

Large π -Aromatic Molecules as Potential Sensitizers for Highly Efficient Dye-Sensitized Solar Cells

HIROSHI IMAHORI,^{*,†,‡,§} TOMOKAZU UMEYAMA,[‡] AND SEIGO ITO^{||}

[†]Institute for Integrated Cell-Material Sciences (iCeMS), Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan, [‡]Department of Molecular Engineering, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan, [§]Fukui Institute for Fundamental Chemistry, Kyoto University, 34-4, Takano-Nishihiraki-cho, Sakyo-ku, Kyoto 606-8103, Japan, ^{||}Department of Electrical Engineering and Computer Sciences, Graduate School of Engineering, University of Hyogo, 2167 Shosha, Himeji, Hyogo 671-2280, Japan

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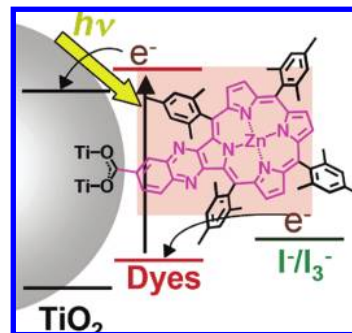
CONSPICUOUS

Recently, dye-sensitized solar cells have attracted much attention relevant to global environmental issues. Thus far, ruthenium(II) bipyridyl complexes have proven to be the most efficient TiO₂ sensitizers in dye-sensitized solar cells. However, a gradual increment in the highest power conversion efficiency has been recognized in the past decade. More importantly, considering that ruthenium is a rare metal, novel dyes without metal or using inexpensive metal are desirable for highly efficient dye-sensitized solar cells. Large π -aromatic molecules, such as porphyrins, phthalocyanines, and perylenes, are important classes of potential sensitizers for highly efficient dye-sensitized solar cells, owing to their photostability and high light-harvesting capabilities that can allow applications in thinner, low-cost dye-sensitized solar cells.

Porphyrins possess an intense Soret band at 400 nm and moderate Q bands at 600 nm. Nevertheless, the poor light-harvesting properties relative to the ruthenium complexes have limited the cell performance of porphyrin-sensitized TiO₂ cells. Elongation of the π conjugation and loss of symmetry in porphyrins cause broadening and a red shift of the absorption bands together with an increasing intensity of the Q bands relative to that of the Soret band. On the basis of the strategy, the cell performance of porphyrin-sensitized solar cells has been improved intensively by the enhanced light absorption. Actually, some push–pull-type porphyrins have disclosed a remarkably high power conversion efficiency (6–7%) that was close to that of the ruthenium complexes.

Phthalocyanines exhibit strong absorption around 300 and 700 nm and redox features that are similar to porphyrins. Moreover, phthalocyanines are transparent over a large region of the visible spectrum, thereby enabling the possibility of using them as “photovoltaic windows”. However, the cell performance was poor, owing to strong aggregation and lack of directionality in the excited state. Novel unsymmetrical zinc phthalocyanine sensitizers with “push” and “pull” groups have made it possible to reduce the aggregation on a TiO₂ surface, tune the level of the excited state, and strengthen the electronic coupling between the phthalocyanine core and the TiO₂ surface. As a result, the power conversion efficiency of up to 3.5% has been achieved.

Perylenes are well-known as chemically, thermally, and photophysically stable dyes and have been used in various optical devices and applications. Nevertheless, the power conversion efficiency remained low compared to other organic dyes. The origin of such limited cell performance is the poor electron-donating abilities of the perylenes, which makes it difficult to inject electrons from the excited singlet state of the perylenes to the conduction band of the TiO₂ electrode efficiently. Strongly electron-donating perylene carboxylic acid derivatives with amine substituents at their perylene core have allowed us to increase the power conversion efficiency of up to ~7% in perylene-sensitized solar cells. The efficiency of large π -aromatic molecule-sensitized solar cells could be improved significantly if the dyes with larger red and near-infrared absorption could be developed.



Introduction

The modern society has intensively consumed energy resources, a large portion of which is accounted for by fossil fuel, such as petroleum, coal, and natural gas. Development of alternative, renewable sources of energy is essential to reduce emission of carbon dioxide and other harmful substances, when fossil fuel is burnt, as well as attain stable energy provision. Solar energy is one of several promising clean energy sources that could contribute to a stable energy supply and mitigate global environmental issues. In particular, the direct creation of electric energy is made possible through a solar cell. Much attention is now being focused on solar cells as potential energy-conversion systems to support society.

Most commercial solar cells today are made from silicon. However, the use of silicon in photovoltaic devices has to date been limited by the high cost of production. In contrast, organic solar cells are defined as photovoltaic devices in which the active layer is made of organic material. Some scientists and engineers believe that organic solar cells will provide a cheaper alternative to conventional inorganic solar cells, because the production cost is expected to go down in comparison to the current costs for the fabrication of inorganic materials. Furthermore, the merits of organic solar cells are color and shape flexibility and lightweight. However, organic solar cells relative to inorganic solar cells exhibit low efficiencies that should be improved notably. Thus far, there have been two representative examples, dye-sensitized^{1,2} and bulk heterojunction solar cells.^{3,4} Specifically, Grätzel et al. developed solar cells based on the sensitization of highly porous TiO₂ by molecular dyes with power conversion efficiencies (η) of 7–11%, making practical applications feasible.^{1,2,5–7} Although ruthenium(II) bipyridyl complexes have proven to be the most efficient TiO₂ sensitizers, a gradual increment in the highest η value has been recognized in recent years.^{5,6} More importantly, considering that ruthenium is a rare metal and the resources are limited, novel dyes without metal or using inexpensive metal (i.e., Cu and Zn) are desirable for highly efficient dye-sensitized solar cells.^{8–12}

Large and stable π -aromatic molecules, such as porphyrins, phthalocyanines, and perylenes, are excellent electron donors and/or acceptors as well as sensitizers and the most frequently employed building blocks in artificial photosynthetic models.^{13–16} Moreover, the optical, photophysical, and electrochemical properties can be systematically tailored by the peripheral substitutions and/or inner metal complexations.

On the other hand, for photovoltaic cells with large π -aromatic molecule-sensitized TiO₂ electrodes, the cell performance has remained poor until recently.^{17–22} Nevertheless, they have the possibility to obtain very high molar absorption coefficients, which could also allow for application in thinner organic solar cells. In this Account, we focus recent advancement in porphyrin-,^{23–43} phthalocyanine-,^{44–50} and perylene-^{51–54} sensitized TiO₂ cells. Because of page limitations, the leading examples including our work in these areas are presented. The literature cited here also contains excellent reviews on the π -aromatic molecule-based solar cells.^{8,21,35,55} For instance, porphyrin-sensitized solar cells reported before 2004 are systematically summarized by Officer et al., with various porphyrin monomer derivatives, dimers, and oligomers.³⁵

Aromatic Ring-Fused, Unsymmetrically π -Extended Porphyrins

Porphyrins possess an intense Soret band at 400–450 nm and moderate Q bands at 500–650 nm, and they have been regarded as potential photosensitizers in dye-sensitized solar cells [e.g., 5-(4-carboxylphenyl)-10,15,20-tetrakis(2,4,6-trimethylphenyl)porphyrinatozinc(II) (Zn-1)^{19,28,33,34} in Figure 1]. For instance, the TiO₂ electrode solar cell with Zn-1 as a sensitizer exhibited the cell performance, a maximal incident photon–current efficiency (IPCE) value of 76%, a short circuit current (J_{SC}) = 9.4 mA cm⁻², an open circuit voltage (V_{OC}) = 0.76 V, a fill factor (ff) = 0.64, and η = 4.6% under standard AM 1.5 sunlight (100 mW cm⁻²), as depicted in Figure 2. The η value (4.6%) is ~70% that of N719-sensitized TiO₂ cell (6.5%) under the same experimental conditions using P-25 TiO₂ nanoparticles (Figure 2a).^{29,33,34} Note that integration of the IPCE values for the Zn-1-sensitized TiO₂ cell with respect to wavenumber is ~70% that of the N719-sensitized TiO₂ cell, which parallels the ratio of the η values in the two cells (Figure 2b). Taking into account the similar ratio together with the virtually identical V_{OC} and ff values, the light-harvesting efficiency of the porphyrin largely limits the cell performance of the porphyrin-sensitized solar cells.

One promising way to surmount the problem relating to the poor light-harvesting properties of porphyrins is to modulate the electronic structures of porphyrins, so that one can match the light-harvesting properties with the solar energy distribution on the earth. Soret and Q bands arise from π - π^* transitions and can be explained in terms of a linear combination of transitions from slightly splitted highest occupied molecular orbital (HOMO) and HOMO-1 to a degenerated pair of lowest unoccupied molecular orbital

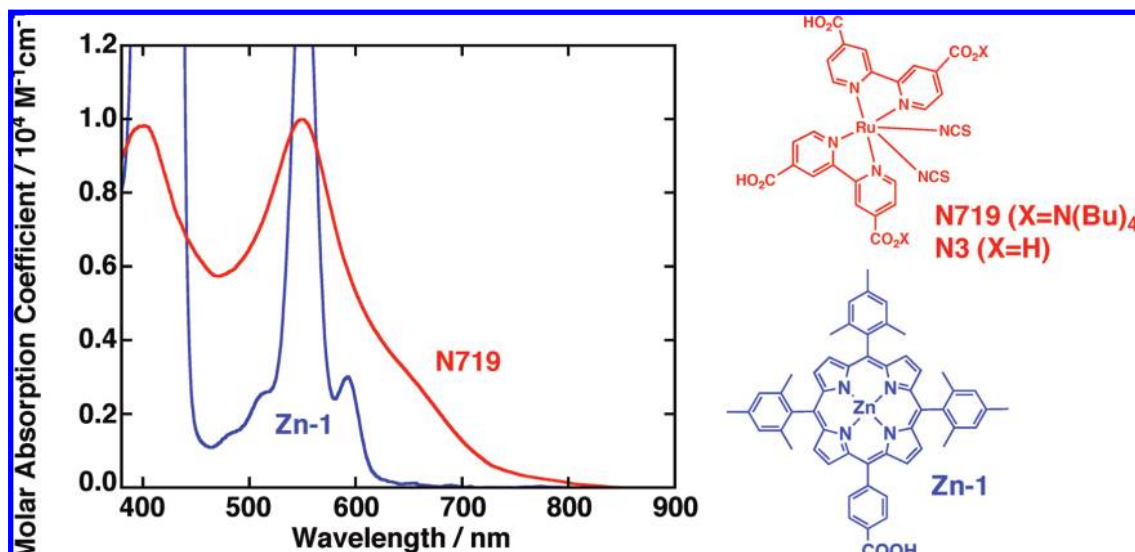


FIGURE 1. Absorption spectra of N719 (red line) and Zn-1 (blue line) in dichloromethane.

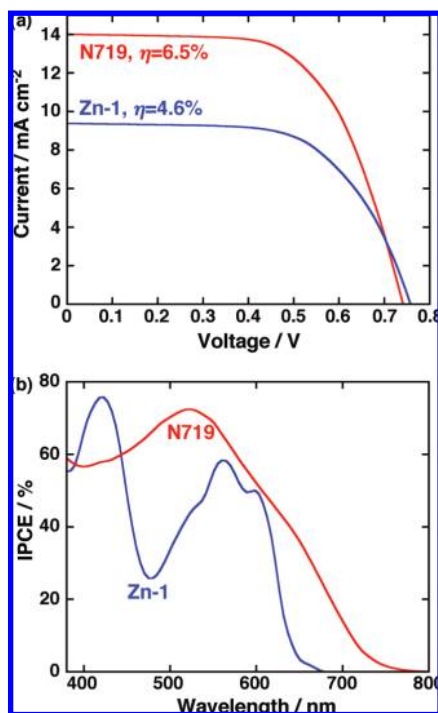


FIGURE 2. (a) Current–voltage characteristics and (b) photocurrent action spectra of N719- (red line) and Zn-1- (blue line) sensitized TiO_2 cells. The N719- and Zn-1-modified TiO_2 electrodes were prepared by immersing the electrodes into a *tert*-butanol/acetonitrile (1:1, v/v) solution of N719 (0.2 mM) for 12 h and a methanol solution of Zn-1 (0.2 mM) for 1 h, respectively. Under standard global AM 1.5 conditions, N719 yielded $\eta = 6.5\%$ ($J_{\text{SC}} = 14.0 \text{ mA cm}^{-2}$, $V_{\text{OC}} = 0.74 \text{ V}$, $\text{ff} = 0.63$).²⁹ Electrolyte: 0.1 M LiI, 0.05 M I_2 , 0.6 M 2,3-dimethyl-1-propylimidazolium iodide, and 0.5 M 4-*tert*-butylpyridine in CH_3CN .

(LUMO) and LUMO-1. The configuration interaction leads to the intense Soret band at the short wavelength and the moderate Q bands at the long wavelength.⁵⁶ Elongation of the π conjugation and loss of symmetry in porphyrins cause

splitting in the π and π^* levels and a decrease in the HOMO–LUMO gap, resulting in broadening and a red shift of the absorption bands together with an increasing intensity of the Q bands relative to that of the Soret band. In such a case, the cell performance of the porphyrin-sensitized solar cells would be improved by the enhanced light absorption. Although there have been several reports on the aromatic ring-fused, π -extended porphyrins, which were synthesized by oxidative coupling between the aromatic ring and the porphyrin core,⁵⁷ they have yet to be applied to organic solar cells.

A naphthyl carboxylic acid group as both bridge and binding moieties was introduced at the meso position of a porphyrin core and then fused at the β position to elongate the π system unsymmetrically (Figure 3).^{30,34} The unsymmetrically π -elongated porphyrin Zn-2 is highly expected to collect visible light efficiently, leading to the improvement of the photovoltaic properties. Bulky mesityl groups were also attached at the other meso positions of the porphyrin core to reduce the porphyrin aggregation on the TiO_2 surface.^{19,28} Nonfused porphyrin reference Zn-3 was also used to evaluate the effects of unsymmetrical π elongation on the photovoltaic properties (Figure 3).^{30,34} As a result of π elongation with low symmetry, Soret and Q bands of Zn-2 were red-shifted and broadened and the intensity of the Q band relative to that of the Soret band was enhanced. A mesoporous P-25-based TiO_2 electrode was immersed in a MeOH solution containing Zn-2 for 0.5 h to yield a porphyrin monolayer-modified TiO_2 electrode. The Zn-2-sensitized TiO_2 solar cell showed $\eta = 4.1\%$ ($J_{\text{SC}} = 10.6 \text{ mA cm}^{-2}$, $V_{\text{OC}} = 0.62 \text{ V}$, $\text{ff} = 0.62$) under stan-

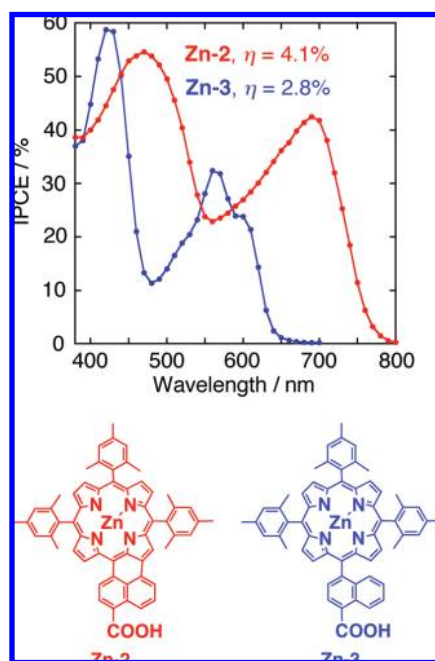


FIGURE 3. Photocurrent action spectra of Zn-2- (red line) and Zn-3- (blue line) sensitized TiO₂ cells.

standard AM 1.5 conditions. The η value of the Zn-2 cell was improved by 50% compared to the reference cell using Zn-3. The Zn-2-sensitized cell revealed a maximum IPCE value of 55% at 470 nm, extending the response of photocurrent generation close to 800 nm (Figure 3). Thus, the improved light-harvesting efficiency and the resulting enhanced photocurrent generation of the Zn-2-sensitized cell relative to the Zn-3-sensitized cell are responsible for the remarkable difference in the η values. To further enhance the cell performance, Zn-1,^{28,33,34} possessing different light-harvesting properties (Figure 2), was co-adsorbed with Zn-2 onto a TiO₂ electrode. Under the optimized conditions, the co-sensitized cell with a molar ratio of Zn-1/Zn-2 = 13:1 yielded a maximal IPCE value of 86%, J_{SC} = 11.7 mA cm⁻², V_{OC} = 0.67 V, ff = 0.64, and η = 5.0%.³⁴ We have also synthesized fused five-membered zinc porphyrin carboxylic acid, in which the benzene ring as a bridge in the phenyl carboxylic acid group was fused to the β position of the meso-tetraphenylporphyrin.³³ Although the fused porphyrin-sensitized TiO₂ cell exhibited the photocurrent generation extending over 800 nm, the η value was found to be poor (0.3%). An insufficient driving force for the electron injection (0.19 eV) for the fused porphyrin cell and/or short lifetime of the porphyrin excited singlet state may be responsible for the low photovoltaic properties.

Another promising way to achieve the unsymmetrical π elongation is to construct β,β' -edge fused porphyrin with an

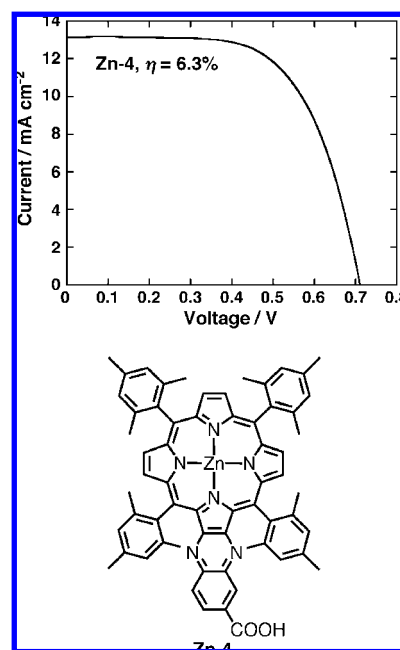


FIGURE 4. Current–voltage characteristic of Zn-4-sensitized TiO₂ cells. The Zn-4-modified TiO₂ electrode was prepared by immersing the electrode into a methanol solution of 0.2 mM Zn-4 containing 2 mM chenodeoxycholic acid (CDCA) for 1 h.

aromatic moiety.^{58,59} This strategy has been employed to construct a variety of model systems, especially for molecular wires.⁵⁸ Tailoring the electrochemical properties, accordingly the electronic properties of the system, by systematic switching of the substituents that are located outside of the porphyrin macrocycle, has been reported.⁵⁹ It typically affords rigid structure and well-defined molecular length as well as relatively broad absorption spectra.

β,β' -edge fused porphyrins with quinoxaline moiety was prepared for dye-sensitized solar cells.³² 5,10,15,20-Tetrakis(2,4,6-trimethylphenyl)-6'-carboxyquinoxalino[2,3- β]porphyrinatozinc(II) (Zn-4 in Figure 4) exhibited broadened and red-shifted light absorption in UV–vis absorption spectra compared to 5,10,15,20-tetrakis(2,4,6-trimethylphenyl)porphyrinatozinc(II) (ZnP). Zn-4 also showed a decrease in the HOMO–LUMO gap because of the extension of the porphyrin π system. From the results of ¹H nuclear magnetic resonance (NMR) spectroscopy and density functional theory (DFT) calculations, Zn-4 was found to adopt a saddle structure. The Zn-4-sensitized TiO₂ cell revealed η = 5.2% (J_{SC} = 11.2 mA cm⁻², V_{OC} = 0.72 V, ff = 0.68). Both device fabrication and dye structure are known to have a large impact on the η value of dye-sensitized solar cells.^{1,2,5–7} Actually, more detailed studies of Zn-4-sensitized TiO₂ cell in a collaboration with Prof. Seigo Ito have led to the higher η value of 6.3% (J_{SC} = 13.2 mA cm⁻², V_{OC} = 0.71 V, ff = 0.67), as illustrated in Figure 4. Thus, fur-

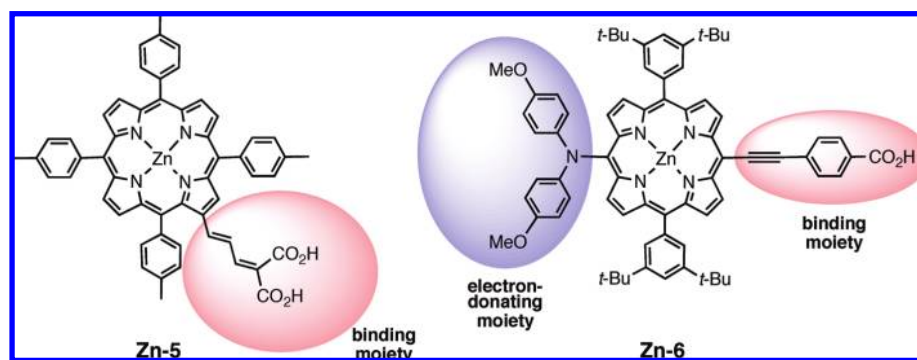


FIGURE 5. β -Substituted porphyrin Zn-5 and push–pull porphyrin Zn-6.

ther improvement of the cell performance in porphyrin-sensitized solar cells may be possible by optimizing the device fabrication as well as the light-harvesting properties.

Other π -Extended Porphyrins

The modification of meso-tetraphenylporphyrins by substitution at the β position with functional groups with extended π systems, such as styryl moiety, leads to the improvement of light-harvesting properties of the porphyrins, as in the case of our strategy. Officer and Grätzel et al. reported a series of meso-tetraphenylporphyrins with the carboxylic acid group as an anchoring moiety via a conjugated double bond as a bridge moiety for dye-sensitized solar cells.^{35–40} Specifically, a combination of a conjugated diethenyl linker at the β -pyrrolic position and two carboxylic acid as binding groups yielded the red-shifted Soret and Q bands of Zn-5 with respect to those of ZnP (Figure 5).³⁹ The Zn-5-modified TiO₂ electrode was prepared by immersing the electrode into an ethanol solution of Zn-5 for 2 h. Under standard global AM 1.5 conditions, Zn-5 yielded $\eta = 7.1\%$ ($J_{SC} = 14.0 \text{ mA cm}^{-2}$, $V_{OC} = 0.68 \text{ V}$, $ff = 0.74$), which, for porphyrin-sensitized solar cells, is unprecedented. Zn-5 also gave $\eta = 3.6\%$ ($J_{SC} = 7.4 \text{ mA cm}^{-2}$, $V_{OC} = 0.78 \text{ V}$, $ff = 0.62$) in a solid-state cell with 2,2',7,7'-tetrakis(*N,N*-dimethoxyphenylamine)-9,9'-spirobifluorene as the hole-transporting component,³⁹ which is highly promising to surmount the problems of liquid electrolyte solvent leakage and the consequent toxicity associated with the liquid electrolyte-based TiO₂ cells.⁷

Very recently, Diao and Yeh et al. reported novel meso-derivatized porphyrins with a carboxylic acid group as a binding moiety connected with a phenylethynyl bridge for dye-sensitized solar cells.⁴¹ The absorption spectra displayed the red shift and broadening of Soret and Q bands with respect to those of ZnP. This behavior is more pronounced for Zn-6, which possesses an electron-donating diarylamino group at the meso position opposite the bind-

ing group (Figure 5). Zn-6 was co-adsorbed with chenodeoxycholic acid (CDCA) on a TiO₂ electrode in ethanol for 2 h. Zn-6 exhibited an excellent cell performance with $\eta = 6.0\%$ ($J_{SC} = 13.6 \text{ mA cm}^{-2}$, $V_{OC} = 0.70 \text{ V}$, $ff = 0.63$). The cell performance is comparable to that of N3- (Figure 1) sensitized solar cell ($J_{SC} = 12.1 \text{ mA cm}^{-2}$, $V_{OC} = 0.76 \text{ V}$, $ff = 0.67$, $\eta = 6.1\%$) under their experimental conditions.⁴¹

Unsymmetrical Phthalocyanines

Phthalocyanines exhibit very high molar absorption coefficients around 300 nm (Soret band) and 700 nm (Q band) and redox features that are similar to porphyrins.²¹ Moreover, phthalocyanines are transparent over a large region of the visible spectrum, thereby enabling the possibility of using them as “photovoltaic windows”. However, the η value was poor, owing to strong aggregation and lack of directionality in the excited state. A combination of catechol axial attachment to a TiO₂ surface, followed by the ligation to titanium(IV) tetra(*tert*-butyl)phthalocyanine without the use of co-adsorbents, with the bulky *tert*-butyl peripheral groups allowed for selective electron injection into the TiO₂ by Soret band excitation, but the η value was 0.2%.⁴⁴

Nazeeruddin et al. developed a novel unsymmetrical zinc phthalocyanine sensitizer Zn-7 with three *tert*-butyl and two carboxylic acid groups that act as “push” and “pull” groups, respectively (Figure 6).⁴⁵ The *tert*-butyl groups allow us to reduce the aggregation on a TiO₂ surface and tune the level of the excited state, whereas the carboxylic acid groups ensure the tight binding of Zn-7 to the TiO₂ surface and the intimate electronic coupling between the phthalocyanine core and the TiO₂ surface. The TiO₂ electrode was dipped into an ethanol solution of Zn-7 with CDCA for 4 h. The Zn-7-sensitized solar cell gave $J_{SC} = 6.5 \text{ mA cm}^{-2}$, $V_{OC} = 0.64 \text{ V}$, and $ff = 0.74$, corresponding to $\eta = 3.1\%$ under standard AM 1.5 conditions.⁴⁵

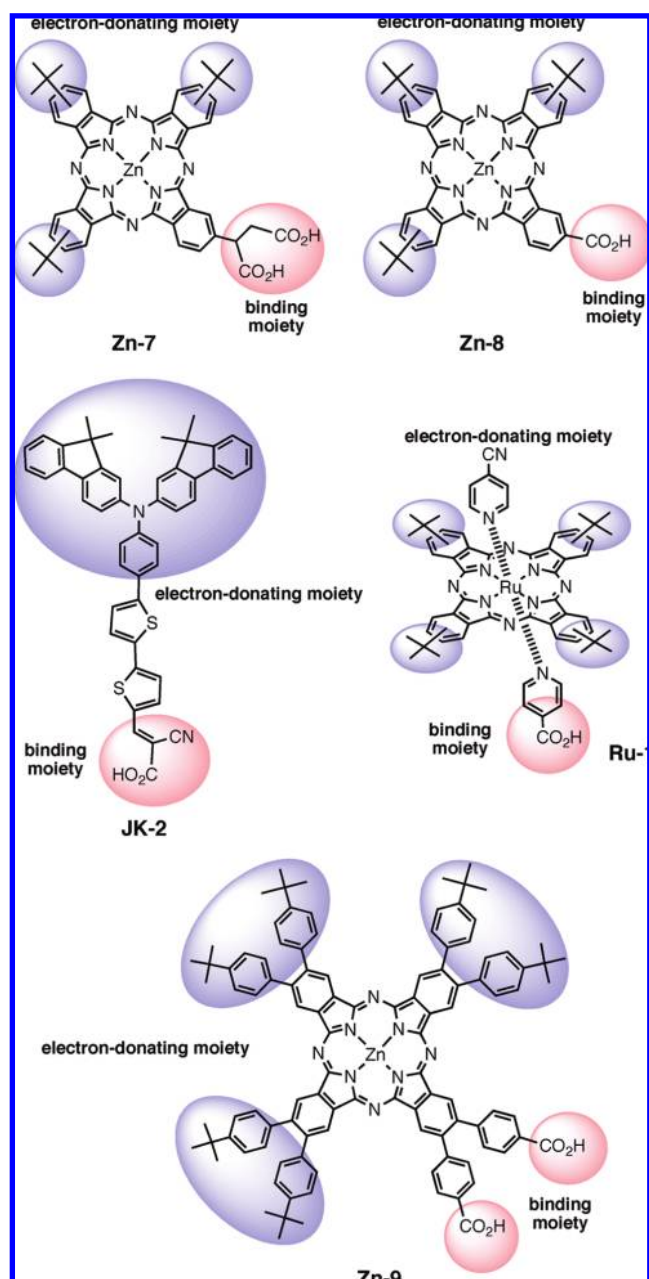


FIGURE 6. Zinc phthalocyanines Zn-7, Zn-8, and Zn-9, ruthenium phthalocyanine Ru-1, and co-sensitizer JK-2 for molecular cocktail.

Nazeeruddin and Torres et al. further extend this concept to prepare a novel unsymmetrical zinc phthalocyanine sensitizer Zn-8 with the same three *tert*-butyl and one carboxylic acid groups that act as “push” and “pull” groups, respectively (Figure 6).^{46,47} To enhance the electronic coupling between the phthalocyanine core and the TiO₂ surface, the carboxylic acid group was directly tethered to the phthalocyanine core. The TiO₂ electrode was immersed into an ethanol solution of Zn-8 with CDCA for 4 h. The Zn-8-sensitized solar cell revealed $\eta = 3.5\%$ ($J_{SC} = 7.6 \text{ mA cm}^{-2}$, $V_{OC} = 0.62 \text{ V}$, $ff = 0.75$). The use of Zn-8 allowed us to

introduce a secondary dye (i.e., JK2 in Figure 6) that complemented the absorption spectra by matching the optical window of the phthalocyanine at 400–550 nm. The photocurrent response corresponded the absorption spectra of the “molecular cocktail” made by Zn-8 and JK2. A η value of 7.7% ($J_{SC} = 16.2 \text{ mA cm}^{-2}$, $V_{OC} = 0.67 \text{ V}$, and $ff = 0.72$) was attained.⁴⁶

Although the power conversion efficiency is the highest among the reported phthalocyanine-sensitized TiO₂ cell,^{46,47} the cell performance is still aided with the co-adsorption of CDCA that is well-known to suppress the dye aggregation on the TiO₂ surface. We prepared novel highly substituted zinc phthalocyanine carboxylic acid Zn-9 for dye-sensitized solar cells (Figure 6).⁴⁸ Zn-9 retains sterically hindered eight phenyl groups, in which the neighboring phenyl rings are rotated about each other with respect to the phthalocyanine plane to avoid the steric congestion around the *ortho* protons. Moreover, the six phenyl groups also possess bulky *tert*-butyl moieties. Actually, Zn-9 showed high solubility in common organic solvents and the reduced tendency of aggregation. Because the two neighboring β positions are occupied by the same functional groups, Zn-9 can be isolated free from the problem of regioisomeric mixtures, unlike the typical synthesis of phthalocyanines, such as Zn-7 and Zn-8. Two carboxylic acid binding groups could guarantee the stable immobilization of Zn-9 onto the TiO₂ surface. Additionally, an intramolecular push–pull character afforded by electron-donating (*tert*-butyl) and electron-withdrawing (carboxylic acid) groups would be anticipated to make the efficient electron transfer from the phthalocyanine excited singlet state to the conduction band (CB) of the TiO₂. The TiO₂ electrode was modified with Zn-9, which was dissolved in THF, for 12 h. Unfortunately, the cell performance of Zn-9-sensitized TiO₂ cell was not high (maximal IPCE = 4.9% at 700 nm, $\eta = 0.57\%$, $J_{SC} = 1.47 \text{ mA cm}^{-2}$, $V_{OC} = 0.54 \text{ V}$, and $ff = 0.71$). Nevertheless, introduction of CDCA as a co-adsorbent revealed no noticeable change in the cell performance, showing that the aggregation of Zn-9 is effectively suppressed by the steric hindrance.⁴⁸ This is marked contrast to the significant effect of co-adsorbent on the photovoltaic properties of other phthalocyanines.^{20,21,45–47} The low cell performance can be rationalized by the small driving force for electron injection from the excited singlet state to the TiO₂ and the poor electronic coupling between the LUMO of the zinc phthalocyanine and the CB of the TiO₂. For most organic dyes, including phthalocyanines, Torres and Durrant et al. proposed that significantly lower output

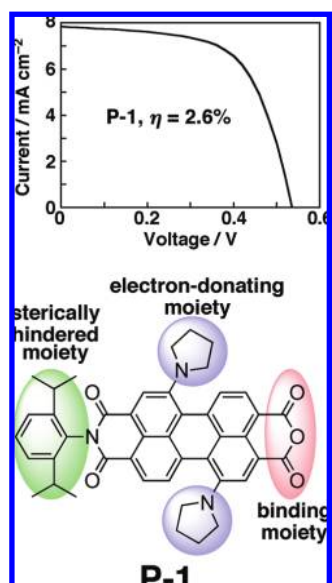


FIGURE 7. Perylene imide acid anhydride P-1.

voltages than equivalent cells made using N719 or its analogues resulted from catalytic electron/electrolyte recombination reactions at both TiO_2 and SnO_2 surfaces.⁴⁹ Such an effect would also lower the cell performance in the Zn-9-sensitized TiO_2 cell. Slow and efficient electron injection is known to take place in ruthenium phthalocyanine-sensitized TiO_2 (Ru-1 in Figure 6) as a consequence of the long-lived triplet excited state that can compete well with the decay to the ground state.⁵⁰ Therefore, optimization of these kinetic competitions is a challenge for improving the efficiency of phthalocyanine-sensitized solar cells.

Electron-Donating Perylenes

Perylenes are well-known as chemically, thermally, and photophysically stable dyes and have been used in various optical devices and applications.^{55,60} Thus far, several perylene-sensitized solar cells have been reported, but the η values remain low ($\eta < 1.9\%$) compared to other organic dyes.²² The origin of such limited cell performance is the poor electron-donating abilities of the perylenes, which makes it difficult to inject electrons from the excited singlet state of the perylenes to the CB of the TiO_2 electrode efficiently. Recently, we⁵¹ and other groups^{52–54} have reported strongly electron-donating perylene tetracarboxylic acid derivatives with amine substituents at their perylene core. The perylene bisimide (PBI) linked to C_{60} has exhibited photoinduced electron transfer from the PBI excited singlet state to C_{60} .⁶¹ On the basis of these results, we designed novel electron-donating perylene tetracarboxylic acid derivative P-1 for dye-sensitized solar cells (Figure 7).⁵¹ In the molecular design, we consider the following crite-

ria: (1) Multiple strongly electron-donating substituents (i.e., two pyrrolidines) at the perylene core shift the first oxidation potential in the negative direction considerably. Thus, we can expect a more exothermic electron injection from the excited singlet state to the CB of the TiO_2 electrode, leading to efficient photocurrent generation. Furthermore, such substitution would vary the light-harvesting ability in the red–NIR region. (2) The degree of the dye aggregation on the TiO_2 electrode can be modulated by the bulky substituents (i.e., 2,6-diisopropylphenyl) at one imide end. It should be noted that the electronic structures of the perylene π systems are not affected by the substituents at the imide nitrogen because the frontier orbitals of these compounds have nodes at the imide nitrogen and the anhydride oxygen atoms. (3) The direct anchoring of the acid anhydride moiety to the TiO_2 surface makes it possible to strengthen the electronic coupling between the perylene core and the TiO_2 surface, leading to the high electron injection efficiency. The P-1-modified TiO_2 electrode was obtained by immersing the TiO_2 electrode into a dichloromethane solution of P-1 in a *tert*-butanol/acetonitrile (1:1, v/v) mixture for 15 h. The TiO_2 electrode solar cell with P-1 as a sensitizer exhibited the cell performance, a maximal IPCE value of 38% at 650 nm, $J_{\text{SC}} = 7.8 \text{ mA cm}^{-2}$, $V_{\text{OC}} = 0.54 \text{ V}$, $\text{ff} = 0.63$, and $\eta = 2.6\%$ under standard AM 1.5 sunlight.⁵¹

Edvinsson and Pschirer et al. presented novel perylene dyes with different intramolecular push–pull characters.⁵² The stronger donors led to a shift of the LUMO to more negative potential versus NHE as well as an increase of the charge separation in the dye upon excitation. The cell performance was improved for the more polar dyes. In particular, a maximal IPCE value reached 70% at 500 nm, and the η value was improved to 3.9% ($J_{\text{SC}} = 10.4 \text{ mA cm}^{-2}$, $V_{\text{OC}} = 0.65 \text{ V}$, and $\text{ff} = 0.58$) for P-2 (Figure 8) with the highest intramolecular charge-transfer character, which can be compared to devices with N719, showing 6% under similar conditions.⁵² The performance of P-2 is a significant improvement compared to that for P-1 and lifts the performance from modest to promising.

Nazeeruddin and Müllen et al. further elaborated P-2 to develop 1,6-dithiophenol-substituted perylene P-3 (Figure 8).⁵⁴ The substituents tune the HOMO and LUMO energies and resulting absorption properties, together with the suppression of aggregation on TiO_2 . The TiO_2 electrode was dipped into a chlorobenzene solution of P-3 for 16–18 h. The P-3-sensitized solar cell attained high cell performance ($\eta = 6.8\%$, $J_{\text{SC}} = 12.6 \text{ mA cm}^{-2}$, $V_{\text{OC}} = 0.73 \text{ V}$, and $\text{ff} = 0.74$).⁵⁴

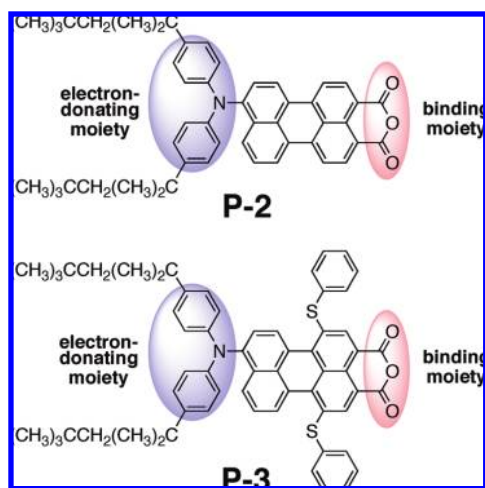


FIGURE 8. Perylene acid anhydrides P-2 and P-3.

Conclusions and Outlook

Considering a recent gradual increment in the highest cell performance of ruthenium dye-sensitized solar cells, it is of utmost importance to reconsider the basic principle of dye-sensitized solar cells for the remarkable breakthrough. Elucidation of the relationship between molecular structure, film structure, photophysics, and photovoltaic properties of dyes would be a prerequisite to overcome the situation. Additionally, ruthenium complexes are likely to become increasingly more expensive as the demand for the noble metal increases. Replacing the ruthenium complexes with fully organic sensitizers or metal complexes using inexpensive metals is an attractive strategy in terms of environmental reasons and low cost. In particular, large π -aromatic molecules, such as porphyrins, phthalocyanines, and perylenes, are important classes of potential sensitizers for highly efficient dye-sensitized solar cells, owing to their marked photostability and high light-harvesting capabilities that can allow for applications in thinner, low-cost dye-sensitized solar cells. Actually, some push-pull-type porphyrins have disclosed a remarkably high cell performance that was comparable or close to that of the ruthenium complexes. The efficiency of large π -aromatic molecule-sensitized solar cells could be improved remarkably if the dyes with larger red and near-infrared absorption could be developed.

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BIOGRAPHICAL INFORMATION

Hiroshi Imahori received his Ph.D. in organic chemistry from Kyoto University. He became an Assistant Professor at ISIR, Osaka University, in 1992, an Associate Professor at the Graduate School of Engineering, Osaka University, in 1999, and a Professor at the Graduate School of Engineering, Kyoto University, in 2002. Since 2007, he has also been a Principal Investigator of iCeMS, Kyoto University. His research interests include novel π -aromatic compounds, carbon nanostructures, self-assembly, photochemistry, organic solar cells, and drug-delivery systems.

Tomokazu Umeyama was born in 1976 and received his B.S. (1999), M.S. (2001), and Ph.D. (2004) in polymer chemistry under the guidance of Prof. Y. Chujo, Kyoto University. Then, he joined Imahori's group as an Assistant Professor. His current interests involve chemical functionalization of nanocarbon materials and their application to photoelectrochemical devices.

Seigo Ito was born in 1970 and studied chemistry at Kyoto University (B.S.). He received his M.S. (1997) and Ph.D. (2000) in chemistry from the University of Tokyo and then joined the research groups of Prof. S. Yanagida (Osaka University), Prof. Y. Koyama (Kwansei Gakuin University), and Prof. M. Grätzel (EPFL). In 2007, he accepted a position of Associate Professor, University of Hyogo. His current interests lie in the fabrication of nanomaterials and their application to solar cells.

FOOTNOTES

* To whom correspondence should be addressed. E-mail: imahori@scl.kyoto-u.ac.jp.

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