

Chapter 10

Proposal for Future Organic Solar Cells



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Recent driving forces for increases in efficiency of organic solar cells have relied on the numerous repeats of the circulation around the syntheses of new organic semiconductors, blends, and performance checks. However, neglect of physical principles, which are hidden in the back of the complicated systems, should be prevented for future long-range development of organic solar cells. In Chapter 10, therefore, the proposals for future organic solar cells are discussed based on the unconventional considerations and the fundamental physical aspects.

10.1 Is Blended Junction Necessary?

The primary question, why a blended junction was inevitably introduced, directly offers the alternative methods for constructing organic solar cells. The first answer is the necessity of combining donor and acceptor molecules to dissociate excitons. A logical consequence is exciton dissociation without combining donor and acceptor molecules, i.e., the use of a single organic semiconductor. The second answer is an extremely short exciton diffusion length of approximately 10 nm. A logical consequence is the use of a material with a long exciton diffusion length. The third answer is the very small relative dielectric constant (ϵ) of about 3 of organic semiconductors, which inhibits exciton dissociation. A logical consequence is the use of the material with large ϵ .

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10.1.1 Bipolar Band-Conductive Organic Semiconductor-Exciton Dissociation Using Single Organic Semiconductor

Carrier generation by doping and light excitation is considered as standard since the liberation process between positive and negative charges can be regarded as identical. In the case of doping, a free carrier is generated by the dissociation of a positive charge of a hole from a negatively ionized dopant ion, which is spatially fixed, and vice versa. In the case of photocarrier generation, free electron and hole are generated by the dissociation of an exciton, i.e., bound electron and hole, which are not spatially fixed.

In the case of acceptor doping to the band-conductive rubrene single crystal, a positive charge of a hole loosely bound around the negatively ionized dopant ion can be liberated by the thermal energy of room temperature; i.e., the Wannier excitonic nature is observed in the band-conductive single crystal (Fig. 10.1a) (Chap. 9, Sect. 9.6.1). A negatively ionized dopant is spatially fixed in the crystal lattice. Therefore, for acceptor and donor doping processes, since the liberated carrier is either a hole or an electron, only hole band-conductive nature or only electron band-conductive nature are required, respectively.

On the other hand, in the case of photocarrier generation, both a hole and an electron should be liberated at room temperature by the Wannier excitonic nature. Therefore, the band-conductive nature is required both for the hole and the electron. When two kinds of organic crystals with hole band conduction and electron band conduction are combined (Fig. 10.1b), exciton automatically dissociates to free electron and hole by the thermal energy of room temperature. When single organic crystal possesses both hole band-conductive and electron band-conductive nature, i.e., possesses bipolar band-conductive nature, exciton automatically dissociates to free electron and hole by thermal energy of room temperature in the single organic crystal (Fig. 10.1c). We presume that the bipolar band-conductive organic semiconductor would dissociate exciton and generate photocurrent without the assistance of donor/acceptor (D/A) sensitization.

Concerning holes, a significant number of band-conductive organic semiconductor crystals, such as rubrene [1] and films such as C8-BTBT [2], has been reported in this decade. However, for electrons, only one organic semiconductor (PDIF-CN₂) has been reported [3]. There has been no report on bipolar band-conductive organic semiconductor. Initially, a sign of bipolar band conduction under very low temperature was reported in naphthalene and perylene single crystals in 1985 by Karl [4] (Fig. 10.2). The mobilities for both hole and electron increased with decreasing temperature, suggesting the bipolar band-conductive nature. The bipolar band-conductive organic semiconductor at room temperature would represent a breakthrough in the field of organic solar cells.

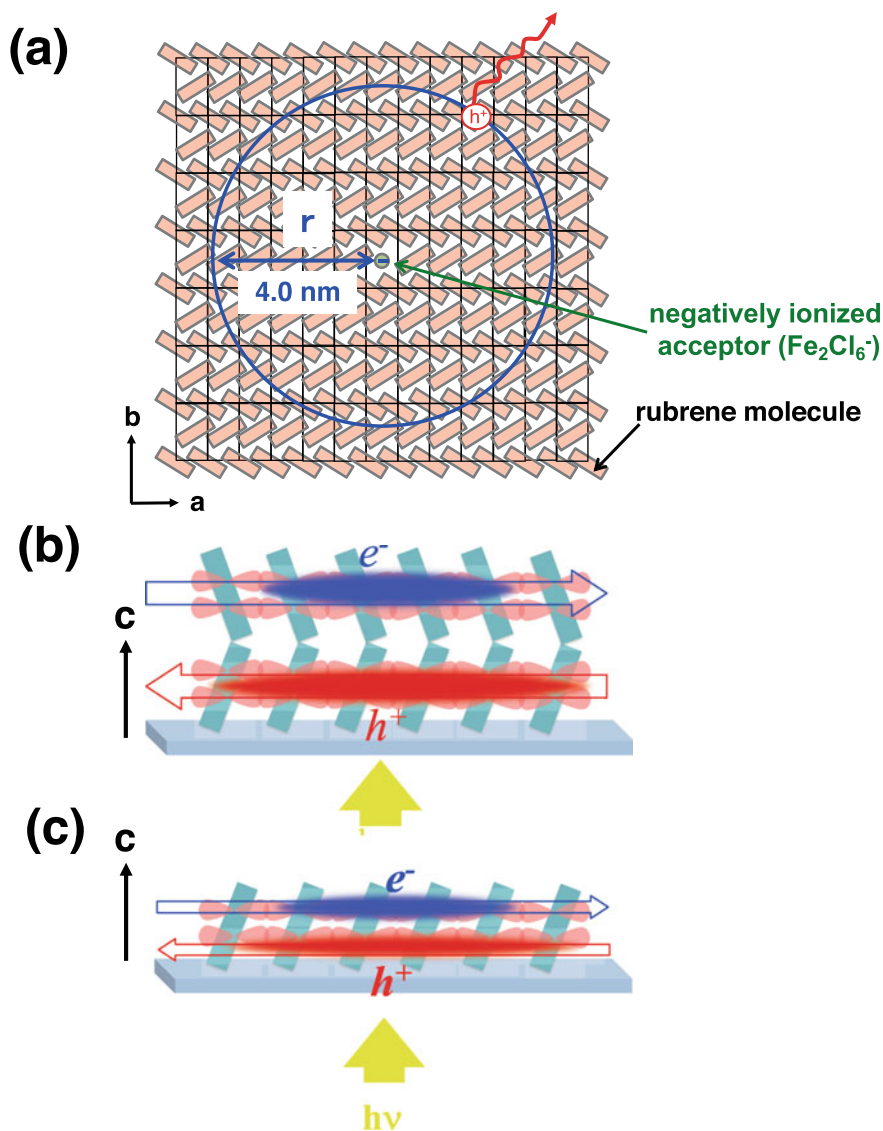


Fig. 10.1 **a** Wannier excitonic nature of doping. A hole loosely bound around the negatively ionized acceptor ion (Fe_2Cl_6^-) in the rubrene single crystal showed 24% doping efficiency. Band conduction promotes the carrier generation by doping. **b** Combination of two types of organic crystals exhibiting hole and electron band conduction. Exciton automatically dissociates into free electron and hole at room temperature. **c** Single organic crystal with bipolar band-conductive nature. Exciton automatically dissociates into free electron and hole in the single organic crystals at room temperature. **a** Reproduced with permission from M. Hiramoto et al., *Adv. Mater* Copyright 2018 John Wiley and Sons

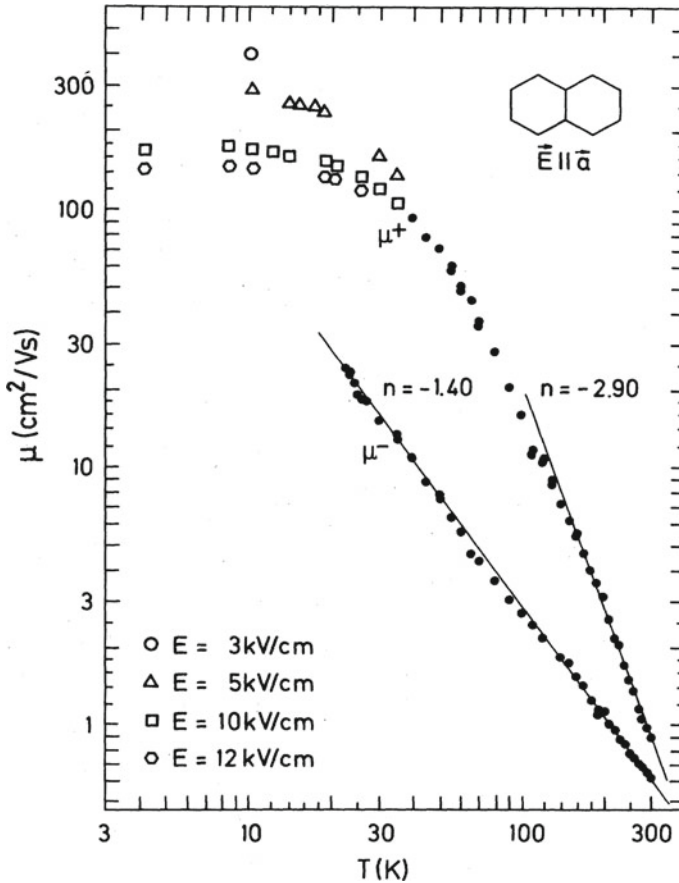


Fig. 10.2 Drift mobility increase of electron and hole by decreasing the temperature observed for naphthalene crystal. Reproduced with permission from W. Warta et al., *Phys. Rev. B*, Copyright 1985 American Physical Society

10.1.2 Long Exciton Diffusion Length—Doped Organic Single-Crystal Solar Cell

If we can use organic semiconductors with significantly long exciton diffusion lengths, exciton diffusion would no longer be a limiting factor for organic solar cells; i.e., the blended junction would not be necessary. A long diffusion length of excitons in organic single crystals, such as anthracene, has been suggested earlier [5–7]. Recently, a long exciton diffusion length of $8 \mu\text{m}$ was reported for rubrene single crystals [8]. This fact shows the possibility of organic single-crystal solar cells without blended junction (Fig. 10.3).

Organic solar cells can be constructed on the *p*-doped rubrene single-crystal substrate acting as a hole transporting substrate. We have already constructed the

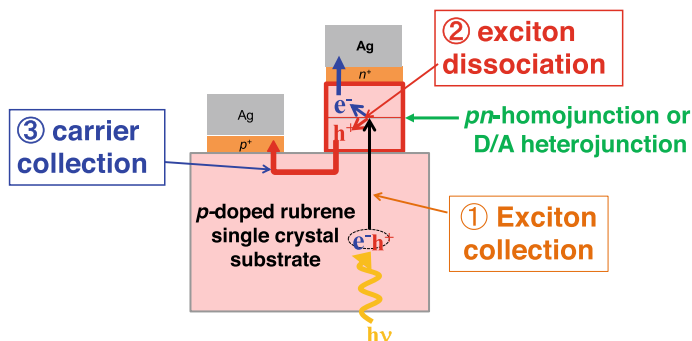


Fig. 10.3 Organic solar cell constructed on the *p*-doped rubrene single-crystal substrate

prototype of the organic single-crystal solar cell [9]. A single-crystal substrate collected excitons to the *pn*-homojunction with the collection efficiency reaching 46%, owing to the long exciton diffusion length of 2.7 μm . Essentially, the blended junction is not necessary when whole excitons are collected to the planar junctions.

The entire photocurrent generated in the *pn*-homojunction with a macroscopic area of 2 mm \times 1 mm was confirmed to be collected through the *p*-doped rubrene substrate. The J_{SC} values were revealed to be dominated by the sheet conductivity (σ_{\square}) of the *p*-doped substrate. To attain a practical value of $J_{\text{SC}} = 20 \text{ mAcm}^{-2}$, the *p*-doped substrate should have a sheet conductivity (σ_{\square}) of $3.1 \times 10^{-5} \text{ S}$. This is equal to the σ_{\square} -value of the entire bulk-doped rubrene single crystals (Fe_2Cl_6 : 100 ppm) with a thickness of approximately 65 μm [10]. An entire bulk doping technology for organic single crystals should be developed for the fabrication of practical organic single-crystal solar cells. Similar to single-crystal Si substrate, the doped organic single-crystal substrate would be a fundamental element in future organic single-crystal solar cells (Fig. 10.4).

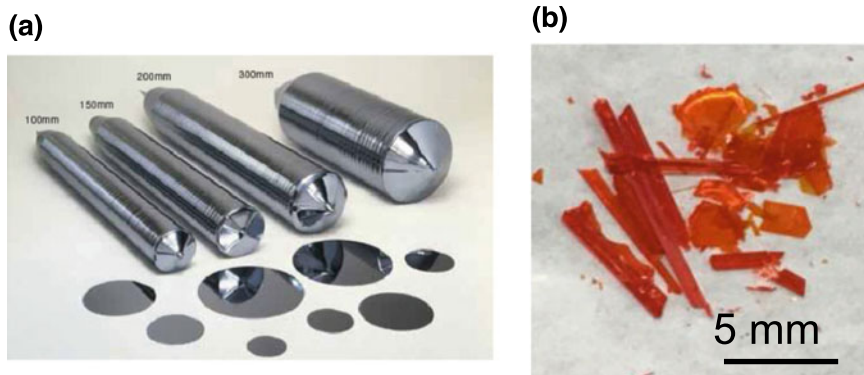


Fig. 10.4 **a** Photograph of doped Si single-crystal ingots and substrates. **b** Photograph of rubrene single crystals

10.1.3 Large Dielectric Constant—Organic/Inorganic Hybrid Cell

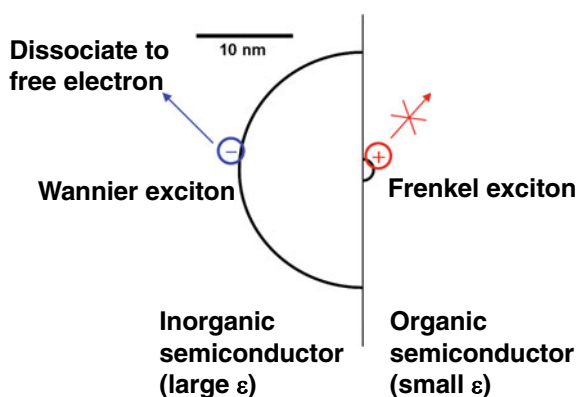
If we can utilize organic semiconductor systems with high ϵ values, exciton dissociation would no longer be a limiting factor for organic solar cells; i.e., exciton would automatically dissociate at room temperature. One possibility is to utilize the heterointerface between the inorganic semiconductor and the organic semiconductor (Fig. 10.5). Since Wannier exciton and Frenkel exciton are formed in the inorganic and organic sides, respectively, an exciton is expected to dissociate efficiently with the assistance of the large ϵ in the inorganic semiconductor, which allows charge to feel weak Coulombic attraction force in the inorganic semiconductor. For example, *n*-type inorganic semiconductor films such as TiO₂ and ZnO can be incorporated in the lateral cell instead of the electron transporting layer (PTCDI-C8).

10.2 Advanced Lateral Junctions—Beyond Shockley–Queisser Limit

Advanced lateral cells composed of organic semiconductor films with high mobilities for holes (C8-BTBT) and electrons (PTCDI-C8) (Chapter 3, Sect. 3.5.4) are shown in Fig. 10.6a. Between C8-BTBT and PTCDI-C8, visible near-infrared absorbers such as DBP and Pc (phthalocyanines), were inserted. Cascade energetic structure is preferable for the choice of absorbers (Fig. 10.6b).

By utilizing the unlimited choices and sharpness of the absorptions of organic semiconductors, the solar spectrum would be divided finely and absorbed by the appropriately designed organic semiconductors (Fig. 10.6c). For lateral junctions, the unlimited number of layers can be stacked, and different photovoltages depending on the bandgap (E_g) are collected using the parallel circuits. For one bandgap system,

Fig. 10.5 Schematic illustration of heterointerface between the inorganic semiconductor and the organic semiconductor. Exciton is expected to dissociate efficiently with the assistance of the large ϵ in the inorganic semiconductor



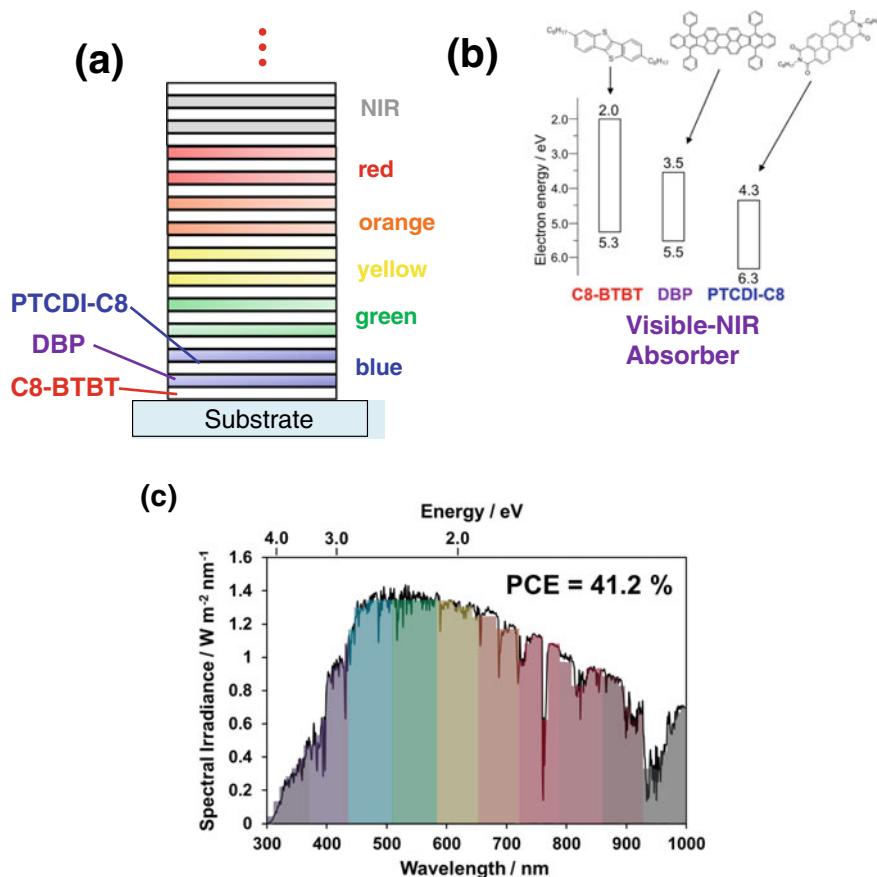


Fig. 10.6 **a** Advanced lateral cell. Between C8-BTBT and PTCDI-C8, visible to near-infrared absorbers such as DBP and Pc (phthalocyanines) are inserted. **b** Cascade energetic structure. **c** Fine division of the solar spectrum into ten regions

the maximum conversion efficiency of 33% was obtained for $E_g = 1.4$ eV (Shockley–Queisser; SQ) limit [11]. When the solar spectrum is divided into ten regions, the conversion efficiency of 41.2% beyond SQ-limit would be obtained under the assumption that the V_{oc} -loss of 0.3 V and the fill factor of 0.8 (Fig. 10.6c).

It should be noted that organic semiconductor is intrinsically suitable for a fine division of the solar spectrum since the sharp absorption can be intentionally tuned to various wavelengths by the molecular design. Moreover, the organic semiconductor is highly suitable for multilayer fabrication at a low price. This would be the utmost advantage of organic solar cells.

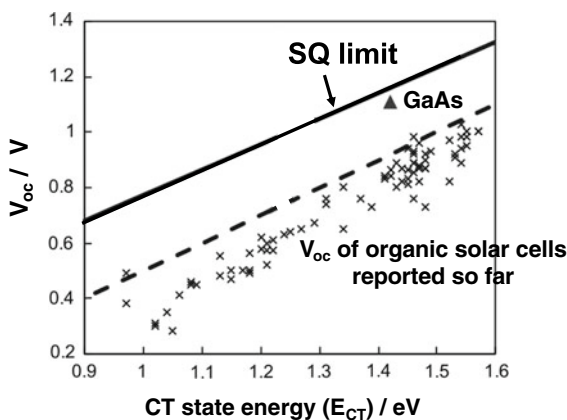
10.3 Recombination Suppression

Recombination suppression has been a priority issue for inorganic solar cells since the recombination is the main leakage of photocurrent. On the other hand, for organic solar cells, the recombination has not attracted considerable attention due to the small magnitude of photocurrent. However, considering that in the past decade, the photocurrent density of organic solar cells exceeded 20 and reached 25 mAcm^{-2} [12], researchers have started to focus on the recombination process in relation to the V_{oc} -loss (Chapter 8). Radiative recombination determines the thermodynamic theoretical limitation of V_{oc} (SQ-limit) (Fig. 10.7). V_{oc} -loss of inorganic solar cells such as GaAs is negligible, and V_{oc} value (triangular-shaped point) has already almost reached the SQ-limit. However, V_{oc} -losses of organic solar cells reported so far are more than 0.5 V, while V_{oc} is far below SQ-limit (crosses). Therefore, non-radiative recombination causing V_{oc} -loss for organic solar cells should be suppressed. Presently, non-radiative recombination suppression is a cutting-edge issue for organic solar cells.

10.3.1 Non-radiative Recombination Dissipated to Molecular Vibration

Non-radiative recombination, which dissipates excited energy to the thermal molecular vibrational energy, is an essential leakage process in the organic solar cells. Conventionally, the carrier generation process of organic semiconductors showing the hopping conduction is represented by the localized model (Fig. 10.8a). In this case, since there is a large Stokes shift (Fig. 10.8c) between the ground state and charge transfer (CT) state due to the considerable reorganization energy, strong vibrational coupling induces the non-radiative recombination (geminate recombination) [13].

Fig. 10.7 Dependence of open-circuit photovoltage (V_{oc}) on the CT state energy (E_{CT}). The black solid line is the theoretical (SQ) limit of V_{oc} . The dashed black line shows $V_{\text{oc}} = E_{\text{CT}}/e - 0.5$ V. The crosses are V_{oc} for all types of organic solar cells reported so far. A closed triangle is V_{oc} for GaAs



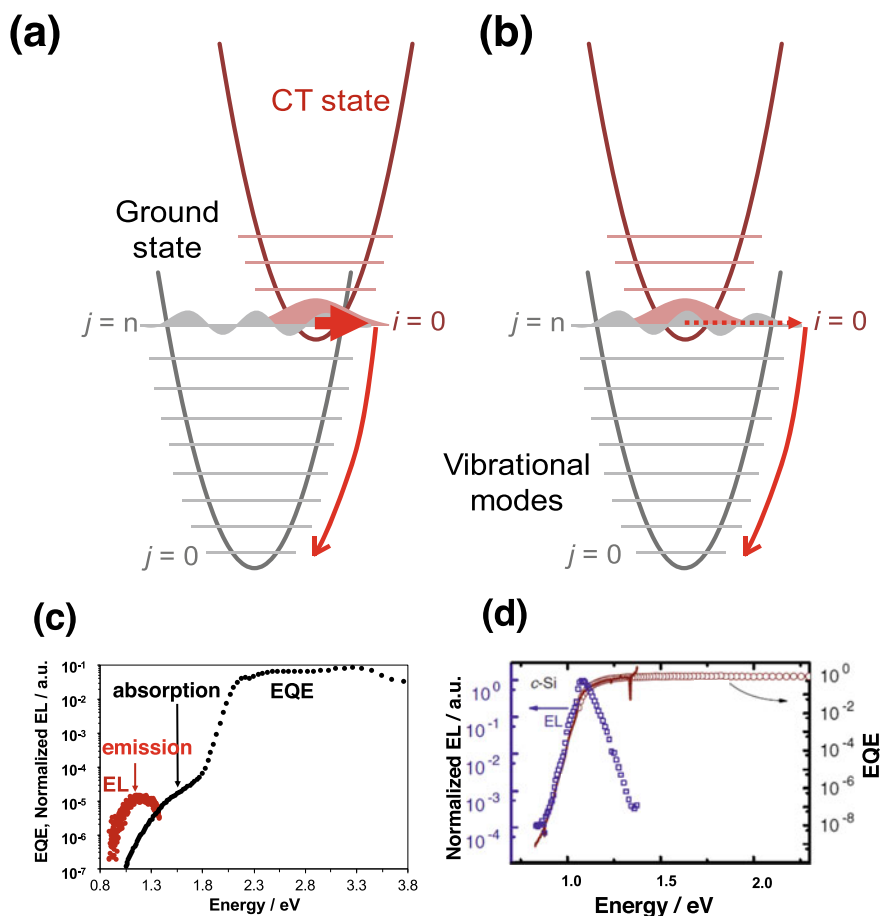
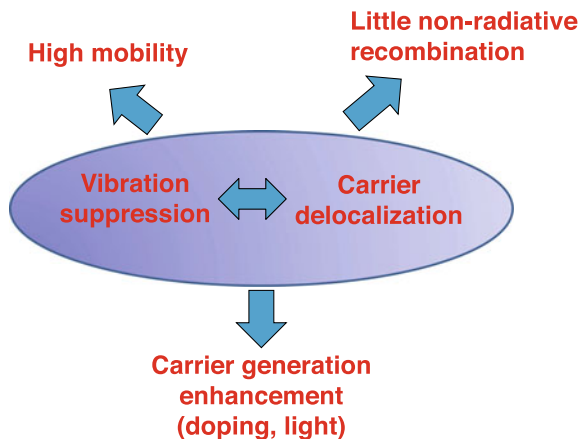


Fig. 10.8 **a** Localized model of the non-radiative recombination from CT state to ground state. **b** Delocalized model of the non-radiative recombination from CT state to ground state. **c** Absorption and EL emission from CT state for 6T/PTCDI-C8 system exhibiting hopping conduction showed a large Stokes shift. Absorption by CT is represented by the edge of the EQE (external quantum efficiency) spectrum. **d** Absorption and EL emission for single-crystal Si exhibiting band conduction showed a little Stokes shift. **d** Reproduced with permission from W. Warta et al., *Phys. Rev. Appl.*, Copyright 2015 American Physical Society

Even if the bimolecular recombination occurs between completely separated electron and hole, non-radiative recombination occurs through the CT state (Fig. 10.8a).

On the other hand, the organic semiconductors showing the band conduction are represented by the delocalized model (Fig. 10.8b). In this case, since there is a small Stokes shift between the ground state and CT state due to the little reorganization energy, little vibrational coupling suppresses the non-radiative recombination. This coincides well with the small Stokes shift observed for the single-crystal Si

Fig. 10.9 Carrier mobility, non-radiative recombination, and carrier generation are closely related to each other with the molecular vibration through carrier delocalization



(Fig. 10.8d) [14]. Thus, organic solar cells using band-conductive organic semiconductors would show little non-radiative recombination dissipated to molecular vibration.

Carrier mobility, non-radiative recombination, and carrier generation are closely related to each other with the molecular vibration through carrier delocalization (Fig. 10.9). Suppression of molecular vibration causes the increase of carrier mobility, the decrease of non-radiative recombination, and presumably, the increase of carrier generation both by light excitation and doping. Detailed clarification of these relationships is the key to the essential breakthrough of organic solar cells.

Intramolecular vibrational modes and inter-molecular vibrational (phonon) modes, which induce the non-radiative recombination, should be identified to design the molecules that can suppress the non-radiative recombination. Suppression of inter-molecular vibration (phonon) might require an innovative approach since there are no chemical bonds among molecules, contrary to the inorganic semiconductors.

In general, the organic semiconductor showing little non-radiative recombination is highly radiative. Namely, the organic semiconductor suitable for efficient organic solar cells is also suitable for the organic electroluminescent device.

10.3.2 *Non-radiative Recombination Via Carrier Traps*

Inorganic crystals inevitably have dangling bonds at the surface, the grain boundary, and the heterojunction, which act as the carrier traps. Thus, for inorganic solar cells, the suppression of trap-induced recombination has been a priority issue, because it is the main leakage mechanism of photocurrent. Passivation of the surface states (Fig. 10.10a), the interfacial states at the grain boundary (Fig. 10.10b), and the interfacial states at heterojunction (Fig. 10.10c) has been a key to obtain efficient solar cells.

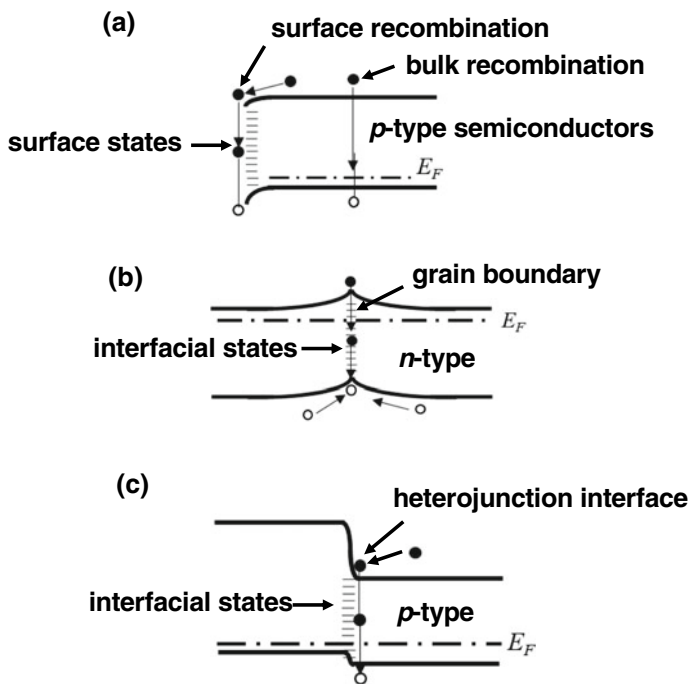


Fig. 10.10 Various recombination processes in the inorganic solar cells. **a** Surface recombination. **b** Recombination at the grain boundary. **c** Recombination at heterojunction interface

On the other hand, organic crystals do not have dangling bonds. However, the various kinds of carrier traps exist in organic crystals. More precisely, they act as carrier traps and accelerate the non-radiative recombination [15] (Fig. 10.11a). The molecular-level spatial structure and energetic structure of these carrier traps can hardly be identified. The concept of traps in organic crystals is not clear. By the analogy of inorganic crystals, they might be a molecular vacancy (Fig. 10.11b) or interstitial molecule (Fig. 10.11c). Steps and kinks at the crystal surface or grain boundary may act as traps (Fig. 10.11d). There should be traps at organic/metal interface and organic/organic heterointerface. Their real nature should close to suppress the trap-induced recombination. This is the next challenge for the field of organic solar cells.

10.4 Conclusion

The following proposal to future organic solar cells based on the fundamental physical aspects is discussed. (i) Exciton dissociation using single bipolar band-conductive organic semiconductors. (ii) The doped organic single-crystal substrates having long

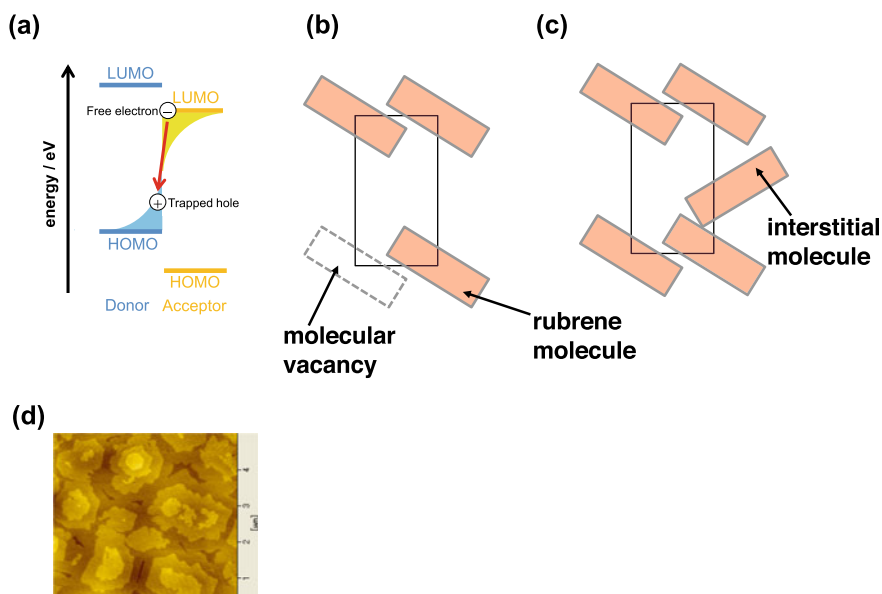


Fig. 10.11 **a** Trap-assisted non-radiative recombination. **b** Molecular vacancy. **c** Interstitial molecule. **d** AFM image of homoepitaxially grown rubrene single crystal. Steps and kinks at the crystal surface or grain boundary may act as traps. **a** Reproduced with permission from [15] Copyright 2018 Elsevier. **d** Reproduced with permission from M. Hiramoto et al., *Adv. Mater.*, Copyright 2018 John Wiley and Sons. Reproduced with permission from C. Ohashi et al., *Adv. Mater.*, Copyright 2017 John Wiley and Sons

exciton diffusion length. (iii) Exciton dissociation using organic/inorganic hybrid cells with a large dielectric constant. (iv) Advanced lateral cells showing the efficiency beyond the SQ-limit. An ultimate advantage of the organic semiconductor is its suitability for a fine division of the solar spectrum.

Suppression of non-radiative recombination is a cutting-edge issue for organic solar cells. V_{oc} -loss by non-radiative recombination would be suppressed close to the SQ-limit. Non-radiative recombination dissipated to molecular vibration would be suppressed by identifying the intramolecular vibrational modes and inter-molecular vibrational phonon modes, related to the non-radiative recombination. Non-radiative recombination via carrier traps has become a key issue for organic solar cells. The spatial and energetic nature of carrier traps would be clarified to suppress the trap-induced recombination.

The research on organic solar cell has advanced gradually, on par with that on inorganic solar cell.

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