Large \(\pi\)-Aromatic Molecules as Potential Sensitizers for Highly Efficient Dye-Sensitized Solar Cells

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**CON SPECTUS**

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 TiO\(_2\) 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 \(\pi\)-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 TiO\(_2\) cells. Elongation of the \(\pi\)-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 TiO\(_2\) surface, tune the level of the excited state, and strengthen the electronic coupling between the phthalocyanine core and the TiO\(_2\) 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 TiO\(_2\) 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 \(\pi\)-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-sensitized1,2 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 virtually identical η values for the Zn-1-sensitized TiO2 cell with respect to N719-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-carboxyphenyl)-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 (JSC) of 9.4 mA cm−2, an open circuit voltage (VOC) of 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 VOC 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
The configuration interaction leads to the intense Soret band at the short wavelength and the moderate Q bands at the long wavelength.\textsuperscript{56} Elongation of the \(\pi\) conjugation and loss of symmetry in porphyrins cause splitting in the \(\pi\) and \(\pi^*\) 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, \(\pi\)-extended porphyrins, which were synthesized by oxidative coupling between the aromatic ring and the porphyrin core,\textsuperscript{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 \(\beta\) position to elongate the \(\pi\) system unsymmetrically (Figure 3).\textsuperscript{30,34} The unsymmetrically \(\pi\)-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\textsubscript{2} surface.\textsuperscript{19,28} Nonfused porphyrin reference Zn-3 was also used to evaluate the effects of unsymmetrical \(\pi\) elongation on the photovoltaic properties (Figure 3).\textsuperscript{30,34} As a result of \(\pi\) 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\textsubscript{2} electrode was immersed in a MeOH solution containing Zn-2 for 0.5 h to yield a porphyrin monolayer-modified TiO\textsubscript{2} electrode. The Zn-2-sensitized TiO\textsubscript{2} solar cell showed \(\eta = 4.1\%\) \((J_{SC} = 10.6 \text{ mA cm}^{-2}, V_{OC} = 0.62 \text{ V}, ff = 0.62)\) under stan-
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, possessing different light-harvesting properties (Figure 2), was co-sorbed 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%, JSC = 11.7 mA cm\(^{-2}\), VOC = 0.67 V, ff = 0.64, and η = 5.0%.\(^{34}\) We have also synthesized 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 photo-voltaic properties.

Another promising way to achieve the unsymmetrical π elongation is to construct β,β’-edge fused porphyrins with an 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.

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. The Zn-4-sensitized TiO2 cell revealed η = 5.2% (JSC = 11.2 mA cm\(^{-2}\), VOC = 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 collaboration with Prof. Seigo Ito have led to the higher η value of 6.3% (JSC = 13.2 mA cm\(^{-2}\), VOC = 0.71 V, ff = 0.67), as illustrated in Figure 4. Thus, fur-
Other $\pi$-Extended Porphyrins

The modification of meso-tetraphenylporphyrins by substitution at the $\beta$ position with functional groups with extended $\pi$ 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 $\beta$-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 TiO$_2$ electrode was prepared by immersing the electrode into an ethanol solution of Zn-5 for 2 h. Zn-6 exhibited an excellent cell performance with $\eta = 6.0\%$ ($\eta_{SC} = 13.6$ mA cm$^{-2}$, $V_{OC} = 0.70$ V, $ff = 0.63$). The cell performance is comparable to that of N3- (Figure 1) sensitized solar cell ($\eta_{SC} = 12.1$ mA cm$^{-2}$, $V_{OC} = 0.76$ 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 $\eta$ value was poor, owing to strong aggregation and lack of directionality in the excited state. A combination of catechol axial attachment to a TiO$_2$ 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 TiO$_2$ by Soret band excitation, but the $\eta$ 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 TiO$_2$ surface and tune the level of the excited state, whereas the carboxylic acid groups ensure the tight binding of Zn-7 to the TiO$_2$ surface and the intimate electronic coupling between the phthalocyanine core and the TiO$_2$ surface. The TiO$_2$ electrode was dipped into an ethanol solution of Zn-7 with CDCA for 4 h. The Zn-7-sensitized solar cell gave $J_{SC} = 6.5$ mA cm$^{-2}$, $V_{OC} = 0.64$ V, and $ff = 0.74$, corresponding to $\eta = 3.1\%$ under standard AM 1.5 conditions.45

![Figure 5: $\beta$-Substituted porphyrin Zn-5 and push–pull porphyrin Zn-6.](image-url)

imahori et al.
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).\(^\text{46,47}\) To enhance the electronic coupling between the phthalocyanine core and the TiO\(_2\) surface, the carboxylic acid group was directly tethered to the phthalocyanine core. The TiO\(_2\) electrode was immersed into an ethanol solution of Zn-8 with CDCA for 4 h. The Zn-8-sensitized solar cell revealed \(\eta = 3.5\% (J_{\text{SC}} = 7.6\, \text{mA cm}^{-2}, V_{\text{OC}} = 0.62\, \text{V}, \text{and } ff = 0.75)\). 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 \(\eta\) value of 7.7\% \((J_{\text{SC}} = 16.2\, \text{mA cm}^{-2}, V_{\text{OC}} = 0.67\, \text{V}, \text{and } ff = 0.72)\) was attained.\(^\text{46}\)

Although the power conversion efficiency is the highest among the reported phthalocyanine-sensitized TiO\(_2\) cell,\(^\text{46,47}\) the cell performance is still aided with the co-adsorption of CDCA that is well-known to suppress the dye aggregation on the TiO\(_2\) surface. We prepared novel highly substituted zinc phthalocyanine carboxylic acid Zn-9 for dye-sensitized solar cells (Figure 6).\(^\text{48}\) 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 \(\beta\) 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 TiO\(_2\) 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 TiO\(_2\). The TiO\(_2\) electrode was modified with Zn-9, which was dissolved in THF, for 12 h. Unfortunately, the cell performance of Zn-9-sensitized TiO\(_2\) cell was not high (maximal IPCE \(= 4.9\%\) at 700 nm, \(\eta = 0.57\%, J_{\text{SC}} = 1.47\, \text{mA cm}^{-2}, V_{\text{OC}} = 0.54\, \text{V}, \text{and } ff = 0.71)\). 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.\(^\text{48}\) This is marked contrast to the significant effect of co-adsorbent on the photovoltaic properties of other phthalocyanines.\(^\text{20,21,45–47}\) The low cell performance can be rationalized by the small driving force for electron injection from the excited singlet state to the TiO\(_2\) and the poor electronic coupling between the LUMO of the zinc phthalocyanine and the CB of the TiO\(_2\). For most organic dyes, including phthalocyanines, Torres and Durrant et al. proposed that significantly lower output
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 $\eta$ 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 groups52−54 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 criteria: (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-disopropylphenyl) at one imide end. It should be noted that the electronic structures of the perylene $\pi$ 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, $V_{OC} = 0.54$ V, $ff = 0.63$, 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 leaded 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 $\eta$ value was improved to 3.9% ($U_{SC} = 10.4$ mA cm$^{-2}$, $V_{OC} = 0.65$ V, and $ff = 0.58$) 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 ($\eta = 6.8\%$, $J_{SC} = 12.6$ mA cm$^{-2}$, $V_{OC} = 0.73$ V, and $ff = 0.74$).54
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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FIGURE 8. Perylene acid anhydrides P-2 and P-3.


