

Review

# Interfacial Charge-Transfer Transitions for Direct Charge-Separation Photovoltaics

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**Abstract:** Photoinduced charge separation (PCS) plays an essential role in various solar energy conversions such as photovoltaic conversion in solar cells. Usually, PCS in solar cells occurs stepwise via solar energy absorption by light absorbers (dyes, inorganic semiconductors, etc.) and the subsequent charge transfer at heterogeneous interfaces. Unfortunately, this two-step PCS occurs with a relatively large amount of the energy loss (at least ca. 0.3 eV). Hence, the exploration of a new PCS mechanism to minimize the energy loss is a high-priority subject to realize efficient solar energy conversion. Interfacial charge-transfer transitions (ICTTs) enable direct PCS at heterogeneous interfaces without energy loss, in principle. Recently, several progresses have been reported for ICTT at organic-inorganic semiconductor interfaces by our group. First of all, new organic-metal oxide complexes have been developed with various organic and metal-oxide semiconductors for ICTT. Through the vigorous material development and fundamental research of ICTT, we successfully demonstrated efficient photovoltaic conversion due to ICTT for the first time. In addition, we revealed that the efficient photoelectric conversion results from the suppression of charge recombination, providing a theoretical guiding principle to control the charge recombination rate in the ICTT system. These results open up a way to the development of ICTT-based photovoltaic cells. Moreover, we showed the important role of ICTT in the reported efficient dye-sensitized solar cells (DSSCs) with carboxy-anchor dyes, particularly, in the solar energy absorption in the near IR region. This result indicates that the combination of dye sensitization and ICTT would lead to the further enhancement of the power conversion efficiency of DSSC. In this feature article, we review the recent progresses of ICTT and its application in solar cells.

**Keywords:** photovoltaic conversion; dye-sensitized solar cell; direct charge separation; interfacial charge-transfer transition

## 1. Introduction

Photoinduced charge separation (PCS) at heterogeneous interfaces between electron-donating (D) and -accepting (A) substances (organic compounds, inorganic semiconductors, metals, etc.) play an important role in various solar energy conversions ranging from photovoltaic conversion in solar cells to photocatalytic reactions such as solar-to-fuel energy conversion. Usually, PCS at heterogeneous interfaces takes place by the following two steps; the absorption of solar energy by light absorbers and the subsequent charge transfer at D–A heterogeneous interfaces, as shown in Figure 1a. In the two-step PCS mechanism, the interfacial charge transfer process requires the energy level offset of at least ca. 0.3 eV between heterogeneous D and A substances. Accordingly, the two-step PCS occurs with a relatively large energy loss of at least ca. 0.3 eV. In order to realize efficient solar energy conversion, the exploration of a new PCS mechanism to minimize the energy loss is of great importance. Interfacial charge-transfer transitions (ICTTs) enable direct PCS at D–A heterogeneous interfaces without energy loss in principle, as shown in Figure 1b. However, the research field of

ICTT has not been cultivated yet. Recently, several progresses have been reported in the research of ICTT between organic compounds and inorganic semiconductors by our group, ranging from the material development to the application of ICTT in solar cells. At first, we developed several new organic-metal oxide hybrids for ICTT. By applying these hybrid materials in photovoltaic cells, we successfully demonstrated efficient photoelectric conversion based on the direct PCS via ICTT for the first time [1]. We revealed that the efficient photoelectric conversion originates from the effective suppression of charge recombination in the hybrid materials, providing a theoretical insight into the control of charge recombination after ICTT [2]. Moreover, we showed that ICTT can be successfully applied to dye-sensitized solar cells (DSSCs), particularly, in the photovoltaic conversion in the near IR region [3]. This result indicates that the appropriate combination of dye sensitization and ICTT would be useful for the improvement of the energy conversion efficiency of DSSC. We introduce the current situation of DSSC concisely below.

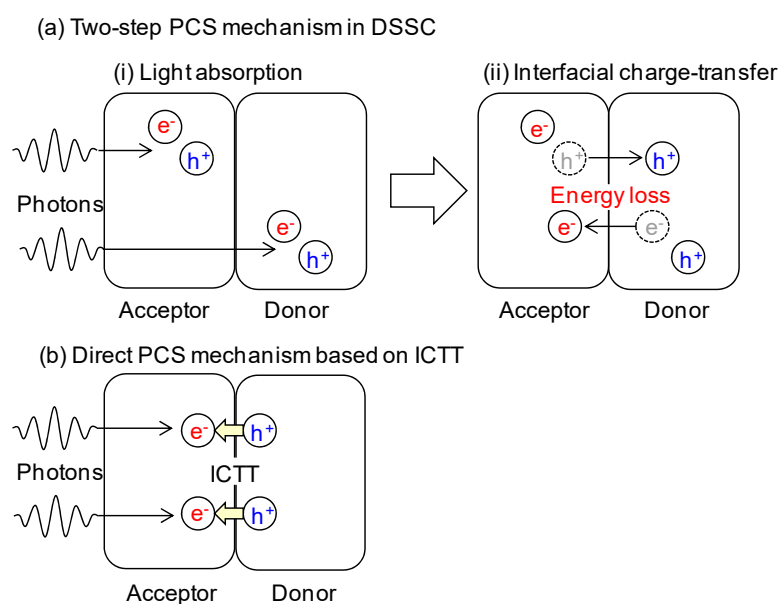


**Figure 1.** Schematic pictures of photoinduced charge separation (PCS) between heterogeneous electron-donating and -accepting substances. (a) Conventional two-step PCS mechanism and (b) direct PCS mechanism based on interfacial charge-transfer transitions (ICTT).

Dye-sensitized solar cells (DSSCs) have attracted much attention as a next-generation solar cell [4–6] and recently gained increasing interest in the potential indoor application, for example, as a power supply for the Internet of Things (IoT) because of the efficient power generation in low light conditions [7–10]. DSSC works by the two-step PCS mechanism via light absorption by dyes and the subsequent electron transfer from excited dyes into the conduction band of wide band-gap semiconductors such as  $\text{TiO}_2$ , as shown in Figure 2a. So far, considerable effort has been devoted to the research and development of DSSC using various dyes (organic dyes and metal-complex dyes) and hole-transporting redox electrolytes [11–19]. Recently, the power conversion efficiency (PCE) over 14% under the standard solar irradiation (AM1.5G, 1 sun) was achieved by two groups [15,19]. In addition, solid-state DSSC with PCE over 11% was developed [20–22]. However, the highest PCE of DSSC is still lower than those (>20%) of other solar cells such as crystalline Si solar cells and perovskite solar cells [23]. To realize more efficient solar energy conversion is a high-priority subject for DSSC. As mentioned above, the two-step PCS occurs with a large amount of energy loss. In DSSC, the electron injection from excited dyes to  $\text{TiO}_2$  occurs with an energy loss of ca. 0.3 eV that corresponds to the energy level offset between the LUMO of dyes and the conduction band minimum (CBM) of  $\text{TiO}_2$  [5,6,24–27], as shown in Figure 2a. ICTT between organic compounds including dyes and inorganic semiconductors is anticipated to overcome the energy loss issue in the electron injection

process due to the direct PCS nature. There are two schemes for the application of ICTT to photovoltaic conversion, in which solar energy is absorbed only by ICTT and by both dye sensitization and ICTT, as shown in Figure 2b,c, respectively. In the former scheme, ICTT opens up a new potentiality of organic compounds for photovoltaic conversion. Photovoltaic materials with two functions of solar energy absorption and direct PCS can be prepared by using low-cost organic compounds with a wide HOMO–LUMO gap. Because of the different PCS mechanisms and light absorbing materials and methods to realize efficient photovoltaic conversion, ICTT-based photovoltaic cells should be distinguished from DSSC. In the latter scheme, on the other hand, ICTT between dyes and  $\text{TiO}_2$  can expand the spectral sensitivity of DSSC on the longer wavelength side. This scheme is included in the framework of DSSC. We have examined the two approaches of ICTT to the development of solar cells. Here, we review the background and the recent progresses in the research of ICTT and the application in solar cells.

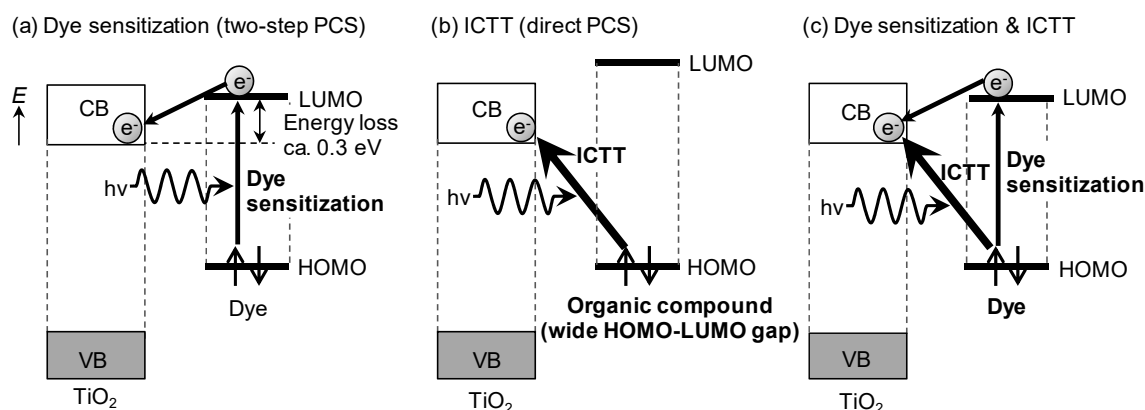


**Figure 2.** Schematic energy level diagrams of (a) dye sensitization of  $\text{TiO}_2$  (two-step PCS), (b) ICTT between an organic compound with a wide HOMO–LUMO gap and  $\text{TiO}_2$  (direct PCS), and (c) dye sensitization and ICTT between a dye and  $\text{TiO}_2$ . CB and VB denote the conduction band and valence band, respectively. HOMO and LUMO stand for the highest occupied molecular orbital and the lowest unoccupied molecular orbital, respectively.

## 2. Interfacial Charge-transfer Transitions and Their Photovoltaic Conversion Properties

First, we briefly introduce the history of the fundamental research of ICTT. To our best knowledge, ICTT between organic compounds and inorganic semiconductors was first reported in 1983 by Houlding et al. [28]. They observed that  $\text{TiO}_2$  nanoparticles were colored bright yellow orange upon the chemisorption of 8-hydroxyquinoline (HOQ) via the hydroxy group and showed a broad absorption band in the visible region. They predicted that the visible light absorption is due to ICTT from the chemisorbed OQ molecule to  $\text{TiO}_2$ . Interestingly, they also demonstrated photocatalytic  $\text{H}_2$  generation via the ICTT excitation, showing the high potentiality of ICTT in the solar energy conversion. Then, Moser et al. and Rajh et al. reported in 1991 and 1999 that catechol (CA) [29] and ascorbic acid (AA) [30] show ICTT bands in the visible region upon the chemisorption on  $\text{TiO}_2$  surfaces via their two hydroxy groups, respectively, as shown in Table 1. Persson et al. computationally verified ICTT between  $\text{TiO}_2$  and CA with quantum chemical calculations [31]. Stimulated by their pioneering studies, ICTTs in the surface complexes of  $\text{TiO}_2$  nanoparticles with aromatic hydroxy compounds (mono-hydroxy compounds [32–36], enediol compounds [37–41], etc.) have been examined in detail.

Against the background, photovoltaic conversion properties of ICTT have been examined from around 1996 employing the surface complexes of  $\text{TiO}_2$  nanoparticles with aromatic hydroxy compounds. In 1996, Tennakone et al. first reported the photocurrent generation by ICTT using  $\text{TiO}_2$ -CA and  $\text{TiO}_2$ -gallic acid surface complexes [42]. Unfortunately, they did not estimate incident photon-to-current conversion efficiencies (IPCEs) in their experiments. Then, Xagas et al. [43] and Sirimanne et al. [44] reported in 2000 and 2003 photovoltaic conversion due to ICTT in the  $\text{TiO}_2$ -AA surface complex and

estimated IPCE to be ca. 5% and ca. 12%, respectively, as shown in Table 2. In 2005, Tae et al. reported low IPCE (ca. 9%) for ICTT in the TiO<sub>2</sub>-CA surface complex [45]. Contrary to the anticipation, it was seen that ICTTs in the TiO<sub>2</sub>-enediol surface complexes give rise to quite inefficient photovoltaic conversion with the low IPCE values. In order to examine the charge recombination process after ICTT, Wang et al. performed femtosecond transient absorption measurements of the TiO<sub>2</sub>-CA complex [46]. They found that the charge recombination occurs very rapidly after the ICTT excitation, in which ca. 80% of electrons injected into the conduction band of TiO<sub>2</sub> by ICTT recombine with holes on the adsorbed CA molecules within ca. 10 psec [46]. This result is consistent with the above IPCE data. Accordingly, the charge recombination should be suppressed for efficient photovoltaic conversion. These results show that enediol compounds such as CA and AA are not suitable for direct PCS photovoltaic conversion. Since organic-inorganic semiconductor hybrids for ICTT were quite limited at that time, there had been no further progress on the photovoltaic conversion based on direct PCS until around 2010.

**Table 1.** Representative organic-inorganic semiconductor complexes for ICTT, bridging atoms, and the year of the first report for each organic-inorganic complex.

| Inorganic Semiconductor | Organic Compound               |                       | Bridging Atom | Year |
|-------------------------|--------------------------------|-----------------------|---------------|------|
| TiO <sub>2</sub>        | Aromatic                       | Mono-hydroxy compound | O             | 1983 |
| TiO <sub>2</sub>        | hydroxy                        | Catechol              | O             | 1991 |
| TiO <sub>2</sub>        | compound                       | Ascorbic acid         | O             | 1999 |
| TiO <sub>2</sub>        | Aromatic carboxylic acid       |                       | O             | 2008 |
| TiO <sub>2</sub>        | Bis(dicyanomethylene) compound |                       | O             | 2009 |
| TiO <sub>2</sub>        | Aromatic amine                 |                       | N             | 2011 |
| TiO <sub>2</sub>        | Benzenedithiol                 |                       | S             | 2015 |
| BaTiO <sub>3</sub>      | Catechol                       |                       | O             | 2016 |
| SrTiO <sub>3</sub>      | Catechol                       |                       | O             | 2018 |
| ZnO                     | Benzenethiol                   |                       | S             | 2020 |

**Table 2.** Incident photon-to-current conversion efficiency (IPCE) maximum values reported for ICTT based photovoltaic conversion in organic-metal oxide complexes.

| Organic-Metal Oxide Complex | IPCE Maximum Value |
|-----------------------------|--------------------|
| TiO <sub>2</sub> -AA        | 5%                 |
| TiO <sub>2</sub> -AA        | 12%                |
| TiO <sub>2</sub> -CA        | 9%                 |
| TiO <sub>2</sub> -TCNQ      | 81%                |
| TiO <sub>2</sub> -ATCA      | 86%                |

New kinds of organic-inorganic semiconductor complexes for ICTT have been developed with various organic compounds and inorganic semiconductors since around 2010, as shown in Table 1 [47–69]. In 2011, our group reported unique surface complexes of bis(dicyanomethylene) compounds (TCNXs) such as tetracyanoquinodimethane (TCNQ), which are well-known to be strong electron acceptors, with TiO<sub>2</sub> nanoparticles [51,52]. As mentioned above, organic compounds typically chemisorb on metal-oxide surfaces (TiO<sub>2</sub>, ZnO, etc.) via their chemical anchoring groups (-OH, -SH, -COOH, -NH<sub>2</sub>, etc.) through the dehydration condensation reaction with surface hydroxy groups on TiO<sub>2</sub>, as shown in Figure 3a. In contrast, TCNQ has no chemical anchoring groups and chemisorbs on TiO<sub>2</sub> surfaces via the nucleophilic addition reaction of a surface hydroxy group, producing the negatively-charged TCNQ adsorbate on TiO<sub>2</sub>, as shown in Figure 2b. Upon the surface complex formation, the color of TiO<sub>2</sub> nanoparticles is drastically changed to violet, as shown in Figure 4. The TiO<sub>2</sub>-TCNQ complex shows a broad ICTT band in the visible region between 400 and ca. 700 nm, in which ICTT takes place from the HOMO of the adsorbed TCNQ to the conduction band of TiO<sub>2</sub>. The coloration and the wavelength range of ICTT band are drastically changed by introducing

electron-donating or -withdrawing substituent groups or modification of the benzene ring, as shown in Figure 4 [52,55]. These spectral changes are directly associated to the variation in the HOMO energy of the adsorbed TCNX due to the chemical modifications [56]. With increasing and decreasing the electron accepting property of TCNX, the ICTT band blue- and red-shifts, respectively. Notably, our research showed that the adsorption mechanism and structure of organic compounds can be clarified by means of FT-IR measurements and density functional theory (DFT) calculations and the electronic structure and ICTT excitation can be clarified by ionization potential measurements based on photoelectron yield spectroscopy (PYS) and DFT and time-dependent DFT (TD-DFT) calculations, which provide a firm basis for the research of ICTT [51–56].

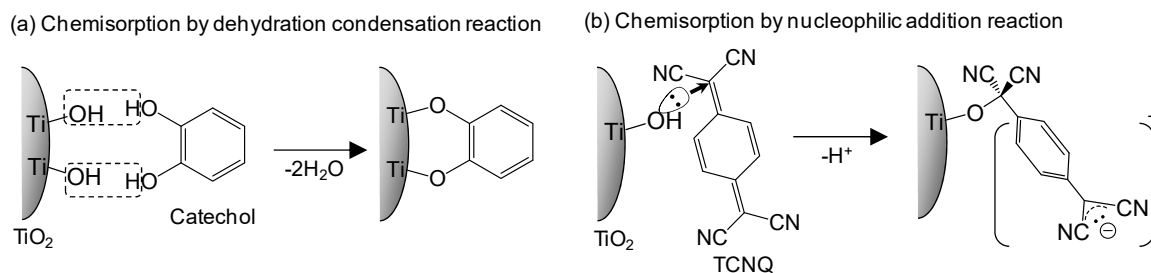


**Figure 3.** Chemisorption reactions of (a) organic compounds bearing proton-donating chemical anchoring groups via dehydration condensation reaction and (b) TCNQ via nucleophilic addition reaction.

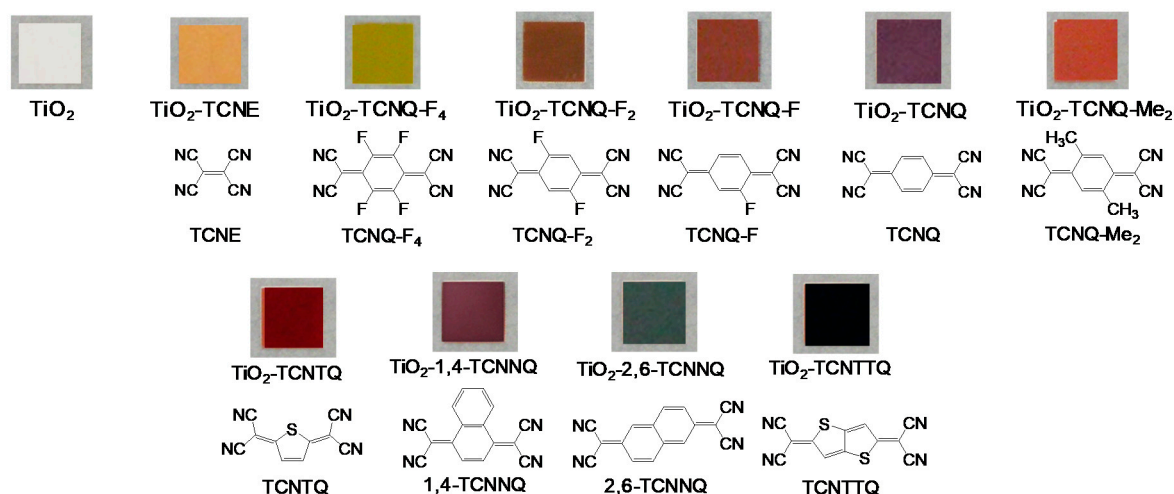


**Figure 4.** Photographs of anatase  $\text{TiO}_2$  nanoparticles immersed in the solution of various TCNXs.

We examined photovoltaic properties of ICTT in the  $\text{TiO}_2\text{-TCNQ}$  surface complex [50]. The  $\text{TiO}_2\text{-TCNQ}$  photovoltaic cell was fabricated with an anatase  $\text{TiO}_2\text{-TCNQ}$  nanoporous photoelectrode and iodide electrolyte ( $\text{I}^-/\text{I}_3^-$  in acetonitrile). The fundamental structure is shown in Figure 5a. We observed efficient photovoltaic conversion with IPCE of ca. 80%, as shown in Figure 5b. This IPCE value is remarkably higher than those (IPCE < ca. 10%) reported for the direct PCS photovoltaics with the  $\text{TiO}_2\text{-enediol}$  complexes. Figure 5c shows the current density-voltage ( $J$ - $V$ ) curve of the  $\text{TiO}_2\text{-TCNQ}$  photovoltaic cell under simulated solar irradiation (AM1.5G, 100  $\text{mW}/\text{cm}^2$ ). The short-circuit current density ( $J_{\text{SC}}$ ), open-circuit voltage ( $V_{\text{OC}}$ ), fill factor ( $FF$ ), and PCE were estimated to be 9.9  $\text{mA}/\text{cm}^2$ , 0.36 V, 0.62, and 2.2%, respectively. Although  $V_{\text{OC}}$  is rather low, this is the first time that such high  $J_{\text{SC}}$  was obtained by ICTT.

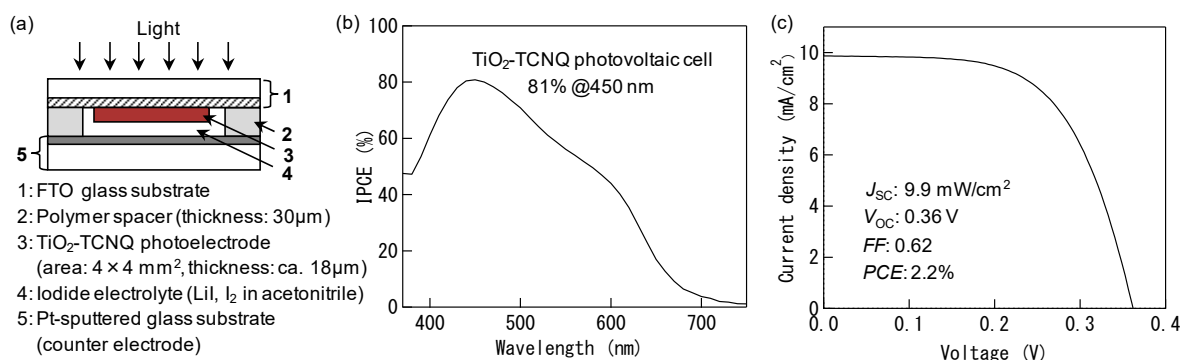


**Figure 5.** (a) Structure of TiO<sub>2</sub>-TCNQ photovoltaic cells fabricated in our study and (b) incident photon-to-current conversion efficiency (IPCE) excitation spectrum and (c) *J*-*V* curve under simulated solar irradiation (AM1.5G, 100 mW/cm<sup>2</sup>) of TiO<sub>2</sub>-TCNQ photovoltaic cell with iodide electrolyte (LiI: ca. 2 M, I<sub>2</sub>: 0.025 M, solvent: acetonitrile).

More efficient photoelectric conversion due to ICTT was achieved by employing the surface complex of TiO<sub>2</sub> with 2-anthracene carboxylic acid (ATCA) [1]. Upon the immersion into the ATCA solution, anatase TiO<sub>2</sub> nanoparticles were colored yellow, as shown in Figure 6a. The TiO<sub>2</sub>-ATCA complex is formed via a carboxy group similarly to the TiO<sub>2</sub>-dye system in DSSC and shows an ICTT band in the visible region between 400 and ca. 650 nm. Figure 6b,c shows IPCE spectrum and *J*-*V* curve under simulated solar irradiation (AM1.5G, 100 mW/cm<sup>2</sup>) of the TiO<sub>2</sub>-ATCA photovoltaic cell with iodide electrolyte (LiI: 1 M, I<sub>2</sub>: 0.025 M, solvent: acetonitrile), respectively, which was fabricated in a similar way to the TiO<sub>2</sub>-TCNQ photovoltaic cell. The TiO<sub>2</sub>-ATCA photovoltaic cell showed higher IPCE (86% at 440 nm) than that obtained for the TiO<sub>2</sub>-TCNQ cell, as shown in Figure 6b. Taking into account the reflection (ca. 90%) of incident light on the FTO surface, almost all incident photons were absorbed by ICTT and converted to photocurrent. *J*<sub>SC</sub>, *V*<sub>OC</sub>, *FF*, and *PCE* were estimated to be 6.6 mA/cm<sup>2</sup>, 0.50 V, 0.66, and 2.2%, respectively [1]. The *J*<sub>SC</sub> value is lower than that of the TiO<sub>2</sub>-TCNQ photovoltaic cell because of the narrower spectral range despite the higher IPCE maximum value. Table 2 summarizes the IPCE values reported for the direct PCS photovoltaic conversion. Inefficient photovoltaic conversion with IPCE values lower than ca. 10% was reported with the enediol compounds. In contrast, efficient photoelectric conversion with high IPCE values was realized with TCNQ and ATCA. Since the low IPCE is attributed to the rapid charge recombination after ICTT, it is likely that charge recombination is suppressed significantly in the TiO<sub>2</sub>-TCNQ and TiO<sub>2</sub>-ATCA systems. We theoretically analyzed the charge recombination process based on the Marcus theory with DFT and TD-DFT calculations [2].

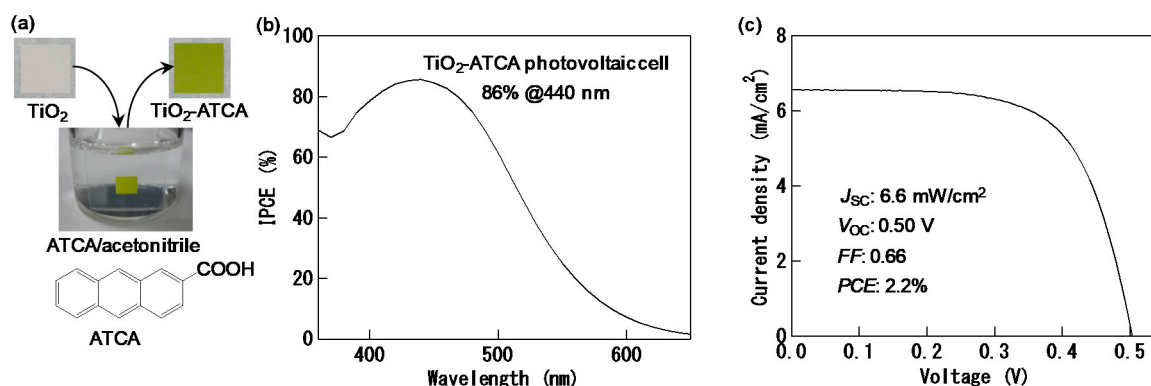


**Figure 6.** (a) Coloration of anatase TiO<sub>2</sub> nanoparticles immersion into the ATCA solution and (b) IPCE spectrum and (c) *J*-*V* curve under simulated solar irradiation (AM1.5G, 100 mW/cm<sup>2</sup>) of TiO<sub>2</sub>-ATCA photovoltaic cell with iodide electrolyte (LiI: 1 M, I<sub>2</sub>: 0.025 M, solvent: acetonitrile). Adapted with permission from Reference 1. Copyright 2015 Elsevier.

### 3. Suppression of Charge Recombination for Direct PCS Photovoltaics

Figure 7a shows the harmonic potential curves of the ground singlet state ( $S_0$ ) and lowest excited charge-separated state ( $S_1$ ) with the same curvature. The aforementioned ICTT systems correspond to the so-called inverted region in the Marcus theory, in which the energy gap ( $\Delta E$ ) between the  $S_0$  and  $S_1$  potential minima is larger than the reorganization energy ( $\lambda$ ) in the  $S_1$  state. Charge recombination occurs via thermal activation in the  $S_1$  state and the subsequent jumping to the  $S_0$  potential curve at the cross point, as shown by the dotted arrows in Figure 7a. The activation energy ( $E_a$ ) for charge recombination is a key factor to reduce the charge recombination rate ( $k_{\text{recom}}$ ).

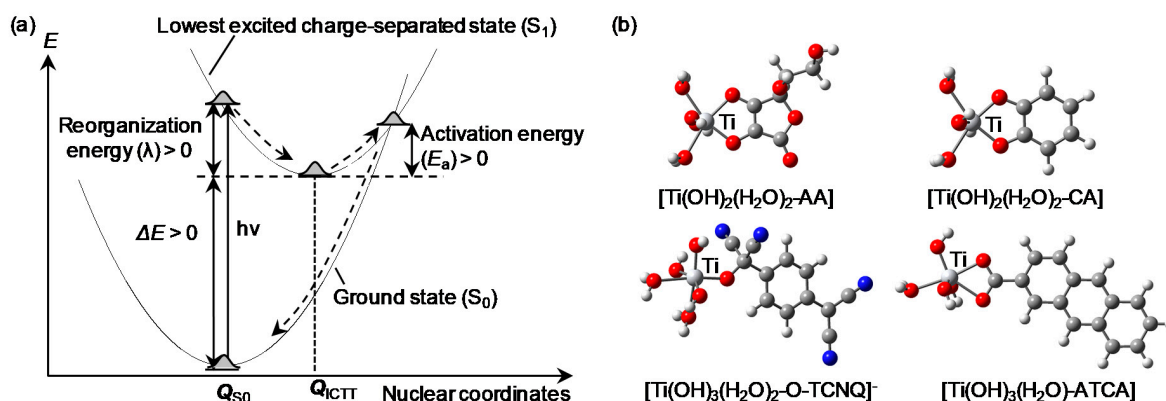


**Figure 7.** (a) Potential energy curves of the ground state ( $S_0$ ) and the lowest excited charge-separated state ( $S_1$ ) and (b) DFT optimized structures of the model complexes in the  $S_0$  state. Gray: carbon, white: hydrogen, blue: nitrogen, red: oxygen, large white: titanium atom. Adapted with permission from Reference 2. Copyright 2015 the PCCP Owner Societies.

According to the Marcus theory,  $k_{\text{recom}}$  after ICTT is given by the following equation.

$$k_{\text{recom}} = \frac{2\pi^2}{h} \frac{\beta^2}{\sqrt{\pi\lambda k_B T}} \exp\left(-\frac{E_a}{k_B T}\right) \quad (1)$$

$h$ ,  $k_B$ ,  $T$ , and  $\beta$  are the Plank constant, Boltzmann constant, absolute temperature, and the transfer integral between the  $S_0$  and  $S_1$  states at the cross point, respectively. From this equation, it is seen that  $k_{\text{recom}}$  is predominantly governed by  $E_a$ , which is given by the following equation.

$$E_a = \frac{(\lambda - \Delta E)^2}{4\lambda} \quad (2)$$

this equation indicates that  $E_a$  increases with decreasing  $\lambda$ , slowing down the charge recombination and vice versa. By DFT and TD-DFT calculations using very simple model complexes shown in Figure 7b,  $\lambda$  values for the four ICTT surface complexes in Table 2 were calculated to be 0.79 eV for AA, 0.71 eV for CA, 0.34 eV for TCNQ, and 0.25 eV for ATCA [2]. Note that the geometrical optimization of each model complex in the  $S_1$  state for the estimation of  $\lambda$  was carried out by fixing the Cartesian coordinates of OH and  $H_2O$  ligands to those in the  $S_0$  optimized structure and relaxing other atoms. Accordingly, the reorganization energies originate from structural changes of the Ti atom and each adsorbed molecule in the  $S_1$  state. Figure 8a shows the relationship between the reported IPCE values and the calculated reorganization energies. The  $TiO_2$ -ATCA and -TCNQ model complexes featuring high IPCE show relatively small reorganization energies, while the  $TiO_2$ -CA and -AA model complexes showing low IPCE exhibit much larger reorganization energies. This correlation is consistent with the tendency predicted from Equations (1) and (2).  $E_a$  for each the organic molecule was estimated from Equation (2) using the calculated  $\lambda$  and  $\Delta E$  experimentally estimated from the absorption onset of the ICTT band. Figure 8b shows the relationship between the reported IPCE values and the calculated

activation energies. We confirm a reasonable correlation between IPCE and  $E_a$ , which indicates that the high IPCE is attributed to the higher activation energy (slow charge recombination) and the low IPCE is due to the low activation energy (fast charge recombination). In addition, it is seen that IPCE abruptly decreases with  $E_a$  around 1.5 eV. In order to understand this behavior, we formulated IPCE based on the two kinetic processes including charge recombination and escape from the  $\text{TiO}_2$  surface generating free electron-hole pairs that are detected as photocurrent, as shown in Figure 9a. Based on the kinetic scheme in Figure 9b, IPCE is given by the following equation [2]:

$$\text{IPCE (\%)} = \frac{100 \times \text{LHE}}{1 + c \times \exp\left(-\frac{E_a}{k_B T}\right)} \quad (3)$$

$$c = \frac{2\pi^2}{k_{\text{escape}} h} \frac{\beta^2}{\sqrt{\pi \lambda k_B T}} \quad (4)$$

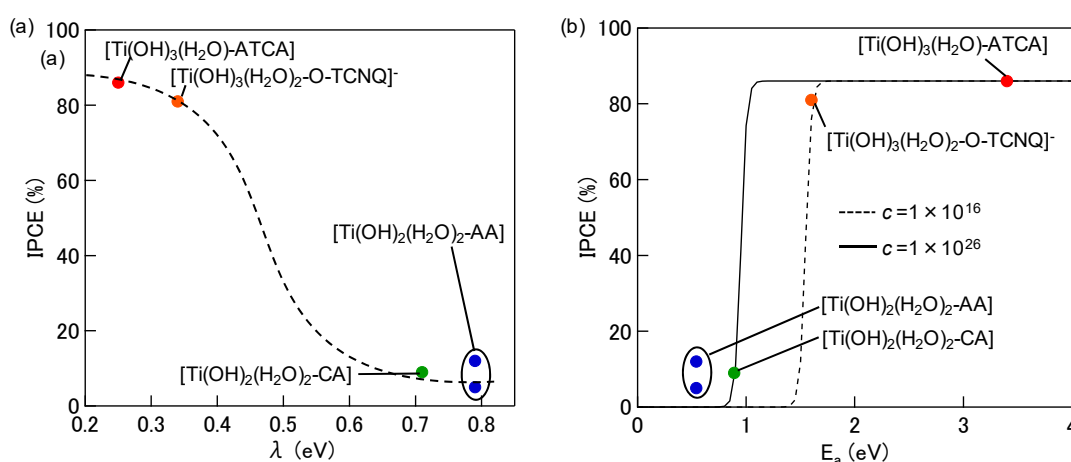


**Figure 8.** (a) Correlation between the reported IPCE and calculated reorganization energy ( $\lambda$ ) and (b) correlation between the reported IPCE and activation energy ( $E_a$ ) calculated with the calculated reorganization energy and experimentally-estimated  $\Delta E$  value. See text for detail. Adapted with permission from Reference 2. Copyright 2015 the PCCP Owner Societies.

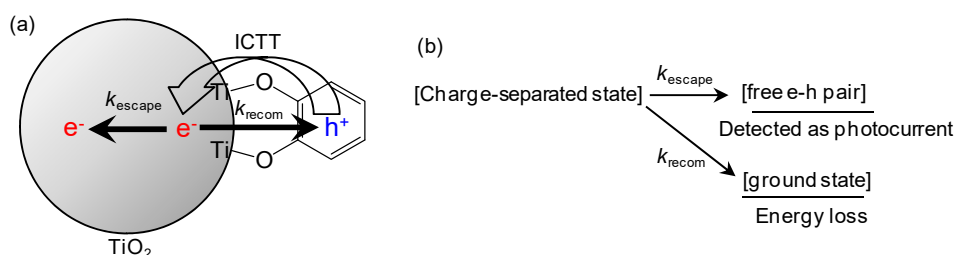


**Figure 9.** (a) Schematic picture of two kinetic processes of electrons injected into  $\text{TiO}_2$  by ICTT and (b) kinetic scheme of the charge-separated state. Adapted with permission from Reference 2. Copyright 2015 the PCCP Owner Societies.

LHE is the light-absorption quantum efficiency. Since the dependence of  $c$  on  $\lambda$  is much weaker than the dependence of IPCE on  $E_a$ , we tentatively treat  $c$  as a constant. Figure 8b shows the dependence of IPCE on  $E_a$  with LHE of 0.86 and  $c$  of  $1 \times 10^{16}$  and  $1 \times 10^{26}$ . The calculated  $E_a$  dependence of IPCE well reproduces the IPCE- $E_a$  correlation. This result clearly reveals that the reorganization energy should be small to suppress charge recombination for obtaining high IPCE. Our DFT analysis indicates that the reorganization energy strongly depends on the kind of chemical anchoring group and a carboxy group is the most useful anchor to suppress the charge recombination [2].

#### 4. Photovoltaic Conversion Based on ICTT in DSSC

Generally, it has been reported that carboxy-anchor dyes adsorbed on  $\text{TiO}_2$  exhibit light absorption at longer wavelengths than their intra-molecular electronic transitions. Figure 10a shows the energy level diagram of  $\text{TiO}_2$  and the LEG4 dye, which was employed in the DSSC achieving the highest PCE (14.3%) [15]. The absorption onset of the LEG4 dye red-shifts from ca. 620 to ca. 780 nm upon the adsorption on  $\text{TiO}_2$ , enabling photovoltaic conversion in the near IR region, as shown in Figure 10b. However, the origin of the near IR light absorption was not unknown. The above-mentioned result of the efficient photoelectric conversion due to ICTT in the  $\text{TiO}_2$ -ATCA complex suggests that the red-shift of the absorption band is attributable to ICTT from LEG4 to  $\text{TiO}_2$ . In fact, the absorption onset energy (1.6 eV) of the  $\text{TiO}_2$ -LEG4 complex well corresponds to the energy difference between the CBM of  $\text{TiO}_2$  and the LUMO of the dye, as shown in Figure 10a. In order to get an insight into the near IR absorption, we examined the absorption properties of the  $\text{TiO}_2$ -LEG4 surface complex with TD-DFT calculations [3]. Figure 11a shows HOMO and LUMO of the bridge- and chelate-type model complexes. For the both models, the HOMO is delocalized over the LEG4 molecule and the LUMO is predominantly distributed in the  $\text{TiO}_2$  cluster, but slightly delocalized on the carboxylate group and cyclopentadithiophene moiety of the dye. Figure 11b shows the TD-DFT calculated electronic excitation spectra of the model complexes. The TD-DFT calculations indicate that dye-to- $\text{TiO}_2$  ICTTs appear at longer wavelengths than the intra-dye electronic transition consistent with the experimental result. Since the lowest electronic excitation is assigned to the  $\text{HOMO} \Rightarrow \text{LUMO}$  transition, the ICTT undergoes direct electron injection into the conduction band. We confirmed that other DSSC dyes bearing a carboxy anchoring group also show ICTT bands on longer wavelength side than their intra-dye absorption. From the DFT analysis, it is seen that the energy levels in the conduction band close in energy to the LUMO of the dyes are strongly coupled with the LUMO, which results in the delocalization on the dyes, rendering ICTT dipole-allowed. The magnitude of the electronic coupling with LUMO for each conduction-band level tends to decrease with increasing the energy difference between them. In addition, the density of states (DOS) of the conduction band of anatase  $\text{TiO}_2$  gradually increases with the energy of the conduction band [70]. Taking into account these factors, the absorption intensity of ICTT decreases as the excitation energy approaches to  $E_{\text{CBM}} - E_{\text{HOMO}}$ , as observed experimentally in the absorption spectra of the  $\text{TiO}_2$ -dye complexes and IPCE spectra of the DSSCs. Based on these results, it is concluded that ICTT plays an important role in the photovoltaic conversion in the near IR region for enhancing PCE of DSSC effectively.

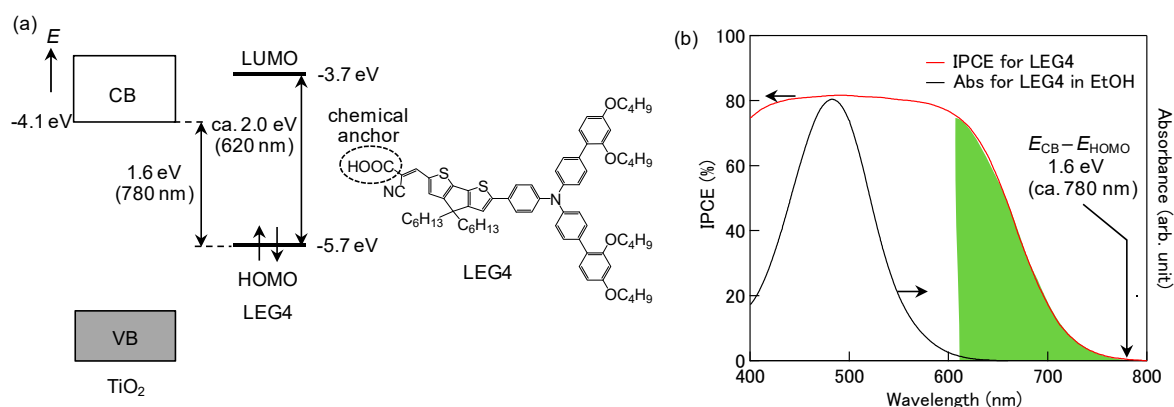


**Figure 10.** (a) Energy level diagram of  $\text{TiO}_2$  and LEG4 along with the molecular structure and (b) absorption spectrum of LEG4 in ethanol and IPCE spectrum of  $\text{TiO}_2$ -LEG4 DSSC. Adapted with permission from Reference 3. Copyright 2018 American Chemical Society.

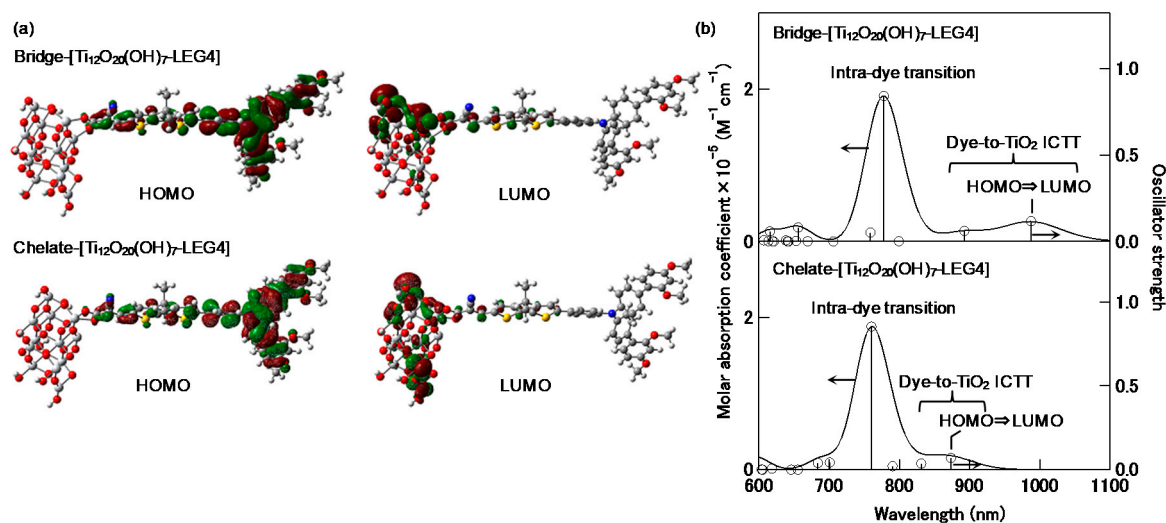


**Figure 11.** (a) Isosurface plots of HOMO and LUMO and (b) TD-DFT calculated electronic excitation spectra of bridge- and chelate-type TiO<sub>2</sub>-LEG4 model complexes. Adapted with permission from Reference 3. Copyright 2018 American Chemical Society.

## 5. Summary

In summary, we reviewed the background and recent progresses on ICTT between organic compounds and metal-oxide semiconductors and its application in solar cells. As mentioned above, there are two approaches of ICTT to solar cells, in which solar energy is absorbed only by ICTT and by both dye sensitization and ICTT. The former approach widely opens up the novel functionality of organic compounds for photovoltaic conversion. ICTT enables to prepare photovoltaic materials with two functions of light absorption and direct PCS using low-cost organic compounds with a large HOMO-LUMO gap. Recently, new organic-metal oxide semiconductor hybrids for ICTT have been developed using various organic compounds and metal-oxide semiconductors. Based on the vigorous material development and fundamental research of ICTT, efficient ICTT-based photovoltaic conversion was demonstrated with the TiO<sub>2</sub>-TCNQ and TiO<sub>2</sub>-ATCA complexes. The obtained IPCE values (>ca. 80%) are much higher than those (<ca. 10%) reported for the TiO<sub>2</sub>-enediol complexes. Our DFT analysis indicates that the efficient photoelectric conversion results from the effective suppression of charge recombination in the surface complexes and reveals that the charge recombination rate strongly depends on the kind of chemical anchoring group. These studies provide an important basis for the development of direct PCS photovoltaic devices. In the latter approach, we found that the carboxy-anchor dyes typically used in DSSC show ICTT in the visible to near IR region. Particularly, ICTT plays a crucial role in the absorption of near IR sunlight in DSSC. This result indicates the possibility that appropriate combination of dye sensitization and ICTT could improve the PCE of DSSC exceeding 14%. For both the approaches, further material development and fundamental research of ICTT is necessary to realize efficient direct PCS photovoltaic conversion.

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## References

1. Fujisawa, J.; Nagata, M. Efficient Light-to-Current Conversion by Organic–Inorganic Interfacial Charge-Transfer Transitions in TiO<sub>2</sub> Chemically Adsorbed with 2-Anthroic Acid. *Chem. Phys. Lett.* **2015**, *619*, 180–184. [[CrossRef](#)]
2. Fujisawa, J. Large Impact of Reorganization Energy on Photovoltaic Conversion due to Interfacial Charge-Transfer Transitions. *Phys. Chem. Chem. Phys.* **2015**, *17*, 12228–12237. [[CrossRef](#)] [[PubMed](#)]
3. Fujisawa, J.; Hanaya, M. Light Harvesting and Direct Electron Injection by Interfacial Charge-Transfer Transitions between TiO<sub>2</sub> and Carboxy-Anchor Dye LEG4 in Dye-Sensitized Solar Cells. *J. Phys. Chem. C* **2018**, *122*, 8–15. [[CrossRef](#)]
4. O'Regan, B.; Grätzel, M. A Low-Cost, High-Efficiency Solar Cell Based on Dye-Sensitized Colloidal TiO<sub>2</sub> Films. *Nature* **1991**, *353*, 737–740. [[CrossRef](#)]
5. Hagfeldt, A.; Grätzel, M. Light-Induced Redox Reactions in Nanocrystalline Systems. *Chem. Rev.* **1995**, *95*, 49–68. [[CrossRef](#)]
6. Hagfeldt, A.; Boschloo, G.; Sun, L.; Kloo, L.; Pettersson, H. Dye-Sensitized Solar Cells. *Chem. Rev.* **2010**, *110*, 6595–6663. [[CrossRef](#)]
7. Freitag, M.; Teuscher, J.; Saygili, Y.; Zhang, X.; Giordano, F.; Liska, P.; Hua, J.; Zakeeruddin, S.M.; Moser, J.-E.; Grätzel, M.; et al. Dye-Sensitized Solar Cells for Efficient Power Generation Under Ambient Lighting. *Nat. Photonics* **2017**, *11*, 372–378. [[CrossRef](#)]
8. Desta, M.B.; Vinh, N.S.; Kumar, C.H.P.; Chaurasia, S.; Wu, W.-T.; Lin, J.T.; Wei, T.-C.; Diau, E.W.-G. Pyrazine-Incorporating Panchromatic Sensitizers for Dye Sensitized Solar Cells Under One Sun and Dim Light. *J. Mater. Chem. A* **2018**, *6*, 13778–13789. [[CrossRef](#)]
9. Chen, C.Y.; Kuo, T.Y.; Huang, C.W.; Jian, Z.H.; Hsiao, P.T.; Wang, C.L.; Lin, J.C.; Chen, C.Y.; Chen, C.H.; Tung, Y.L.; et al. Thermal and Angular Dependence of Next-Generation Photovoltaics Under Indoor Lighting. *Prog. Photovolt. Res. Appl.* **2019**, *28*, 1–11. [[CrossRef](#)]
10. Michaels, H.; Rinderle, M.; Freitag, R.; Benesperi, I.; Edvinsson, T.; Socher, R.; Gagliardi, A.; Freitag, M. Dye-Sensitized Solar Cells Under Ambient Light Powering Machine Learning: Towards Autonomous Smart Sensors for the Internet of Things. *Chem. Sci.* **2020**, *11*, 2895–2906. [[CrossRef](#)]
11. Horiuchi, T.; Fujisawa, J.; Uchida, S.; Grätzel, M. *Data Book on Dye-Sensitized Solar Cells*; CMC Publishing Co.: Tokyo, Japan, 2009.
12. Yella, A.; Lee, H.-W.; Tsao, H.N.; Yi, C.; Chandiran, A.K.; Nazeeruddin, M.K.; Diau, E.W.-G.; Yeh, C.-Y.; Zakeeruddin, S.M.; Grätzel, M. Porphyrin-Sensitized Solar Cells with Cobalt (II/III)-Based Redox Electrolyte Exceed 12 Percent Efficiency. *Science* **2011**, *334*, 629–634. [[CrossRef](#)] [[PubMed](#)]
13. Mathew, S.; Yella, A.; Gao, P.; Humphry-Baker, R.; Curchod, B.F.E.; Ashari-Astani, N.; Tavernelli, I.; Rothlisberger, U.; Nazeeruddin, M.K.; Grätzel, M. Dye-Sensitized Solar Cells with 13% Efficiency Achieved Through the Molecular Engineering of Porphyrin Sensitizers. *Nat. Chem.* **2014**, *6*, 242–247. [[CrossRef](#)] [[PubMed](#)]
14. Kakiage, K.; Aoyama, Y.; Yano, T.; Otsuka, T.; Kyômen, T.; Unno, M.; Hanaya, M. An Achievement of Over 12 Percent Efficiency in an Organic Dye-Sensitized Solar Cell. *Chem. Commun.* **2014**, *50*, 6379–6381. [[CrossRef](#)]
15. Kakiage, K.; Aoyama, Y.; Yano, T.; Oya, K.; Fujisawa, J.; Hanaya, M. Highly-Efficient Dye-Sensitized Solar Cells with Collaborative Sensitization by Silyl-Anchor and Carboxy-Anchor Dyes. *Chem. Commun.* **2015**, *51*, 15894–15897. [[CrossRef](#)] [[PubMed](#)]
16. Kakiage, K.; Osada, H.; Aoyama, Y.; Yano, T.; Oya, K.; Iwamoto, S.; Fujisawa, J.; Hanaya, M. Achievement of Over 1.4 V Photovoltage in a Dye-Sensitized Solar Cell by the Application of a Silyl-Anchor Coumarin Dye. *Sci. Rep.* **2016**, *6*, 35888. [[CrossRef](#)] [[PubMed](#)]
17. Ren, Y.; Sun, D.; Cao, Y.; Tsao, H.N.; Yuan, Y.; Zakeeruddin, S.M.; Wang, P.; Grätzel, M. A Stable Blue Photosensitizer for Color Palette of Dye-Sensitized Solar Cells Reaching 12.6% Efficiency. *J. Am. Chem. Soc.* **2018**, *140*, 2405–2408. [[CrossRef](#)]
18. Zhang, L.; Yang, X.; Wang, W.; Gurzadyan, G.G.; Li, J.; Li, X.; An, J.; Yu, Z.; Wang, H.; Cai, B.; et al. 13.6% Efficient Organic Dye-Sensitized Solar Cells by Minimizing Energy Losses of the Excited State. *ACS Energy Lett.* **2019**, *4*, 943–951. [[CrossRef](#)]

19. Ji, J.-M.; Zhou, H.; Eom, Y.K.; Kim, C.H.; Kim, H.K. 14.2% Efficiency Dye-Sensitized Solar Cells by Co-Sensitizing Novel Thieno[3,2-*b*]indole-Based Organic Dyes with a Promising Porphyrin Sensitizer. *Adv. Energy Mater.* **2020**, *10*, 2000124. [[CrossRef](#)]
20. Cao, Y.; Saygili, Y.; Ummadisingu, A.; Teuscher, J.; Luo, J.; Pellet, N.; Giordano, F.; Zakeeruddin, S.M.; Moser, J.-E.; Freitag, M.; et al. 11% Efficiency Solid-State Dye-Sensitized Solar Cells with Copper(II/I) Hole Transport Materials. *Nat. Commun.* **2017**, *8*, 15390. [[CrossRef](#)]
21. Benesperi, I.; Michaels, H.; Freitag, M. The Researcher's Guide to Solid-State Dye-Sensitized Solar Cells. *J. Mater. Chem. C* **2018**, *6*, 11903–11942. [[CrossRef](#)]
22. Zhang, W.; Wu, Y.; Bahng, H.W.; Cao, Y.; Yi, C.; Saygili, Y.; Luo, J.; Liu, Y.; Kavan, L.; Moser, J.-E.; et al. Comprehensive Control of Voltage Loss Enables 11.7% Efficient Solid-State Dye-Sensitized Solar Cells. *Energy Environ. Sci.* **2018**, *11*, 1779–1787. [[CrossRef](#)]
23. Green, M.A.; Dunlop, E.D.; Hohl-Ebinger, J.; Yoshita, M.; Kopidakis, N.; Ho-Baillie, A.W.Y. Solar Cell Efficiency Tables (Version 55). *Prog. Photovolt. Res. Appl.* **2020**, *28*, 3–15. [[CrossRef](#)]
24. Katoh, R.; Furube, A.; Hara, K.; Murata, S.; Sugihara, H.; Arakawa, H.; Tachiya, M. Efficiencies of Electron Injection from Excited Sensitizer Dyes to Nanocrystalline ZnO Films as Studied by Near-IR Optical Absorption of Injected Electrons. *J. Phys. Chem. B* **2002**, *106*, 12957–12964. [[CrossRef](#)]
25. Hara, K.; Sato, T.; Katoh, R.; Furube, A.; Ohga, Y.; Shinpo, A.; Suga, S.; Sayama, K.; Sugihara, H.; Arakawa, H. Molecular Design of Coumarin Dyes for Efficient Dye-Sensitized Solar Cells. *J. Phys. Chem. B* **2003**, *107*, 597–606. [[CrossRef](#)]
26. Katoh, R.; Furube, A.; Yoshihara, T.; Hara, K.; Fujihashi, G.; Takano, S.; Murata, S.; Arakawa, H.; Tachiya, M. Efficiencies of Electron Injection from Excited N3 Dye into Nanocrystalline Semiconductor (ZrO<sub>2</sub>, TiO<sub>2</sub>, ZnO, Nb<sub>2</sub>O<sub>5</sub>, SnO<sub>2</sub>, In<sub>2</sub>O<sub>3</sub>) Films. *J. Phys. Chem. B* **2004**, *108*, 4818–4822. [[CrossRef](#)]
27. Fujisawa, J.; Osawa, A.; Hanaya, M. A Strategy to Minimize the Energy Offset in Carrier Injection from Excited Dyes to Inorganic Semiconductors for Efficient Dye-Sensitized Solar Energy Conversion. *Phys. Chem. Chem. Phys.* **2016**, *18*, 22244–22253. [[CrossRef](#)]
28. Houlding, V.H.; Grätzel, M. Photochemical Hydrogen Generation by Visible Light. Sensitization of Titanium Dioxide Particles by Surface Complexation with 8-Hydroxyquinoline. *J. Am. Chem. Soc.* **1983**, *105*, 5695–5696. [[CrossRef](#)]
29. Moser, J.; Punchihewa, S.; Infelta, P.P.; Grätzel, M. Surface Complexation of Colloidal Semiconductors Strongly Enhances Interfacial Electron-Transfer Rates. *Langmuir* **1991**, *7*, 3012–3018. [[CrossRef](#)]
30. Rajh, T.; Nedeljkovic, J.M.; Chen, L.X.; Poluektov, O.; Thurnauer, M.C. Improving Optical and Charge Separation Properties of Nanocrystalline TiO<sub>2</sub> by Surface Modification with Vitamin C. *J. Phys. Chem. B* **1999**, *103*, 3515–3519. [[CrossRef](#)]
31. Persson, P.; Bergström, R.; Lunell, S. Quantum Chemical Study of Photoinjection Processes in Dye-Sensitized TiO<sub>2</sub> Nanoparticles. *J. Phys. Chem. B* **2000**, *104*, 10348–10351. [[CrossRef](#)]
32. Tachikawa, T.; Tojo, S.; Fujitsuka, M.; Majima, T. Photocatalytic One-Electron Oxidation of Biphenyl Derivatives Strongly Coupled with the TiO<sub>2</sub> Surface. *Langmuir* **2004**, *20*, 2753–2759. [[CrossRef](#)] [[PubMed](#)]
33. Kim, S.; Choi, W. Visible-Light-Induced Photocatalytic Degradation of 4-Chlorophenol and Phenolic Compounds in Aqueous Suspension of Pure Titania: Demonstrating the Existence of a Surface-Complex-Mediated Path. *J. Phys. Chem. B* **2005**, *109*, 5143–5149. [[CrossRef](#)] [[PubMed](#)]
34. Fujisawa, J.; Matsumura, S.; Hanaya, M. A Single Ti-O-C Linkage Induces Interfacial Charge-Transfer Transitions between TiO<sub>2</sub> and a  $\pi$ -Conjugated Molecule. *Chem. Phys. Lett.* **2016**, *657*, 172–176. [[CrossRef](#)]
35. Fujisawa, J.; Eda, T.; Giorgi, G.; Hanaya, M. Visible-to-Near-IR Wide-Range Light Harvesting by Interfacial Charge-Transfer Transitions between TiO<sub>2</sub> and *p*-Aminophenol and Evidence of Direct Electron Injection to the Conduction Band of TiO<sub>2</sub>. *J. Phys. Chem. C* **2017**, *121*, 18710–18716. [[CrossRef](#)]
36. Sredojević, D.N.; Kovač, T.; Džunuzović, E.; Đorđević, V.; Grgur, B.N.; Nedeljković, J.M. Surface-Modified TiO<sub>2</sub> Powders with Phenol Derivatives: A Comparative DFT and Experimental Study. *Chem. Phys. Lett.* **2017**, *686*, 167–172. [[CrossRef](#)]
37. Rodríguez, R.; Blesa, M.A.; Regazzoni, A.E. Surface Complexation at the TiO<sub>2</sub>(anatase)/Aqueous Solution Interface: Chemisorption of Catechol. *J. Colloid Interface Sci.* **1996**, *177*, 122–131. [[CrossRef](#)]
38. Liu, Y.; Dadap, J.I.; Zimdars, D.; Eisenthal, K.B. Study of Interfacial Charge-Transfer Complex on TiO<sub>2</sub> Particles in Aqueous Suspension by Second-Harmonic Generation. *J. Phys. Chem. B* **1999**, *103*, 2480–2486. [[CrossRef](#)]

39. Rajh, T.; Chen, L.X.; Lukas, K.; Liu, T.; Thurnauer, M.C.; Tiede, D.M. Surface Restructuring of Nanoparticles: An Efficient Route for Ligand–Metal Oxide Crosstalk. *J. Phys. Chem. B* **2002**, *106*, 10543–10552. [[CrossRef](#)]
40. de la Garza, L.; Saponjic, Z.V.; Dimitrijevic, N.M.; Thurnauer, M.C.; Rajh, T. Surface States of Titanium Dioxide Nanoparticles Modified with Enediol Ligands. *J. Phys. Chem. B* **2006**, *110*, 680–686. [[CrossRef](#)]
41. Murata, Y.; Hori, H.; Taga, A.; Tada, H. Surface Charge-Transfer Complex Formation of Catechol on Titanium(IV) Oxide and the Application to Bio-Sensing. *J. Colloid Interface Sci.* **2015**, *458*, 305–309. [[CrossRef](#)]
42. Tennakone, K.; Kumara, G.R.R.A.; Kumarasinghe, A.R.; Sirimanne, P.M.; Wijayantha, K.G.U. Efficient Photosensitization of Nanocrystalline TiO<sub>2</sub> Films by Tannins and Related Phenolic Substances. *J. Photochem. Photobiol. A* **1996**, *94*, 217–220. [[CrossRef](#)]
43. Xagas, A.P.; Bernard, M.C.; Hugot-Le Goff, A.; Spyrellis, N.; Loizos, Z.; Falaras, P. Surface Modification and Photosensitization of TiO<sub>2</sub> Nanocrystalline Films with Ascorbic Acid. *J. Photochem. Photobiol. A* **2000**, *132*, 115–120. [[CrossRef](#)]
44. Sirimanne, P.M.; Soga, T. Fabrication of a Solid-State Cell Using Vitamin C as Sensitizer. *Sol. Energy Mater. Sol. Cells* **2003**, *80*, 383–389. [[CrossRef](#)]
45. Tae, E.L.; Lee, S.H.; Lee, J.K.; Yoo, S.S.; Kang, E.J.; Yoon, K.B. A Strategy to Increase the Efficiency of the Dye-Sensitized TiO<sub>2</sub> Solar Cells Operated by Photoexcitation of Dye-to-TiO<sub>2</sub> Charge-Transfer Bands. *J. Phys. Chem. B* **2005**, *109*, 22513–22522. [[CrossRef](#)] [[PubMed](#)]
46. Wang, Y.; Hang, K.; Anderson, N.A.; Lian, T. Comparison of Electron Transfer Dynamics in Molecule-to-Nanoparticle and Intramolecular Charge Transfer Complexes. *J. Phys. Chem. B* **2003**, *107*, 9434–9440. [[CrossRef](#)]
47. Rahal, R.; Daniele, S.; Hubert-Pfalzgraf, L.G.; Guyot-Ferréol, V.; Tranchant, J.-F. Synthesis of *para*-Amino Benzoic Acid–TiO<sub>2</sub> Hybrid Nanostructures of Controlled Functionality by an Aqueous One-Step Process. *Eur. J. Inorg. Chem.* **2008**, 980–987. [[CrossRef](#)]
48. Thomas, A.G.; Jackman, M.J.; Wagstaffe, M.; Radtke, H.; Syres, K.; Adell, J.; Lévy, A.; Martinsovich, N. Adsorption Studies of *p*-Aminobenzoic Acid on the Anatase TiO<sub>2</sub>(101) Surface. *Langmuir* **2014**, *30*, 12306–12314. [[CrossRef](#)]
49. Manzhos, S.; Kotsis, K. Computational Study of Interfacial Charge Transfer Complexes of 2-Anthraic Acid Adsorbed on a Titania Nanocluster for Direct Injection Solar Cells. *Chem. Phys. Lett.* **2016**, *660*, 69–75. [[CrossRef](#)]
50. Kubo, T.; Fujisawa, J.; Segawa, H. 有機無機ハイブリッド太陽電池の新展開. *Electrochemistry* **2009**, *2009*, 977–980.
51. Jono, R.; Fujisawa, J.; Segawa, H.; Yamashita, K. Theoretical Study of the Surface Complex between TiO<sub>2</sub> and TCNQ Showing Interfacial Charge-Transfer Transitions. *J. Phys. Chem. Lett.* **2011**, *2*, 1167–1170. [[CrossRef](#)]
52. Manzhos, S.; Jono, R.; Yamashita, K.; Fujisawa, J.; Nagata, M.; Segawa, H. Study of Interfacial Charge Transfer Bands and Electron Recombination in the Surface Complexes of TCNE, TCNQ, and TCNAQ with TiO<sub>2</sub>. *J. Phys. Chem. C* **2011**, *115*, 21487–21493. [[CrossRef](#)]
53. Jono, R.; Fujisawa, J.; Segawa, H.; Yamashita, K. The Origin of the Strong Interfacial Charge-Transfer Absorption in the Surface Complex Between TiO<sub>2</sub> and Dicyanomethylene Compounds. *Phys. Chem. Chem. Phys.* **2013**, *15*, 18584–18588. [[CrossRef](#)] [[PubMed](#)]
54. Fujisawa, J.; Hanaya, M. Extremely Strong Organic–Metal Oxide Electronic Coupling Caused by Nucleophilic Addition Reaction. *Phys. Chem. Chem. Phys.* **2015**, *17*, 16285–16293. [[CrossRef](#)] [[PubMed](#)]
55. Fujisawa, J.; Nagata, M.; Hanaya, M. Charge-Transfer Complex *versus*  $\sigma$ -Complex Formed Between TiO<sub>2</sub> and Bis(dicyanomethylene) Electron Acceptors. *Phys. Chem. Chem. Phys.* **2015**, *17*, 27343–27356. [[CrossRef](#)]
56. Fujisawa, J.; Hanaya, M. Electronic Structures of TiO<sub>2</sub>-TCNE, -TCNQ, and -2,6-TCNAQ Surface Complexes Studied by Ionization Potential Measurements and DFT Calculations: Mechanism of the Shift of Interfacial Charge-Transfer Bands. *Chem. Phys. Lett.* **2016**, *653*, 11–16. [[CrossRef](#)]
57. Bledowski, M.; Wang, L.; Ramakrishnan, A.; Khavryuchenko, O.V.; Khavryuchenko, V.D.; Ricci, P.C.; Strunk, J.; Cremer, T.; Kolbeck, C.; Beranek, R. Visible-light photocurrent response of TiO<sub>2</sub>-polyheptazine hybrids: Evidence for interfacial charge-transfer absorption. *Phys. Chem. Chem. Phys.* **2011**, *13*, 21511–21519. [[CrossRef](#)]
58. Pitre, S.P.; Yoon, T.P.; Scaiano, J.C. Titanium Dioxide Visible Light Photocatalysis: Surface Association Enables Photocatalysis with Visible Light Irradiation. *Chem. Commun.* **2017**, *53*, 4335–4338. [[CrossRef](#)]

59. Fujisawa, J. Interfacial Charge-Transfer Transitions Between  $\text{TiO}_2$  and Indole. *Chem. Phys. Lett.* **2020**, *739*, 136974. [[CrossRef](#)]
60. Fujisawa, J.; Muroga, R.; Hanaya, M. Interfacial Charge-Transfer Transitions in a  $\text{TiO}_2$ -Benzenedithiol Complex with Ti–S–C Linkages. *Phys. Chem. Chem. Phys.* **2015**, *17*, 29867–29873. [[CrossRef](#)]
61. Fujisawa, J.; Muroga, R.; Hanaya, M. Interfacial Charge-Transfer Transitions and Reorganization Energies in Sulfur-Bridged  $\text{TiO}_2$ -x-Benzenedithiol Complexes (x: o, m, p). *Phys. Chem. Chem. Phys.* **2016**, *18*, 22286–22292. [[CrossRef](#)]
62. Fujisawa, J.; Eda, T.; Hanaya, M. Interfacial Charge-Transfer Transitions in  $\text{BaTiO}_3$  Nanoparticles Adsorbed with Catechol. *J. Phys. Chem. C* **2016**, *120*, 21162–21168. [[CrossRef](#)]
63. Eda, T.; Fujisawa, J.; Hanaya, M. Inorganic Control of Interfacial Charge-Transfer Transitions in Catechol-Functionalized Titanium Oxides Using  $\text{SrTiO}_3$ ,  $\text{BaTiO}_3$ , and  $\text{TiO}_2$ . *J. Phys. Chem. C* **2018**, *122*, 16216–16220. [[CrossRef](#)]
64. Fujisawa, J.; Kaneko, N.; Hanaya, M. Interfacial Charge-Transfer Transitions in  $\text{ZnO}$  Induced Exclusively by Adsorption of Aromatic Thiols. *Chem. Commun.* **2020**, *56*, 4090–4093. [[CrossRef](#)] [[PubMed](#)]
65. Varaganti, S.; Ramakrishna, G. Dynamics of Interfacial Charge Transfer Emission in Small Molecule Sensitized  $\text{TiO}_2$  Nanoparticles: Is It Localized or Delocalized? *J. Phys. Chem. C* **2010**, *114*, 13917–13925. [[CrossRef](#)]
66. Kim, G.; Choi, W. Charge-Transfer Surface Complex of EDTA- $\text{TiO}_2$  and its Effect on Photocatalysis Under Visible Light. *Appl. Catal. B* **2010**, *100*, 77–83. [[CrossRef](#)]
67. Kim, G.; Lee, S.-H.; Choi, W. Glucose- $\text{TiO}_2$  Charge Transfer Complex-Mediated Photocatalysis Under Visible Light. *Appl. Catal. B* **2015**, *162*, 463–469. [[CrossRef](#)]
68. Seo, Y.S.; Lee, C.; Lee, K.H.; Yoon, K.B. 1:1 and 2:1 Charge-Transfer Complexes Between Aromatic Hydrocarbons and Dry Titanium Dioxide. *Angew. Chem. Int. Ed.* **2005**, *44*, 910–913. [[CrossRef](#)]
69. Haeldermans, I.; Vandewal, K.; Oosterbaan, W.D.; Gadisa, A.; D'Haen, J.; Van Bael, M.K.; Manca, J.V.; Mullens, J. Ground-State Charge-Transfer Complex Formation in Hybrid Poly(3-hexyl thiophene):Titanium Dioxide Solar Cells. *Appl. Phys. Lett.* **2008**, *93*, 223302. [[CrossRef](#)]
70. Asahi, R.; Taga, Y.; Mannstadt, W.; Freeman, A.J. Electronic and Optical Properties of Anatase  $\text{TiO}_2$ . *Phys. Rev. B* **2000**, *61*, 7459–7465. [[CrossRef](#)]



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