy of [6,6]-phenyl C71-butyric acid methyl ester (PC71BM), and the voltage losses of the PTB7-Th: PC71BM, TQ1: PC71BM locate in the minimal region. The trap states induced by charge transfer between donor TQ1and acceptors PC71BM are confirmed by both photoinduced absorption and electron paramagnetic resonance (EPR)[96]. When PC71BM is chose as the acceptor, the positive pining energy of the donors should be around 4.35 eV such as PBDTTS-FTAZ[97,98]. This empirical designing rule is also checked in the state-of-the art non-fullerene acceptor OSCs and finds that the positive pining energy of the donor is approximately equal to the negative pining energy of the non-fullerene acceptors in many efficient organic solar cells. In PM6: Y6 system (Poly[(2,6-(4,8-bis(5-(2-ethylhexyl-3-fluoro)thiophen-2-yl)-benzo[1,2-b:4,5-b’]dithiophene))-alt-(5,5-(1’,3’-di-2-thienyl-5’,7’-bis(2-ethylhexyl)benzo[1’,2’-c:4’,5’-c’]dithiophene-4,8-dione)] (PM6), 2,2'-((2Z,2'Z)-((12,13-bis(2-ethylhexyl)-3,9-diundecyl-12,13-dihydro-[1,2,5]thiadiazolo[3,4-e]thieno[2",3’':4’,5']thieno[2',3':4,5]pyrrolo[3,2-g]thieno[2',3':4,5]thieno[3,2-b]indole-2,10-diyl)bis(methanylylidene))bis(5,6-difluoro-3-oxo-2,3-dihydro-1H-indene-2,1-diylidene))dimalononitrile (Y6)), the positive pining energy of polymer donor PM6 is around 4.6 eV, approximately equal to the negative pining energy of non-fullerene acceptor Y6[13,40,99,100]. The positive pining energy of the polymer donor poly[(2,6-(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)-benzo[1,2-b:4,5-b’]dithiophene))-alt-(5,5-(1’,3’-di-2-thienyl-5’,7’-bis(2-ethylhexyl)benzo[1’,2’-c:4’,5’-c’]dithiophene-4,8-dione)] (PBDB-T) is equal to the negative pining energy of non-fullerene acceptor 3,9-bis(2-methylene-(3-(1,1-dicyanomethylene)-indanone))-5,5,11,11-tetrakis(4-hexylphenyl)-dithieno[2,3-d:2’,3’-d’]-s-indaceno[1,2-b:5,6-b’]dithiophene (ITIC) and annealed 3,9-bis(2-methylene-((3-(1,1-dicyanomethylene)-6/7-methyl)-indanone))-5,5,11,11-tetrakis(4-hexylphenyl)-dithieno[2,3-d:2’,3’-d’]-s-indaceno[1,2-b:5,6-b’]dithiophene (IT-M)[86]. We also privately checked the positive pining energy of polymer PTB7-Th and non-fullerene acceptor of CO*i*8DFC (O6T-4F)[101,102], and confirmed that the positive pining energy of the donor is equal to the negative pining energy of the acceptor. In all polymer solar cell PBDBT: N2200 (Poly{[N,N'-bis(2-octyldodecyl)naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-alt-5,5'-(2,2'-bithiophene)}), the positive pining energy of polymer donor PBDB-T is equal to the negative pining energy of polymer acceptor N2200[86]. However, different from the fullerene based organic solar cell where the potential step at D-A interface is around zero when *E*ICT+, D is approximately equal to *E*ICT-, A. Falman et al. studied the energy level alignment between PBDB-T and ITIC, PBDB-T and IT-4F, PM6 and ITIC, PM6 and IT-4F (3,9-bis(2-methylene-((3-(1,1-dicyanomethylene)-6,7-difluoro)-indanone))-5,5,11,11-tetrakis(4-hexylphenyl)-dithieno[2,3-d:2’,3’-d’]-s-indaceno[1,2-b:5,6-b’]dithiophene). The results demonstrate that though the energy level alignment between polymer donor or non-fullerene acceptor and conducting substrates still follow the ICT model, an extra potential step exists at donor and non-fullerene acceptor interfaces in addition to potential steps introduced by ground integer charge transfer between donor and acceptor,and the value of the extra potential step is as large as 0.7 eV when the potential step via ICT state is around zero[13]. The increased potential step at D-A interfaces compared to the predicted potential steps based on ICT model is explained theoretically by electrostatic potential, probably widely existing in the push-pull molecular system. The extra potential steps at interfaces can move up the HOMO and LUMO energy levels and decrease the HOMO or LUMO offset between donor and acceptor, and enlarge the effective transport gap or charge transfer states energy, in accordance with the phenomena that efficient exciton dissociation and high open-circuit voltage are achieved in efficient non-fullerene OSCs[103].

A screenshot of a computer screen

Description automatically generated with low confidence(a) (b)

(c) (d)

**Figure 3** Energy level alignment between donor and acceptor interfaces before and after contact when (a) *E*ICT+ > *E*ICT-, and (b) *E*ICT+ ≤ *E*ICT-. and (c)-(d) voltage losses diagram taken from Bao et al. and Wang et al.[96,97].

Photoactive layers composed of ternary blends have resulted in record efficiency in single junction ternary OSCs because the addition of the third component can improve charge generation and/or charge transport when the location of the third component is well controlled both horizontally and vertically and the energy level alignment of the three different components are appropriate in the ternary blends[104-107]. The ICT model and the empirical rule that guide the choice of the donor and acceptor in binary solar cells can work well in optimizing the energy level alignment of ternary blends to design efficient ternary OSCs. Wang et al. reported a ternary OSC with minimal voltage losses via optimizing interface energetic properties between donors and acceptor[97]. Double polymer donors PTB7-Th (A1) and PBDTTS-FTAZ (A2) possess the same *IP* value around 4.95 eV and the same positive pining energy value around 4.35 eV, and the fullerene PC71BM (D) with the negative pining energy around 4.35 eV was chosen as the acceptor. In this case, the positive pining energies of the donors are equal to the negative pining energy of the fullerene acceptor (*E*ICT+, A1 ≈ *E*ICT+, A1 ≈ *E*ICT-, D ≈ 4.35 eV). Both binary solar cells PTB7-Th: PC71BM, PBDTTS-FTAZ: PC71BM and ternary solar cell PTB7- h: PBDTTS-FTAZ: PC71BM with the minimal voltage losses were obtained[97]. Though the trap assisted recombination is minimized when the positive pining energy of the donor is equal to the negative pining energy of the acceptor, the minimized trap assisted recombination probably still contributes to voltage losses. The development of the planner norfullerene acceptors allows us to reduce this kind of trap states at interfaces further without sacrificing exciton dissociation efficiency because proper surface energy of the NFAs allows them self-assembling at interfaces of host donor and fullerene acceptor. Based on this assumption, a ternary organic solar cell with enhanced open-circuit voltage was achieved[108]. Polymer donor PTB7-Th and fullerene acceptor PC71BM were chosen as the host donor and acceptor because the *E*ICT+ of PTB7-Th is equal to the *E*ICT- of PC71BM, and planner NFA *m*-ITIC with lower negative pinning energy was chosen as the third component. NFA *m*-ITIC was forced to self-organize at interfaces of host donor and acceptor and can form a discontinuous interface layer between host donor and acceptor when there are small amounts of *m*-ITIC in ternary blends because the wetting coefficient of *m*-ITIC calculated from water contact angles locates between -1 and 1(-1< ω <1). In this case, cascade energy heterojunction is formed in photoactive layer, and the ternary OSCs will work through cascade charge transfer mechanism. The holes and electrons were transported separately in host donor PTB7-Th and acceptor PC71BM and the bimolecular recombination was reduced by reducing the chances of holes and electrons meeting with each other in the separated channels. *m*-ITIC located at interfaces can also hinder spontaneous dark ground state charge transfer between host donor and acceptor, so the ICT states in the photoactive layer and the corresponding trap assisted recombination via ICT states in ternary solar cell were reduced. Both reduced bimolecular recombination and trap assisted recombination contributed to the increased open-circuit voltage in ternary OSCs [94,109]. The increased open-circuit voltage in ternary OSCs exceeds the small different values of open circuit voltages between two binary OSCs and hence enhanced open-circuit voltage is observed in ternary OSCs. In non-fullerene small molecular acceptor OSC design, this strategy has also been proved reliable and useful. Bao et. al. designed a ternary OSC with increased exciton dissociation and suppressed charge recombination by choosing matched interface pining energy[100]. PM6 and Y6 were chosen as the host donor and acceptor because the positive pining energy of the donor PM6 is equal to the negative pining energy of the acceptor Y6. The non-fullerene acceptor ITIC-M was chosen as the third component because the negative pining energy of ITIC-M is smaller than Y6, and the surface energy of ITIC-M allows it to self-organize at the interface of host donor and acceptor PM6: Y6. In this case, the cascade charge transport channel is formed, and hence the exciton dissociation is improved, and trap assisted recombination through ICT states is potentially reduced in the ternary device. Similarly, when a polymer donor DRTB-T-C4 with a larger positive pining energy and proper surface energy (-1< ω <1) was added to the host binary blend PM6: Y6 where the positive pining energy of the donor PM6 equal to the negative pining energy of the acceptor Y6, the DRTB-T-C4 can self-organize at the interface to increase the exciton dissociation and reduce the trap assisted recombination of the ternary solar cells[110]. In ternary blends, when the *IP* and positive pining energy of the third filler component is larger than the *IP* and positive pinning energy of the host donor and acceptor, and the *EA* and negative pining energy of the third component is smaller than the *EA* and negative pining energy of the host donor and acceptor, the third filler component will not take part in charge transport and charge transfer because of the energetic barrier across the interfaces. The filler will not act as exciton or charge traps from energetic view[104]. If the D-A interface for exciton dissociation and the penetrated network for charge transport were not disturbed in the matrix of the filler, a diluted solar cell can be obtained. polymer donor PBDB-T and polymer acceptor N2200 were chosen as a model binary system, when the poly(9-vinylcarbazole) (PVK) or polystyrene (PS) was added to the blends, the hole mobility of the diluted ternary blends was increased by one order of the magnitude. The thermal stability is also increased as indicated by absence of the trap states in diluted film with 50% PVK when the annealed temperature was increased to 220 ℃. The improved thermal stability probably is attributed to the improved geometric stability of the semiconductors in the diluted ternary blends because of the composite effect of the insulator, and hence the trap density is suppressed under high temperature [111,112]. This diluted strategy can also improve the other properties of the solar cell such as the increased open-circuit voltage and power conversion efficiency, suppressed fullerene aggregation, or improved stretchability[113-116], and variety effects of different fillers on OSC properties has been reported by Hao e.g. al. in a recent review paper[117].

 (a) (b)

(c) (d)

**Figure 4.** Energy level diagram in ternary OSC: (a) double donor OSC with the same *IP* and *E*ICT+, (b) double acceptor OSC with the cascade energy level diagram, (c) double donor OSC with the cascade energy level diagram, (d) insulated OSC.

**Environmental Effects on Energy Levels and Photovoltaic Properties**

The energy levels and energy level alignment at interfaces involved in the photoactive layer of OSCs are determined fundamentally by molecular/polymer structure[118-124], but the measured energy level and energy level alignment of the same kind of molecule or same batch of polymer can also be affected by different molecular/polymer conformations or molecular/polymer orders in the condensed films[60,84,125-127]. Thus, environmental factors that result in molecular/polymer structure, conformation or molecular order changes can probably affect the energy levels and energy level alignment, and consequently the corresponding device efficiency and stability will be affected. The main environmental factors affecting the molecules/polymers in the photoactive layers involved in OSC preparation or operation include water vapor, oxygen, and thermal stress[128-131]. The evolution of the electronic properties and energy level alignment of organic semiconductors can be recorded by in-situ or ex-situ photoelectron spectroscopy when they are exposed to air or experienced thermal annealing. To investigate the sensitivity of fullerene acceptors to water vapor and oxygen, semiconductor films should be handled under inert conditions and the evolution of the electronic structure should be detected under dark conditions by controlling the volume of the water vapor or oxygen gas to exclude photochemical degradation[132-135], Bao et al. studied in situ oxygen and water vapor effects on fullerene acceptor [6,6]-Phenyl C61 butyric acid methyl ester (PC61BM)[136]. The frontier electronic structures mapped by UPS show no changes when the PC61BM films deposited on different conducting substrates with a wide range of work functions were exposed to oxygen under the controlled oxygen gas pressure, neither in the distribution nor in the intensity of the spectra, and the *IPs* keep constant. But the work functions and the hole injection barriers shifted to the higher binding energy together, i.e., the UPS spectra moved to higher binding energy. The changes caused by oxygen exposure can be recovered after removal of the oxygen through thermal annealing, indicating weak interaction between oxygen and fullerene acceptor PC61BM. The interface energy level alignment of the PC61BM can be predicted and described by ICT model, and the energy level diagram, i.e., the ICT curve of the pristine PC61BM, moved down by 0.15 eV around as a whole and stabilized after 3 hours exposure to oxygen (Figure 5a). The changes of the energy level alignment caused by oxygen can be explained by the double dipole effect at interface (Figure 5b)[137]. The oxygen can dope the fullerene films as an n-dopant. After occurring of doping effect, the small size oxygen anions tend to move closer to the electrodes compared to the fullerene cations and result in dipoles with the negative side pointing to the electrodes, and subsequently image dipoles are induced in the metal close to the interface with the positive pole pointing to the interface. The double dipole layers downshift the vacuum levels and the work functions at the interface independent on the work functions of the bare conducting substrates, downshifting the energy level diagram[138,139]. Different from oxygen effects, the degradation of PC61BM caused by the water vapor is chemical degradation as demonstrated by irreversible changed UPS spectra and XPS spectra. The frontier electronic structure in UPS spectra is bleached gradually and both IP and work function were reduced, and a new feature is observed in XPS spectra of C1S core level. The degradation of PC61BM under water vapor condition cannot be recovered by thermal annealing, indicating a strong interaction between water vapor and PC61BM. The same degradation effect is observed when C60 was exposed to water vapor, indicating the chemical interaction between water vapor and fullerene PC61BM occurs at fullerene cage instead of side chain. Same with PC61BM, the interaction of oxygen and n-type polymer acceptor N2200 is weak[140], and the oxygen caused degradation effects on N2200 can be removed by thermal annealing. The *IP* and the frontier electronic structure keep constant, but the work function or energy level diagram downshift around 0.15 eV as shown in Figure 5c. The mechanism of the decreased work function or the downshifted energy level alignment curve can also be explained by the double dipole effect. The oxygens dope polymer acceptor N2200 as an n dopant and more mobile oxygen anions move closer to the electrodes where the double dipole is formed. Different from PC61BM, Wang et al. demonstrated that non-fullerene small molecules show higher stability and different types of interaction with water vapor and oxygen[141]. Compared with PC61BM, all three non-fullerene acceptors o-IDTBR, *m*-ITIC and *p*-ITIC show higher resistance to water vapor and the interactions between water vapor and three non-fullerene acceptors are weak and reversable. There is no chemical interaction between water vapor and non-fullerene acceptors o-IDTBR as demonstrated by XPS spectra in Figure 5d. After thermal annealing following water vapor exposure, the C1s, N1s, S2p and O 1s XPS spectra of o-IDTBR can overlap with the spectra of the pristine film. After water exposure, the core levels of p-ITIC show no changes as demonstrated by the completely overlapped C1s, N1s, S2p and O 1s XPS spectra before and after water vapor exposure (Figure 5e). Different from PC61BM, both pining energy and ionization potential are hardly changed by water vapor as shown in Figure 5 f-h, and the frontier electronic structure degraded quite slower than PC61BM. The changes in frontier electronic structure of o-IDTBR caused by water vapor can be removed by thermal annealing and no changes was observed in the frontier electronic structure of p/m-ITIC, indicating weak removable interactions between water vapor and three non-fullerene acceptors. Oxygen mainly interacted with the terminal groups of the three non-fullerene acceptors. The frontier electronic structures degraded slowly under oxygen atmosphere because the HOMO is less relevant to the terminal group. The *IP* keeps constant till the HOMO feature bleached completely. The LUMO and negative pining energy are affected more because the LUMO and the negative pining states are mainly determined by the terminal groups where oxygen molecules mainly interacted with the non-fullerene molecules. Interestingly, the water vapor has an oxygen passivation effect as an oxygen blocker under dark air atmosphere, probably contributing to the stability of the non-fullerene acceptor based solar cells. The spectra studies are in consistent with the device study results that the degradation speed of the NFA solar cells in atmosphere under dark conditions is slower than the corresponding fullerene organic solar cells with the same donor[130,142-144]. However, Zhang et al. recently revealed by in-situ near-ambient pressure XPS (NAP-XPS) that non-fullerene acceptor Y6 is more sensitive to water vapor than oxygen gas under near-ambient pressure[145]. When the pristine Y6 film was exposed to water vapor or oxygen gas, negligible changes of C1s, S 2p and F1s was observed, and only the N1s cyano feature of the pristine Y6 films were decreased accompanied by an additional peak appeared in higher binding energy, indicating interaction between water vapor or oxygen and the cyano at the end group of the NFA. The extra peak induced by oxygen gas can be removed by pumping, but the extra peak after water exposure cannot be removed by pumping, indicating stronger interaction between water vapor and Y6. Thermal annealing during solar cell preparation or working process can affect the energy levels and energy level alignment of the photoactive layer. For rr-P3HT and rra-P3HT, thermal annealing can decrease positive pining energy and promote dark ground state charge transfer between P3HT and PCBM, introducing a dipole layer between

and acceptor with the negative side pointing to the acceptor PCBM[91]. The interface dipole with the negative side pointing to PCBM can increase the exciton dissociation efficiency and decrease the geminate recombination at D-A interfaces. Recently Wang et al. prove that thermal annealing can promote dark ground integer charge transfer between polymer donor TQ1 and polymer acceptor N2200[86]. In all polymer solar cell, positive pining energy of the pristine polymer donor TQ1 is larger than negative pining energy of the pristine acceptor N2200, and there should be no ground integer charge transfer between donor and acceptor based on ICT model, thus vacuum level is aligned at D-A interface. However, the *IP* and positive pining energy of TQ1 become smaller after thermal annealing compared with the raw film without thermal annealing because of the geometric changes of TQ1. The *IP* of N2200 keep constant but the negative pining energy is decreased with the increasing of the temperature. The positive pinning energy of polymer donor become equal with the negative pinning energy of polymer acceptor when annealing temperature is around 100 ℃-120 ℃ (Figure 5e). We predicted there probably is spontaneous ground state integer charge transfer between polymer donor and polymer acceptor, and this charge transfer prediction is confirmed by EPR measurement with the increased single electron signal[86]. The introduction of interface dipole at D-A interfaces can assist exciton dissociation and reduce geminate recombination and the corresponding energy losses in all polymer solar cells. Consequently, the energy losses in all-polymer solar cell TQ1: N2200 was reduced by 0.18 eV and reduced to 0.25 eV, a comparable minimized value with TQ1: PC71BM or other donor acceptor recipes with *E*ICT+, D ≈ *E*ICT+, A in Figure 3 c and d. The reduced germinate recombination was also demonstrated by a series of advanced technologies and devices studies in previous reports by Wang et al. and Laquai et al..[146,147].

(a) (b) (c)

(d) (e)

(f) (g) (h)

(i) (j) (k)

**Figure 5 (**a) ICT curve of pristine and oxygen exposed PC61BM. Data taken from Bao et al.[136], (b) Double dipole potential step at interfaces, (c) ICT curve of pristine and oxygen exposed N2200. Data taken from Bao et al.[140], (d) Evolution of XPS spectra of (d) o-IDTBR and (e) p-ITIC, and UPS spectra of (f) o-IDTBR, (g) p-ITIC and (h) m-ITIC, (i), Evolution of the UPS spectra of TQ1 and N2200 and (j) the corresponding evolution of *IP* and *E*ICT± of TQ1and N2200, (k) evolution of energy level alignment between TQ1 and N2200 before and after thermal annealing. Date take from Wang et al.[141].

**Conclusion**

In this review, we have first presented two usually used technologies for measuring and calculating energy levels of organic semiconductors used in organic photovoltaics or organic electronics, and summarized the relationships between values obtained from photoelectron spectroscopy and electrochemical methods. We then have shown the energy level alignment at interfaces when the photoactive layer physically absorbed on the conducting substrates and presented the ICT model in explaining and predicting the energy level alignment at both organic photoactive layer-conducting substrates and semiconductor D-A interfaces. We also have shown how we employ the ICT model to design both binary and ternary OSCs with various advantages such as enhanced charge generation and minimized voltage losses. Finally, we show the three common parameters oxygen, water vapor and thermal annealing effect on energy level and energy level alignment involved in both fullerene or non-fullerene photoactive layer, and the subsequent effect on OSC performance.

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**Conflict of Interest**

The authors declare no competing interests.

**References**

[1] S. Park, S. W. Heo, W. Lee, D. Inoue, Z. Jiang, K. Yu, H. Jinno, D. Hashizume, M. Sekino, T. Yokota, K. Fukuda, K. Tajima, T. Someya, "Self-powered ultra-flexible electronics via nano-grating-patterned organic photovoltaics" *Nature* **2018**, *561*, 516.

[2] K. F. Hiroaki Jinno, Xiaomin Xu, Sungjun Park, Yasuhito Suzuki, Mari Koizumi, , I. O. Tomoyuki Yokota, Kazuo Takimiya, Takao Someya, "Stretchable and waterproof elastomer-coated organic photovoltaics for washable electronic textile applications" *Nat. Energy* **2017**, *2*, 780.

[3] G. Yu, J. Gao, J. C. Hummelen, F. Wudl, A. J. Heeger, "Polymer Photovoltaic Cells - Enhanced Efficiencies Via a Network of Internal Donor-Acceptor Heterojunctions" *Science* **1995**, *270*, 1789.

[4] H. Yao, J. Hou, "Recent Advances in Single-Junction Organic Solar Cells" *Angew Chem Int Edit* **2022**, *61*, e202209021.

[5] N. Gasparini, A. Salleo, I. McCulloch, D. Baran, "The role of the third component in ternary organic solar cells" *Nat. Rev. Mater.* **2019**, *4*, 229.

[6] L. Zhu, M. Zhang, J. Xu, C. Li, J. Yan, G. Zhou, W. Zhong, T. Hao, J. Song, X. Xue, Z. Zhou, R. Zeng, H. Zhu, C. C. Chen, R. C. I. MacKenzie, Y. Zou, J. Nelson, Y. Zhang, Y. Sun, F. Liu, "Single-junction organic solar cells with over 19% efficiency enabled by a refined double-fibril network morphology" *Nat Mater* **2022**, *21*, 656.

[7] Q. He, W. Sheng, M. Zhang, G. Xu, P. Zhu, H. Zhang, Z. Yao, F. Gao, F. Liu, X. Liao, Y. Chen, "Revealing Morphology Evolution in Highly Efficient Bulk Heterojunction and Pseudo-Planar Heterojunction Solar Cells by Additives Treatment" *Adv. Energy Mater.* **2021**, *11*, 2003390.

[8] K. Jiang, J. Zhang, Z. Peng, F. Lin, S. Wu, Z. Li, Y. Chen, H. Yan, H. Ade, Z. Zhu, A. K. Jen, "Pseudo-bilayer architecture enables high-performance organic solar cells with enhanced exciton diffusion length" *Nat Commun* **2021**, *12*, 468.

[9] X. Xu, W. Jing, H. Meng, Y. Guo, L. Yu, R. Li, Q. Peng, "Sequential Deposition of Multicomponent Bulk Heterojunctions Increases Efficiency of Organic Solar Cells" *Adv Mater* **2023**, *35*, e2208997.

[10] K. Cnops, B. P. Rand, D. Cheyns, B. Verreet, M. A. Empl, P. Heremans, "8.4% efficient fullerene-free organic solar cells exploiting long-range exciton energy transfer" *Nat Commun* **2014**, *5*, 3406.

[11] M. Fahlman, P. Sehati, W. Osikowicz, S. Braun, M. P. de Jong, G. Brocks, "Photoelectron spectroscopy and modeling of interface properties related to organic photovoltaic cells" *J. Electron Spectrosc. Relat.* **2013**, *190*, 33.

[12] S. Karuthedath, J. Gorenflot, Y. Firdaus, N. Chaturvedi, C. S. P. De Castro, G. T. Harrison, J. I. Khan, A. Markina, A. H. Balawi, T. A. D. Pena, W. Liu, R. Z. Liang, A. Sharma, S. H. K. Paleti, W. Zhang, Y. Lin, E. Alarousu, S. Lopatin, D. H. Anjum, P. M. Beaujuge, S. De Wolf, I. McCulloch, T. D. Anthopoulos, D. Baran, D. Andrienko, F. Laquai, "Intrinsic efficiency limits in low-bandgap non-fullerene acceptor organic solar cells" *Nat Mater* **2021**, *20*, 378.

[13] X. Li, Q. Zhang, J. Yu, Y. Xu, R. Zhang, C. Wang, H. Zhang, S. Fabiano, X. Liu, J. Hou, F. Gao, M. Fahlman, "Mapping the energy level alignment at donor/acceptor interfaces in non-fullerene organic solar cells" *Nat. Commun.* **2022**, *13*, 2046.

[14] C. W. Tang, "Two-layer organic photovoltaic cell" *Appl.Phys.Lett.* **1986**, *48*, 183.

[15] Z. Zheng, J. Wang, P. Bi, J. Ren, Y. Wang, Y. Yang, X. Liu, S. Zhang, J. Hou, "Tandem organic solar cell with 20.2% efficiency" *Joule* **2022**, *6*, 171.

[16] Y. Cui, Y. Xu, H. Yao, P. Bi, L. Hong, J. Zhang, Y. Zu, T. Zhang, J. Qin, J. Ren, Z. Chen, C. He, X. Hao, Z. Wei, J. Hou, "Single-Junction Organic Photovoltaic Cell with 19% Efficiency" *Adv Mater* **2021**, *33*, e2102420.

[17] Y. Wei, Z. Chen, G. Lu, N. Yu, C. Li, J. Gao, X. Gu, X. Hao, G. Lu, Z. Tang, J. Zhang, Z. Wei, X. Zhang, H. Huang, "Binary Organic Solar Cells Breaking 19% via Manipulating the Vertical Component Distribution" *Adv Mater* **2022**, *34*, e2204718.

[18] C. Han, J. Wang, S. Zhang, L. Chen, F. Bi, J. Wang, C. Yang, P. Wang, Y. Li, X. Bao, "Over 19% Efficiency Organic Solar Cells by Regulating Multidimensional Intermolecular Interactions" *Adv Mater* **2023**, *35*, e2208986.

[19] D. Li, N. Deng, Y. Fu, C. Guo, B. Zhou, L. Wang, J. Zhou, D. Liu, W. Li, K. Wang, Y. Sun, T. Wang, "Fibrillization of Non-Fullerene Acceptors Enables 19% Efficiency Pseudo-Bulk Heterojunction Organic Solar Cells" *Adv Mater* **2023**, *35*, e2208211.

[20] L. Zhan, S. Li, Y. Li, R. Sun, J. Min, Z. Bi, W. Ma, Z. Chen, G. Zhou, M. Shi, L. Zuo, H. Chen, "Desired open-circuit voltage increase enables efficiencies approaching 19% in symmetric-asymmetric molecule ternary organic photovoltaics" *Joule* **2022**, *6*, 662.

[21] Y. Lin, J. Wang, Z. G. Zhang, H. Bai, Y. Li, D. Zhu, X. Zhan, "An electron acceptor challenging fullerenes for efficient polymer solar cells" *Adv Mater* **2015**, *27*, 1170.

[22] K. Weng, L. Ye, L. Zhu, J. Xu, J. Zhou, X. Feng, G. Lu, S. Tan, F. Liu, Y. Sun, "Optimized active layer morphology toward efficient and polymer batch insensitive organic solar cells" *Nat Commun* **2020**, *11*, 2855.

[23] C. Yan, S. Barlow, Z. Wang, H. Yan, A. K. Y. Jen, S. R. Marder, X. Zhan, "Non-fullerene acceptors for organic solar cells" *Nat. Rev. Mater.* **2018**, *3*, 18003.

[24] R. Xue, J. Zhang, Y. Li, Y. Li, "Organic Solar Cell Materials toward Commercialization" *Small* **2018**, *14*, e1801793.

[25] J. Miao, Y. Wang, J. Liu, L. Wang, "Organoboron molecules and polymers for organic solar cell applications" *Chem Soc Rev* **2022**, *51*, 153.

[26] H. Fu, Z. Wang, Y. Sun, "Polymer Donors for High-Performance Non-Fullerene Organic Solar Cells" *Angew Chem Int Edit* **2019**, *58*, 4442.

[27] N. Ahmad, H. Q. Zhou, P. Fan, G. X. Liang, "Recent progress in cathode interlayer materials for non-fullerene organic solar cells" *Ecomat.* **2022**, *4*, e12156.

[28] J. Hou, O. Inganas, R. H. Friend, F. Gao, "Organic solar cells based on non-fullerene acceptors" *Nat. Mater.* **2018**, *17*, 119.

[29] Y. Wang, D. Qian, Y. Cui, H. Zhang, J. Hou, K. Vandewal, T. Kirchartz, F. Gao, "Optical Gaps of Organic Solar Cells as a Reference for Comparing Voltage Losses" *Adv. Energy Mater.* **2018**, *8*, 1801352.

[30] I. Ramirez, M. Causa, Y. F. Zhong, N. Banerji, M. Riede, "Key Tradeoffs Limiting the Performance of Organic Photovoltaics" *Adv. Energy Mater.* **2018**, *8*, 1703551.

[31] S. D. Collins, N. A. Ran, M. C. Heiber, T. Q. Nguyen, "Small is Powerful: Recent Progress in Solution-Processed Small Molecule Solar Cells" *Adv. Energy Mater.* **2017**, *7*, 1602242.

[32] F. Zhao, C. Wang, X. Zhan, "Morphology Control in Organic Solar Cells" *Adv. Energy Mater.* **2018**, *8*, 1703147.

[33] X. Xu, Y. Li, Q. Peng, "Ternary Blend Organic Solar Cells: Understanding the Morphology from Recent Progress" *Adv Mater* **2022**, *34*, e2107476.

[34] L. Zhu, M. Zhang, W. K. Zhong, S. F. Leng, G. Q. Zhou, Y. C. Zou, X. Su, H. Ding, P. Y. Gu, F. Liu, Y. M. Zhang, "Progress and prospects of the morphology of non-fullerene acceptor based high-efficiency organic solar cells" *Energy Environ. Sci.* **2021**, *14*, 4341.

[35] K. Gao, Y. Kan, X. Chen, F. Liu, B. Kan, L. Nian, X. Wan, Y. Chen, X. Peng, T. P. Russell, Y. Cao, A. K. Jen, "Low-Bandgap Porphyrins for Highly Efficient Organic Solar Cells: Materials, Morphology, and Applications" *Adv Mater* **2020**, *32*, e1906129.

[36] W. R. Salaneck, "Intermolecular Relaxation Energies in Anthracene" *Phys. Rev. Lett.* **1978**, *40*, 60.

[37] M. Fahlman, S. Fabiano, V. Gueskine, D. Simon, M. Berggren, X. Crispin, "Interfaces in organic electronics" *Nat. Rev. Mater.* **2019**, *4*, 627.

[38] Q. Bao, S. Braun, C. Wang, X. Liu, M. Fahlman, "Interfaces of (Ultra)thin Polymer Films in Organic Electronics" *Adv. Mater. Interfaces* **2019**, *6*, 1800897.

[39] L. Zhu, J. Zhang, Y. Guo, C. Yang, Y. Yi, Z. Wei, "Small Exciton Binding Energies Enabling Direct Charge Photogeneration Towards Low-Driving-Force Organic Solar Cells" *Angew Chem Int Edit* **2021**, *60*, 15348.

[40] J. Yuan, Y. Zhang, L. Zhou, G. Zhang, H.-L. Yip, T.-K. Lau, X. Lu, C. Zhu, H. Peng, P. A. Johnson, M. Leclerc, Y. Cao, J. Ulanski, Y. Li, Y. Zou, "Single-Junction Organic Solar Cell with over 15% Efficiency Using Fused-Ring Acceptor with Electron-Deficient Core" *Joule* **2019**, *3*, 1140.

[41] J. L. Brédas, D. Beljonne, V. Coropceanu, J. Cornil, "Charge-Transfer and Energy-Transfer Processes in π-Conjugated Oligomers and Polymers:  A Molecular Picture" *Chem. Rev.* **2004**, *104*, 4917.

[42] E. T. Hoke, K. Vandewal, J. A. Bartelt, W. R. Mateker, J. D. Douglas, R. Noriega, K. R. Graham, J. M. J. Frechet, A. Salleo, M. D. McGehee, "Recombination in Polymer:Fullerene Solar Cells with Open-Circuit Voltages Approaching and Exceeding 1.0 V" *Adv. Energy Mater.* **2013**, *3*, 220.

[43] H. Cha, S. Wheeler, S. Holliday, S. D. Dimitrov, A. Wadsworth, H. H. Lee, D. Baran, I. McCulloch, J. R. Durrant, "Influence of Blend Morphology and Energetics on Charge Separation and Recombination Dynamics in Organic Solar Cells Incorporating a Nonfullerene Acceptor" *Adv. Funct. Mater.* **2017**, *28*, 1704389.

[44] Y. Cai, H. Zhang, L. Ye, R. Zhang, J. Xu, K. Zhang, P. Bi, T. Li, K. Weng, K. Xu, J. Xia, Q. Bao, F. Liu, X. Hao, S. Tan, F. Gao, X. Zhan, Y. Sun, "Effect of the Energy Offset on the Charge Dynamics in Nonfullerene Organic Solar Cells" *Acs Appl. Mater. Interfaces* **2020**, *12*, 43984.

[45] J. Zhang, W. Liu, G. Zhou, Y. Yi, S. Xu, Feng Liu, H. Zhu, X. Zhu, "Accurate Determination of the Minimum HOMO Offset for Efficient Charge Generation using Organic Semiconducting Alloys" *Adv. Energy Mater.* **2020**, *10*, 1903298.

[46] D. Qian, Z. Zheng, H. Yao, W. Tress, T. R. Hopper, S. Chen, S. Li, J. Liu, S. Chen, J. Zhang, X. K. Liu, B. Gao, L. Ouyang, Y. Jin, G. Pozina, I. A. Buyanova, W. M. Chen, O. Inganas, V. Coropceanu, J. L. Bredas, H. Yan, J. Hou, F. Zhang, A. A. Bakulin, F. Gao, "Design rules for minimizing voltage losses in high-efficiency organic solar cells" *Nat Mater* **2018**, *17*, 703.

[47] C. Sun, S. Qin, R. Wang, S. Chen, F. Pan, B. Qiu, Z. Shang, L. Meng, C. Zhang, M. Xiao, C. Yang, Y. Li, "High Efficiency Polymer Solar Cells with Efficient Hole Transfer at Zero Highest Occupied Molecular Orbital Offset between Methylated Polymer Donor and Brominated Acceptor" *J. Am. Chem. Soc.* **2020**, *142*, 1465.

[48] S. Li, L. Zhan, C. Sun, H. Zhu, G. Zhou, W. Yang, M. Shi, C. Z. Li, J. Hou, Y. Li, H. Chen, "Highly Efficient Fullerene-Free Organic Solar Cells Operate at Near Zero Highest Occupied Molecular Orbital Offsets" *J Am Chem Soc* **2019**, *141*, 3073.

[49] S. Chen, Y. Wang, L. Zhang, J. Zhao, Y. Chen, D. Zhu, H. Yao, G. Zhang, W. Ma, R. H. Friend, P. C. Y. Chow, F. Gao, H. Yan, "Efficient Nonfullerene Organic Solar Cells with Small Driving Forces for Both Hole and Electron Transfer" *Adv Mater* **2018**, *30*, e1804215.

[50] J. Bertrandie, J. Han, C. S. P. De Castro, E. Yengel, J. Gorenflot, T. Anthopoulos, F. Laquai, A. Sharma, D. Baran, "The Energy Level Conundrum of Organic Semiconductors in Solar Cells" *Adv Mater* **2022**, *34*, e2202575.

[51] T.-Q. Nguyen, "Barrier to charge generation" *Nat. Energy* **2022**, *7*, 1120.

[52] R. E. M. Willems, C. H. L. Weijtens, X. de Vries, R. Coehoorn, R. A. J. Janssen, "Relating Frontier Orbital Energies from Voltammetry and Photoelectron Spectroscopy to the Open-Circuit Voltage of Organic Solar Cells" *Adv. Energy Mater.* **2019**, *9*, 1803677.

[53] M. C. Scharber, D. Mühlbacher, M. Koppe, P. Denk, C. Waldauf, A. J. Heeger, C. J. Brabec, "Design Rules for Donors in Bulk-Heterojunction Solar Cells—Towards 10 % Energy-Conversion Efficiency" *Adv. Mater.* **2006**, *18*, 789.

[54] Z. Guan, H. W. Li, Y. Cheng, Q. Yang, M.-F. Lo, T. W. Ng, S. W. Tsang, C. S. Lee, "Charge-Transfer State Energy and Its Relationship with Open-Circuit Voltage in an Organic Photovoltaic Device" *J. Phys. Chem. C* **2016**, *120*, 14059.

[55] H. Yoshida, "Low-Energy Inverse Photoemission Study on the Electron Affinities of Fullerene Derivatives for Organic Photovoltaic Cells" *J. Phys. Chem. C* **2014**, *118*, 24377.

[56] H. Ishii, K. Sugiyama, E. Ito, K. Seki, "Energy Level Alignment and Interfacial Electronic Structures at Organic/Metal and Organic/Organic Interfaces" *Adv. Mater.* **1999**, *11*, 605.

[57] S. Braun, W. R. Salaneck, M. Fahlman, "Energy-Level Alignment at Organic/Metal and Organic/Organic Interfaces" *Adv. Mater.* **2009**, *21*, 1450.

[58] N. B. Kotadiya, A. Mondal, P. W. M. Blom, D. Andrienko, G. A. H. Wetzelaer, "A window to trap-free charge transport in organic semiconducting thin films" *Nat Mater* **2019**, *18*, 1182.

[59] H. Yoshida, "Principle and application of low energy inverse photoemission spectroscopy: A new method for measuring unoccupied states of organic semiconductors" *J. Electron Spectrosc. Relat.* **2015**, *204*, 116.

[60] A. Sugie, W. N. Han, N. Shioya, T. Hasegawa, H. Yoshida, "Structure-Dependent Electron Affinities of Perylene Diimide-Based Acceptors" *J. Phys. Chem. C* **2020**, *124*, 9765.

[61] S. Hellstrom, F. Zhang, O. Inganas, M. R. Andersson, "Structure-property relationships of small bandgap conjugated polymers for solar cells" *Dalton Trans* **2009**, 10032.

[62] S. Admassie, O. Inganas, W. Mammo, E. Perzon, M. R. Andersson, "Electrochemical and optical studies of the band gaps of alternating polyfluorene copolymers" *Synth. Met.* **2006**, *156*, 614.

[63] X. Liu, M. Fahlman, "Electronic Structure Characterization of Soft Semiconductors" *Adv. Mater. Interfaces* **2019**, *6*, 1900439.

[64] H. Yoshida, "Near-ultraviolet inverse photoemission spectroscopy using ultra-low energy electrons" *Chem. Phys. Lett.* **2012**, *539*, 180.

[65] C. M. Cardona, W. Li, A. E. Kaifer, D. Stockdale, G. C. Bazan, "Electrochemical considerations for determining absolute frontier orbital energy levels of conjugated polymers for solar cell applications" *Adv Mater* **2011**, *23*, 2367.

[66] T. Johansson, W. Mammo, M. Svensson, M. R. Andersson, O. Inganas, "Electrochemical bandgaps of substituted polythiophenes" *J. Mater. Chem.* **2003**, *13*, 1316.

[67] S. Athanasopoulos, F. Schauer, V. Nádaždy, M. Weiß, F. J. Kahle, U. Scherf, H. Bässler, A. Köhler, "What is the Binding Energy of a Charge Transfer State in an Organic Solar Cell?" *Adv. Energy Mater.* **2019**, *9*, 1900814.

[68] V. Nadazdy, F. Schauer, K. Gmucova, "Energy resolved electrochemical impedance spectroscopy for electronic structure mapping in organic semiconductors" *Appl. Phys. Lett.* **2014**, *105*, 142109.

[69] H. Bässler, D. Kroh, F. Schauer, V. Nádaždy, A. Köhler, "Mapping the Density of States Distribution of Organic Semiconductors by Employing Energy Resolved–Electrochemical Impedance Spectroscopy" *Adv. Funct. Mater.* **2020**, *31*, 2007738.

[70] C. Wang, L. Ouyang, X. Xu, S. Braun, X. Liu, M. Fahlman, "Relationship of Ionization Potential and Oxidation Potential of Organic Semiconductor Films Used in Photovoltaics" *Sol. RRL* **2018**, *2*, 1800122.

[71] B. W. D'Andrade, S. Datta, S. R. Forrest, P. Djurovich, E. Polikarpov, M. E. Thompson, "Relationship between the ionization and oxidation potentials of molecular organic semiconductors" *Org. Electron.* **2005**, *6*, 11.

[72] P. I. Djurovich, E. I. Mayo, S. R. Forrest, M. E. Thompson, "Measurement of the lowest unoccupied molecular orbital energies of molecular organic semiconductors" *Org. Electron.* **2009**, *10*, 515.

[73] J. Sworakowski, J. Lipinski, K. Janus, "On the reliability of determination of energies of HOMO and LUMO levels in organic semiconductors from electrochemical measurements. A simple picture based on the electrostatic model" *Org. Electron.* **2016**, *33*, 300.

[74] J. Sworakowski, K. Janus, "On the reliability of determination of energies of HOMO levels in organic semiconducting polymers from electrochemical measurements" *Org. Electron.* **2017**, *48*, 46.

[75] K. Vandewal, K. Tvingstedt, A. Gadisa, O. Inganas, J. V. Manca, "Relating the open-circuit voltage to interface molecular properties of donor:acceptor bulk heterojunction solar cells" *Phys. Rev. B* **2010**, *81*, 125204.

[76] T. S. Zhai, R. B. Wang, T. Katase, F. Quigley, H. Ohta, P. Amsalem, N. Koch, S. Duhm, "Substrate-Independent Energy-Level Pinning of an Organic Semiconductor Providing Versatile Hole-Injection Electrodes" *Acs Appl Electron Ma* **2020**, *2*, 3994.

[77] Q. Bao, S. Fabiano, M. Andersson, S. Braun, Z. Sun, X. Crispin, M. Berggren, X. Liu, M. Fahlman, "Energy Level Bending in Ultrathin Polymer Layers Obtained through Langmuir-Shafer Deposition" *Adv. Funct. Mater.* **2016**, *26*, 1077.

[78] L. Lindell, C. Vahlberg, K. Uvdal, M. Fahlman, S. Braun, "Self-assembled monolayer engineered interfaces: Energy level alignment tuning through chain length and end-group polarity" *J. Electron Spectrosc. Relat.* **2015**, *204*, 140.

[79] N. B. Kotadiya, H. Lu, A. Mondal, Y. Ie, D. Andrienko, P. W. M. Blom, G. A. H. Wetzelaer, "Universal strategy for Ohmic hole injection into organic semiconductors with high ionization energies" *Nat Mater* **2018**, *17*, 329.

[80] K. Ding, S. R. Forrest, "Reducing Energy Losses at the Organic-anode-buffer Interface of Organic Photovoltaics" *Phys. Rev. Appl.* **2020**, *13*, 054046.

[81] G. A. H. Wetzelaer, P. W. M. Blom, "Comment on "Enhanced Charge Selectivity via Anodic-C(60) Layer Reduces Nonradiative Losses in Organic Solar Cells"" *ACS Appl Mater Interfaces* **2022**, *14*, 7523.

[82] C. Yang, J. Zhang, N. Liang, H. Yao, Z. Wei, C. He, X. Yuan, J. Hou, "Effects of energy-level offset between a donor and acceptor on the photovoltaic performance of non-fullerene organic solar cells" *J. Mater. Chem. A* **2019**, *7*, 18889.

[83] X. Li, Q. Zhang, J. Yu, Y. Xu, R. Zhang, C. Wang, H. Zhang, S. Fabiano, X. Liu, J. Hou, F. Gao, M. Fahlman, "Mapping the energy level alignment at donor/acceptor interfaces in non-fullerene organic solar cells" *Nat Commun* **2022**, *13*, 2046.

[84] Y. Li, P. Li, Z.-H. Lu, "Molecular Orientation and Energy Levels at Organic Interfaces" *Adv. Electron. Mater.* **2016**, *2*, 1600306.

[85] M. Oehzelt, K. Akaike, N. Koch, G. Heimel, "Energy-level alignment at organic heterointerfaces" *Sci Adv* **2015**, *1*, e1501127.

[86] C. Wang, F. Moro, S. Ni, Q. Zhang, G. X. Pan, J. Yang, F. Zhang, I. A. Buyanova, W. M. M. Chen, X. Liu, M. Fahlman, "Thermal-annealing effects on energy level alignment at organic heterojunctions and corresponding voltage losses in all-polymer solar cells" *Nano Energy* **2020**, *72*, 104677.

[87] K. Xu, H. Sun, T. P. Ruoko, G. Wang, R. Kroon, N. B. Kolhe, Y. Puttisong, X. Liu, D. Fazzi, K. Shibata, C. Y. Yang, N. Sun, G. Persson, A. B. Yankovich, E. Olsson, H. Yoshida, W. M. Chen, M. Fahlman, M. Kemerink, S. A. Jenekhe, C. Muller, M. Berggren, S. Fabiano, "Ground-state electron transfer in all-polymer donor-acceptor heterojunctions" *Nat Mater* **2020**, *19*, 738.

[88] H. Yao, D. Qian, H. Zhang, Y. Qin, B. Xu, Y. Cui, R. Yu, F. Gao, J. Hou, "Critical Role of Molecular Electrostatic Potential on Charge Generation in Organic Solar Cells" *Chinese Journal of Chemistry* **2018**, *36*, 491.

[89] H. Yao, Y. Cui, D. Qian, C. S. Ponseca Jr., A. Honarfar, Y. Xu, J. Xin, Z. Chen, L. Hong, B. Gao, R. Yu, Y. Zu, W. Ma, P. Chabera, T. Pullerits, A. Yartsev, F. Gao, J. Hou, "14.7% Efficiency Organic Photovoltaic Cells Enabled by Active Materials with a Large Electrostatic Potential Difference" **2019**, *141*, 7743.

[90] W. Osikowicz, M. P. de Jong, W. R. Salaneck, "Formation of the interfacial dipole at organic-organic interfaces: C-60/polymer interfaces" *Adv. Mater.* **2007**, *19*, 4213.

[91] H. Aarnio, P. Sehati, S. Braun, M. Nyman, M. P. de Jong, M. Fahlman, R. Osterbacka, "Spontaneous Charge Transfer and Dipole Formation at the Interface Between P3HT and PCBM" *Adv. Energy Mater.* **2011**, *1*, 792.

[92] V. I. Arkhipov, P. Heremans, H. Bässler, "Why is exciton dissociation so efficient at the interface between a conjugated polymer and an electron acceptor?" *Appl. Phys. Lett.* **2003**, *82*, 4605.

[93] M. Kuik, L. J. Koster, G. A. Wetzelaer, P. W. Blom, "Trap-assisted recombination in disordered organic semiconductors" *Phys Rev Lett* **2011**, *107*, 256805.

[94] C. M. Proctor, M. Kuik, T. Q. Nguyen, "Charge carrier recombination in organic solar cells" *Prog. Polym. Sci.* **2013**, *38*, 1941.

[95] S. Zeiske, O. J. Sandberg, N. Zarrabi, W. Li, P. Meredith, A. Armin, "Direct observation of trap-assisted recombination in organic photovoltaic devices" *Nat. Commun.* **2021**, *12*, 3603.

[96] Q. Bao, O. Sandberg, D. Dagnelund, S. Sanden, S. Braun, H. Aarnio, X. Liu, W. M. M. Chen, R. Osterbacka, M. Fahlman, "Trap-Assisted Recombination via Integer Charge Transfer States in Organic Bulk Heterojunction Photovoltaics" *Adv. Funct. Mater.* **2014**, *24*, 6309.

[97] C. Wang, W. Zhang, X. Meng, J. Bergqvist, X. Liu, Z. Genene, X. Xu, A. Yartsev, O. Inganas, W. Ma, E. Wang, M. Fahlman, "Ternary Organic Solar Cells with Minimum Voltage Losses" *Adv. Energy Mater.* **2017**, *7*, 1700390.

[98] J. W. Zewdneh Genene, Xiangyi Meng, Wei Ma, Xiaofeng Xu, Renqiang Yang, Wendimagegn Mammo, Ergang Wang, "High Bandgap (1.9 eV) Polymer with Over 8% Efficiency in Bulk Heterojunction Solar Cells" *Adv. Electron. Mater.* **2016**, *2*, 1600084.

[99] X. Li, Q. Zhang, X. Liu, M. Fahlman, "Pinning energies of organic semiconductors in high-efficiency organic solar cells" *Journal of Semiconductor* **2022**, *44*, 032201.

[100] Y. Zeng, D. Li, H. Wu, Z. Chen, S. Leng, T. Hao, S. Xiong, Q. Xue, Z. Ma, H. Zhu, Q. Bao, "Enhanced Charge Transport and Broad Absorption Enabling Record 18.13% Efficiency of PM6:Y6 Based Ternary Organic Photovoltaics with a High Fill Factor Over 80%" *Adv. Funct. Mater.* **2022**, *32*, 2110743.

[101] H. Li, Z. Xiao, L. Ding, J. Wang, "Thermostable single-junction organic solar cells with a power conversion efficiency of 14.62" *Sci Bull (Beijing)* **2018**, *63*, 340.

[102] L. Meng, Y. Zhang, X. Wan, C. Li, X. Zhang, Y. Wang, X. Ke, Z. Xiao, L. Ding, R. Xia, H. L. Yip, Y. Cao, Y. Chen, "Organic and solution-processed tandem solar cells with 17.3% efficiency" *Science* **2018**, *361*, 1094.

[103] L. Perdigon-Toro, H. Zhang, A. Markina, J. Yuan, S. M. Hosseini, C. M. Wolff, G. Zuo, M. Stolterfoht, Y. Zou, F. Gao, D. Andrienko, S. Shoaee, D. Neher, "Barrierless Free Charge Generation in the High-Performance PM6:Y6 Bulk Heterojunction Non-Fullerene Solar Cell" *Adv Mater* **2020**, *32*, e1906763.

[104] B. Lim, J. T. Bloking, A. Ponec, M. D. McGehee, A. Sellinger, "Ternary bulk heterojunction solar cells: addition of soluble NIR dyes for photocurrent generation beyond 800 nm" *ACS Appl Mater Interfaces* **2014**, *6*, 6905.

[105] N. K. Marcella Günther, Dominic Blätte, Jose Dario Perea, Barry C. Thompson, Tayebeh Ameri, "Models and mechanisms of ternary organic solar cells" *Nat. Rev. Mater.* **2023**, [*https://doi.org/10.1038/s41578-023-00545-1*](https://doi.org/10.1038/s41578-023-00545-1).

[106] L. Zuo, S. B. Jo, Y. Li, Y. Meng, R. J. Stoddard, Y. Liu, F. Lin, X. Shi, F. Liu, H. W. Hillhouse, D. S. Ginger, H. Chen, A. K. Jen, "Dilution effect for highly efficient multiple-component organic solar cells" *Nat. Nanotechnol.* **2022**, *17*, 53.

[107] S. Honda, H. Ohkita, H. Benten, S. Ito, "Selective Dye Loading at the Heterojunction in Polymer/Fullerene Solar Cells" *Adv. Energy Mater.* **2011**, *1*, 588.

[108] C. Wang, X. Xu, W. Zhang, S. Ben Dkhil, X. Meng, X. Liu, O. Margeat, A. Yartsev, W. Ma, J. Ackermann, E. Wang, M. Fahlman, "Ternary organic solar cells with enhanced open circuit voltage" *Nano Energy* **2017**, *37*, 24.

[109] W. Huang, P. Cheng, Y. Yang, G. Li, Y. Yang, "High-Performance Organic Bulk-Heterojunction Solar Cells Based on Multiple-Donor or Multiple-Acceptor Components" *Adv. Mater.* **2018**, *30*, 1705706.

[110] D. Li, L. Zhu, X. Liu, W. Xiao, J. Yang, R. Ma, L. Ding, F. Liu, C. Duan, M. Fahlman, Q. Bao, "Enhanced and Balanced Charge Transport Boosting Ternary Solar Cells Over 17% Efficiency" *Adv. Mater.* **2020**, *32*, 2002344.

[111] C. Wang, X. J. Liu, Y. Xiao, J. Bergqvist, X. Lu, F. Gao, M. Fahlman, "Diluted Organic Semiconductors in Photovoltaics" *Sol. RRL* **2020**, *4*, 2000261.

[112] A. Gumyusenge, D. T. Tran, X. Luo, G. M. Pitch, Y. Zhao, K. A. Jenkins, T. J. Dunn, A. L. Ayzner, B. M. Savoie, J. Mei, "Semiconducting polymer blends that exhibit stable charge transport at high temperatures" *Science* **2018**, *362*, 1131.

[113] Q. Zhang, H. Zhang, Z. Wu, C. Wang, R. Zhang, C.-Y. Yang, F. Gao, S. Fabiano, H. Y. Woo, M. Ek, X. Liu, M. Fahlman, "Natural Product Betulin-Based Insulating Polymer Filler in Organic Solar Cells" *Sol. RRL* **2022**, *6*, 2200381.

[114] F. Bao, J. Han, D. Huang, C. Yang, J. Wang, X. Bao, X. Jian, J. Wang, "Synergistic Effect of Poly(aryl ether ketone) Matrices via Rational Ternary Copolymerization Enables Efficient and Stable Organic Solar Cells" *Chem. Mater.* **2021**, *34*, 430.

[115] J. Xu, S. Wang, G. N. Wang, C. Zhu, S. Luo, L. Jin, X. Gu, S. Chen, V. R. Feig, J. W. To, S. Rondeau-Gagne, J. Park, B. C. Schroeder, C. Lu, J. Y. Oh, Y. Wang, Y. H. Kim, H. Yan, R. Sinclair, D. Zhou, G. Xue, B. Murmann, C. Linder, W. Cai, J. B. Tok, J. W. Chung, Z. Bao, "Highly stretchable polymer semiconductor films through the nanoconfinement effect" *Science* **2017**, *355*, 59.

[116] S. Chen, S. Jung, H. J. Cho, N. H. Kim, S. Jung, J. Xu, J. Oh, Y. Cho, H. Kim, B. Lee, Y. An, C. Zhang, M. Xiao, H. Ki, Z. G. Zhang, J. Y. Kim, Y. Li, H. Park, C. Yang, "Highly Flexible and Efficient All-Polymer Solar Cells with High-Viscosity Processing Polymer Additive toward Potential of Stretchable Devices" *Angew Chem Int Edit* **2018**, *57*, 13277.

[117] T. Wang, J.-Q. Liu, X.-T. Hao, "Recent Progress of Organic Solar Cells with Insulating Polymers" *Sol. RRL* **2020**, *4*, 2070124.

[118] Y. Li, "Molecular design of photovoltaic materials for polymer solar cells: toward suitable electronic energy levels and broad absorption" *Acc Chem Res* **2012**, *45*, 723.

[119] Z. Ji, X. Xu, G. Zhang, Y. Li, Q. Peng, "Synergistic effect of halogenation on molecular energy level and photovoltaic performance modulations of highly efficient small molecular materials" *Nano Energy* **2017**, *40*, 214.

[120] S. Li, L. Ye, W. Zhao, S. Zhang, S. Mukherjee, H. Ade, J. Hou, "Energy-Level Modulation of Small-Molecule Electron Acceptors to Achieve over 12% Efficiency in Polymer Solar Cells" *Adv. Mater.* **2016**, *28*, 9423.

[121] R. Wang, J. Yuan, G. Han, T. Huang, W. Huang, J. Xue, H.-C. Wang, C. Zhang, C. Zhu, P. Cheng, D. Meng, Y. P. Yi, K. W. Wei, Y. P. Zou, Y. Yang, "Rational Tuning of Molecular Interaction and Energy Level Alignment Enables High-Performance Organic Photovoltaics" *Adv. Mater.* **2019**, *31*, 1904215.

[122] Bin Kan, Jiangbin Zhang, Feng Liu, Xiangjian Wan, Chenxi Li, Xin Ke, H. F. Yunchuang Wang, Yamin Zhang, Guankui Long, A. A. B. Richard H. Friend, Yongsheng Chen, "Fine-Tuning the Energy Levels of a Nonfullerene Small-Molecule Acceptor to Achieve a High Short-Circuit Current and a Power Conversion Efficiency over 12% in Organic Solar Cells" *Adv. Mater.* **2018**, *30*, 1704904.

[123] Z. Luo, H. Bin, T. Liu, Z.-G. Zhang, Y. Yang, C. Zhong, B. Qiu, G. Li, W. Gao, D. Xie, K. Wu, Y. Sun, F. Liu, Y. Li, C. Yang, "Fine-Tuning of Molecular Packing and Energy Level through Methyl Substitution Enabling Excellent Small Molecule Acceptors for Nonfullerene Polymer Solar Cells with Efficiency up to 12.54%" *Adv. Mater.* **2018**, *30*, 1706124.

[124] Z. Luo, R. Ma , T. Liu , J. Yu, Y. Xiao, R. Sun, G. Xie, J. Yuan, Y. Chen, K. Chen, G. Chai, H. Sun, J. Min, J. Zhang, Y. Zou, C. Yang, X. Lu, F. Gao, H. Yan, "Fine-Tuning Energy Levels via Asymmetric End Groups Enables Polymer Solar Cells with Efficiencies over 17%" *Joule* **2020**, *4*, 1236.

[125] S. Duhm, G. Heimel, I. Salzmann, H. Glowatzki, R. L. Johnson, A. Vollmer, J. P. Rabe, N. Koch, "Orientation-dependent ionization energies and interface dipoles in ordered molecular assemblies" *Nat Mater* **2008**, *7*, 326.

[126] N. A. Ran, S. Roland, J. A. Love, V. Savikhin, C. J. Takacs, Y. T. Fu, H. Li, V. Coropceanu, X. Liu, J. L. Bredas, G. C. Bazan, M. F. Toney, D. Neher, T. Q. Nguyen, "Impact of interfacial molecular orientation on radiative recombination and charge generation efficiency" *Nat Commun* **2017**, *8*, 79.

[127] M. Schwarze, K. S. Schellhammer, K. Ortstein, J. Benduhn, C. Gaul, A. Hinderhofer, L. P. Toro, R. Scholz, J. Kublitski, S. Roland, M. Lau, C. Poelking, D. Andrienko, G. Cuniberti, F. Schreiber, D. Neher, K. Vandewal, F. Ortmann, K. Leo, "Impact of molecular quadrupole moments on the energy levels at organic heterojunctions" *Nat. Commun.* **2019**, *10*, 2466.

[128] B. Zhou, L. Wang, Y. Liu, C. Guo, D. Li, J. Cai, Y. Fu, C. Chen, D. Liu, Y. Zhou, W. Li, T. Wang, "On the Stability of Non-fullerene Acceptors and Their Corresponding Organic Solar Cells: Influence of Side Chains" *Adv. Funct. Mater.* **2022**, *32*, 2206042.

[129] C.-T. Lin, C.-T. Hsieh, T. J. Macdonald, J.-F. Chang, P.-C. Lin, H. Cha, L. Steier, A. Wadsworth, I. McCulloch, C.-C. Chueh, J. R. Durrant, "Water-Insensitive Electron Transport and Photoactive Layers for Improved Underwater Stability of Organic Photovoltaics" *Adv. Funct. Mater.* **2022**, *32*, 2203487.

[130] L. P. Duan, A. Uddin, "Progress in Stability of Organic Solar Cells" *Adv. Sci.* **2020**, *7*, 1903259.

[131] G. Zuo, M. Linares, T. Upreti, M. Kemerink, "General rule for the energy of water-induced traps in organic semiconductors" *Nat. Mater.* **2019**, *18*, 588.

[132] V. Blazinic, L. K. E. Ericsson, S. A. Muntean, E. Moons, "Photo-degradation in air of spin-coated PC60BM and PC70BM films" *Synth. Met.* **2018**, *241*, 26.

[133] A. S. Anselmo, A. Dzwilewski, K. Svensson, E. Moons, "Photodegradation of the electronic structure of PCBM and C60 films in air" *Chem. Phys. Lett.* **2016**, *652*, 220.

[134] V. Blazinic, L. K. E. Ericsson, I. Levine, R. Hansson, A. Opitz, E. Moons, "Impact of intentional photo-oxidation of a donor polymer and PC70BM on solar cell performance" *Phys. Chem. Chem. Phys.* **2019**, *21*, 22259.

[135] I. E. Brumboiu, L. K. E. Ericsson, V. Blazinic, R. Hansson, A. Opitz, B. Brena, E. Moons, "Photooxidation of PC60BM: new insights from spectroscopy" *Phys. Chem. Chem. Phys.* **2022**, *24*, 25753.

[136] Q. Bao, X. Liu, S. Braun, M. Fahlman, "Oxygen-and Water-Based Degradation in [6,6]-Phenyl-C61-Butyric Acid Methyl Ester (PCBM) Films" *Adv. Energy Mater.* **2014**, *4*, 1301272.

[137] Q. Bao, X. Liu, E. Wang, J. Fang, F. Gao, S. Braun, M. Fahlman, "Regular Energetics at Conjugated Electrolyte/Electrode Modifi er for Organic Electronics and their Implications on Design Rules" *Adv. Mater. Interfaces* **2015**, *2*, 1500204.

[138] Q. Bao, X. Liu, S. Braun, F. Gao, M. Fahlman, "Energetics at Doped Conjugated Polymer/Electrode Interfaces" *Adv. Mater. Interfaces* **2015**, *2*, 1400403.

[139] S. van Reenen, S. Kouijzer, R. A. J. Janssen, M. M. Wienk, M. Kemerink, "Origin of Work Function Modification by Ionic and Amine-Based Interface Layers" *Adv. Mater. Interfaces* **2014**, *1*, 1400189.

[140] Q. Bao, X. Liu, S. Braun, J. Yang, Y. Li, J. Tang, C. Duan, M. Fahlman, "The Effect of Oxygen Uptake on Charge Injection Barriers in Conjugated Polymer Films" *ACS Appl Mater Interfaces* **2018**, *10*, 6491.

[141] C. Wang, S. Ni, S. Braun, M. Fahlman, X. Liu, "Effects of water vapor and oxygen on non-fullerene small molecule acceptors" *J. Mater. Chem. C* **2019**, *7*, 879.

[142] W. Li, D. Liu, T. Wang, "Stability Of Non-Fullerene Electron Acceptors and Their Photovoltaic Devices" *Adv. Funct. Mater.* **2021**, *31*, 2104552.

[143] D. Baran, R. S. Ashraf, D. A. Hanifi, M. Abdelsamie, N. Gasparini, J. A. Rohr, S. Holliday, A. Wadsworth, S. Lockett, M. Neophytou, C. J. Emmott, J. Nelson, C. J. Brabec, A. Amassian, A. Salleo, T. Kirchartz, J. R. Durrant, I. McCulloch, "Reducing the efficiency-stability-cost gap of organic photovoltaics with highly efficient and stable small molecule acceptor ternary solar cells" *Nat Mater* **2017**, *16*, 363.

[144] P. Cheng, X. W. Zhan, "Stability of organic solar cells: challenges and strategies" *Chem. Soc. Rev.* **2016**, *45*, 2544.

[145] Q. Zhang, Y. Chen, X. Liu, M. Fahlman, "In situ near-ambient pressure X-ray photoelectron spectroscopy reveals the effects of water, oxygen and light on the stability of PM6:Y6 photoactive layers" *J. Mater. Chem. C* **2023**, *11*, 3112.

[146] S. Karuthedath, A. Melianas, Z. Kan, V. Pranculis, M. Wohlfahrt, J. I. Khan, J. Gorenflot, Y. Xia, O. Inganas, V. Gulbinas, M. Kemerink, F. Laquai, "Thermal annealing reduces geminate recombination in TQ1:N2200 all-polymer solar cells" *J. Mater. Chem. A* **2018**, *6*, 7428.

[147] Y. Xia, C. Musumeci, J. Bergqvist, W. Ma, F. Gao, Z. Tang, S. Bai, Y. Jin, C. Zhu, R. Kroon, C. Wang, M. R. Andersson, L. Hou, O. Inganas, E. Wang, "Inverted all-polymer solar cells based on a quinoxaline-thiophene/naphthalene-diimide polymer blend improved by annealing" *J. Mater. Chem. A* **2016**, *4*, 3835.