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Energy Conversion

Dye Molecules for Simple Co-Sensitization Process: Fabrication of Mixed-Dye-Sensitized Solar Cells[**]

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Dye-sensitized solar cells (DSSCs) made from mesoporous TiO_2 electrodes have been intensely investigated as a promising candidate for low-cost, lightweight, and scalable solar cells.[1] To date, the highest conversion efficiencies above 11 % have been achieved with panchromatic polypyridylruthenium complex sensitizers.[2] The high efficiency of the ruthenium complexes can be attributed to their wide absorption range from the visible to near-infrared (IR) regions.[3] However, the issue with the ruthenium complexes is the difficulty of further improvement in the conversion efficiencies, because of their low molar extinction coefficients (e.g., $\varepsilon < 10\,000\,\text{M}^{-1}\,\text{cm}^{-1}$ at the metal to ligand charge-transfer (MLCT) band of black dye) and the limited use of precious ruthenium metal for the practical applications. To avoid these issues, much effort has been devoted to the development of organic dye molecules which possess no metal or utilize nonprecious metals.[4] So far, the conversion efficiencies of DSSCs with organic dye molecules are modest compared to those with the ruthenium complexes, partially because of their insufficient light-harvesting ability in the near-IR region.

Metallophthalocyanines (MPcs) show potential for near-IR sensitizers because of their intense Q bands ($\lambda = 600$–700 nm), high molar extinction coefficients ($\varepsilon > 100\,000\,\text{M}^{-1}\,\text{cm}^{-1}$), and good thermal, chemical, and photolytic stabilities.[5] Nevertheless, MPc sensitizers displayed rather low conversion efficiencies in DSSCs. Major factors for the low efficiency of MPcs were the formation of aggregates on the surface of the TiO_2 crystal and the lack of electron-transfer directionality in the excited state. In 2007, Nazeeruddin et al. and Torres et al. reported high conversion efficiencies ($\eta = 3.1$ and 3.6 %) for DSSCs using unsymmetrical the zinc phthalocyanines (ZnPcs) PCH001 and TT1, which have three *tert*-butyl groups and one carboxylic acid moiety.[6–8] Unsymmetrical substitution of ZnPcs provides electron-transfer directionality, thus giving high incident photon-to-current conversion efficiency (IPCE) in the near-IR region, whereas little sensitization was observed in the blue and green spectral regions.

To exploit such dyes, co-sensitization with different dyes (cocktail-type) has been applied.[9] The combination of two dyes, which have complementary absorption properties in the visible region, could result in broad responses to the solar spectrum, thus improving conversion efficiencies. However, mixing two dyes usually resulted in a decrease of efficiency, which is probably due to the decreased injection efficiency caused by intermolecular interactions between the two dyes. Thus, prevention of electronic interactions between the dyes on the TiO_2 surface is important for the development of efficient cocktail-type DSSCs. A simple way is to separate the adsorption sites on the TiO_2; various methods have been proposed, for example, sensitization using two separate layers,[10,11] and sensitization using a double dye layer.[12] However these methods require complex processes. Another way is to use a co-adsorbant, and as in the case for the TT1 dye, which was co-sensitized with the organic red dye JK2 to cover the blue and green regions.[8] The efficiency of the TT1/JK2 cocktail-type DSSC was higher than that of the DSSCs using each dye separately. While the co-adsorbant, chenodeoxycholoc acid (CDCA), was used to suppress the aggregation of ZnPcs and to suppress interaction between TT1 and JK2, complete suppression of aggregation by CDCA was hard to achieve.

Recently, we reported the photovoltaic properties of the unsymmetrical ZnPc PcS6, which has one benzoic acid on one side of the macrocycle and six bulky 2,6-diphenylphenol groups on the other positions.[13] Three-dimensional (3D) enlargement of the molecular structure prevented the cofacial aggregation of ZnPcs adsorbed onto the TiO_2 surface and PcS6 gave a high efficiency of 4.6 % without the addition of a coadsorbent. Such non-interacting features of the dye would be desirable for cocktail-type DSSCs. The introduction of electron-donating phenoxy groups onto a ZnPc core led to significant improvement of the IPCE for the entire absorption range. The IPCE could be further improved by adding greater directional electron-transfer features (pushing ability).

Herein, we report the novel ZnPc dye PcS15 having a 5.3 % efficiency, which is achieved by enhancing the unsymmetrical and 3D ZnPc structure. The introduction of electron-donating methoxy groups to the peripheral 2,6-diphenylphenol units increased the photoresponse in the $\lambda =$ 400–500 nm range and improved the solubility. We then applied PcS15 to the cocktail-type DSSCs through combination with red or orange organic dyes, D102 and D131, respectively. The co-sensitization of the TiO_2 electrode by PcS15 and D131 showed little interaction between the dyes, thus resulting in a dramatic enhancement of the photocurrent response throughout the entire visible-light region.

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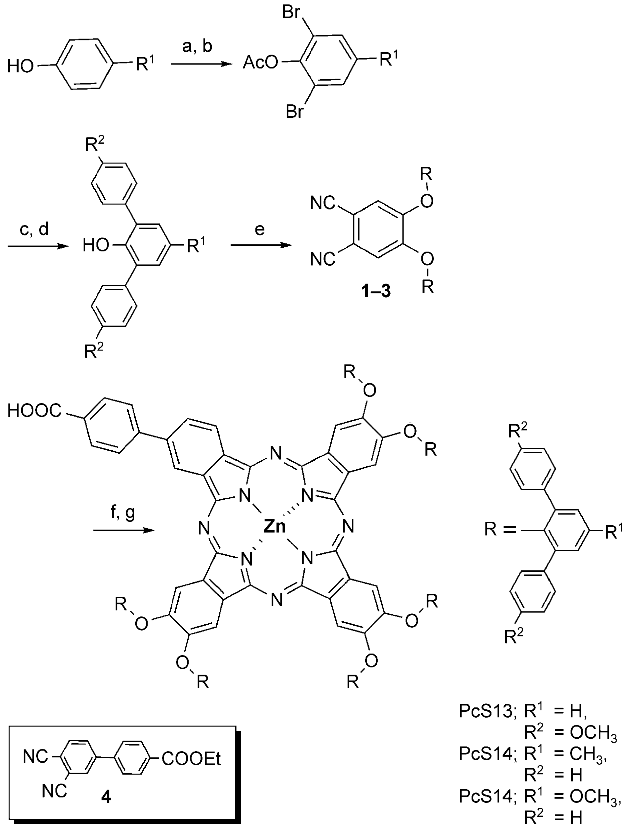
Scheme 1 illustrates the synthesis of the ZnPc PcS15. The phthalocyanine precursor **3** was synthesized from 4-methoxyphenol ($R^1 = OMe$) in five steps. Reaction of 4-methoxyphenol with tetrabutylammonium tribromide in a CH_2Cl_2/methanol readily gave 2,6-dibromo-4-methoxyphenol.[14] After the acetylation of the phenol group, a palladium-catalyzed coupling reaction between the 2,6-dibromophenol derivatives and phenylboronic acid gave 2,6-diphenyl-4-methoxyphenol ($R^1 = OMe$, $R^2 = H$), which was was reacted with 4,5-dichlorophthalonitrile in the presence of K_2CO_3 to afford 4,5-di(2′,6′-diphenyl-4′-methoxyphenoxy)phthalonitirile (**3**).[15] The unsymmetrical ZnPc PcS15 was prepared through a mixed cyclo-tetramerization reaction of **3** and **4** in a 3:1 ratio by heating to reflux in 2-(dimethylamino)ethanol (DMAE) in the presence of $Zn(OAc)_2$, and subsequent hydrolysis with an aqueous alkaline solution. The other ZnPcs, PcS13 and PcS14, were synthesized from **1** and **2** by the same procedure of PcS15.



Scheme 1. Synthesis of PcS13–15. Reagents and conditions: a) nBu_4NBr_3, CH_2Cl_2/MeOH (5:2); b) $(CH_3CO)_2O$, pyridine; c) Suzuki coupling, $[Pd(PPh_3)_4]$, phenyl boronic acid, toluene/THF/2 M Na_2CO_3 (aq.); d) aq NaOH; e) 4,5-dichlorophthalonitirile, K_2CO_3, DMF; f) **4**, $Zn(CH_3COO)_2$, DMAE, reflux; g) aq. NaOH. See the Supporting Information for details.

The peripheral 2,6-diphenyl-4-methoxyphenoxy units in PcS15, which are perpendicular to a planar phthalocyanine ring, introduces severe steric crowding adjacent to the phthalocyanine core, thus avoiding cofacial self-association (see Figure S4 in the Supporting Information). The prevention of intermolecular aggregation leads to high solubility and single-site isolation in the respective physical environments. Whereas PcS6, possessing 2,6-diphenylphenoxy units, did not dissolve in toluene, the introduction of methyl and methoxy groups to the 2,6-diphenylphenoxy units improved the solubility in toluene. The absorption spectrum of PcS15 in toluene showed a sharp and strong peak at $\lambda_{max} = 686$ nm ($\log \varepsilon = 4.97$) and a relatively weak peak at $\lambda_{max} = 360$ nm as the Q band and the Soret band of ZnPcs.[16] The synthesized ZnPc exhibited a broad absorption band around $\lambda = 450$ nm, which was attributed to the intramolecular charge transfer between the ZnPc core and the electron-donating phenoxy units.[16] When PcS15 was excited at the Soret band of the ZnPc core in a degassed toluene solution, it exhibited a strong fluorescence at $\lambda = 702$ nm. The Q bands, Soret bands, and the emission maxima of the ZnPcs remained unaltered for PcS13, PcS14, and PcS15, each of which possess different peripheral units, thus suggesting that the electronic conditions in all ZnPcs were similar to each other.

The porous TiO_2 electrodes were immersed in toluene solutions of PcS13–15 to obtain the phthalocyanine-stained TiO_2 electrode. The absorption spectrum of PcS15 adsorbed on a 4 μm TiO_2 film shows a sharp Q band at $\lambda = 699$ nm and the intensity ratio between the peaks at $\lambda = 699$ and 624 nm was in fare agreement with that in toluene solution, thus revealing the prevention of molecular aggregation among ZnPc cores within the adsorbed PcS15 monolayer on the TiO_2 surface (see Figure S5 in the Supporting Information).[16] The fluorescence of adsorbed PcS15 was completely quenched, thereby implying an efficient electron transfer from the excited PcS15 to TiO_2. The molecular enclosure of a ZnPc core with six bulky 2,6-diphenylphenoxy units in PcS13–15 enables steric isolation of the photoactive ZnPcs within the adsorbed monolayer on the TiO_2 surface.

The DSSC performance of PcS13–15 was examined using double-layered TiO_2 electrodes. The TiO_2 electrodes were immersed in toluene solutions of PcS13–15 for 48 hours at 25 °C. Figure 1a shows the photocurrent density-voltage curve of the DSSCs using PcS15-adsorbed TiO_2 electrodes under a standard global AM 1.5 solar condition and Table 1 shows the short-circuit current density (J_{sc}), open-circuit voltage (V_{oc}), fill factor (FF), and overall power conversion efficient (PCE) of PcS6 and PcS13–15. The PcS15 cell showed the highest PCE value of 5.3 % among the ZnPcs. This efficiency is the highest for the DSSCs using ZnPcs as a light-harvesting dye. Whereas the V_{oc} values of the PcS6 and PcS15 cells were the same, the J_{sc} value for the PcS15 cell was higher than that of PcS6 cell.

The IPCE spectrum of the PcS15 cell was similar to the absorption feature of PcS15 adsorbed onto the TiO_2 electrode (Figure 1b). The onset of the IPCE spectrum was at $\lambda = 800$ nm and the maximum IPCE was 72 % at $\lambda = 600$–720 nm, which correspond to the Q band of ZnPc. The IPCE was higher than those values obtained with the previously reported PcS6 in all visible-light regions (see Figure S7 in the Supporting Information). Noticeably, the IPCE values for the PcS15 cell in the region between $\lambda = 400$ and 520 nm was significantly increased by the introduction of

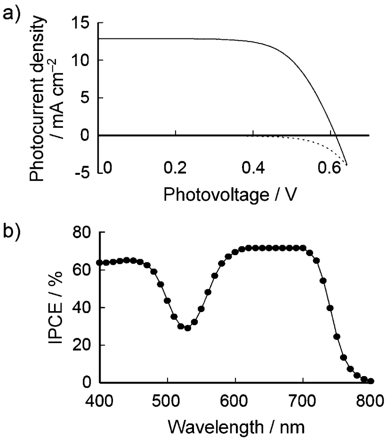


Figure 1. a) Photocurrent-voltage curve obtained with the DSSC derived from PcS15 under a standard global AM 1.5 solar conditions (solid line) and dark current (dotted line). b) IPCE spectrum for DSSC based on PcS15.

Table 1: Photovoltaic performance of DSSCs based on PcS6 and PcS13-15, compared to N719 dye.[a]

Dyes	V_{oc} [mV]	J_{sc} [mA cm^{-1}]	FF	PCE [%]
PcS6	610	11.0	0.70	4.7
PcS13	610	10.9	0.70	4.7
PcS14	600	11.5	0.70	4.8
PcS15	610	12.8	0.68	5.3
N719	640	15.3	0.68	6.7

[a] See the Supporting Information for details.

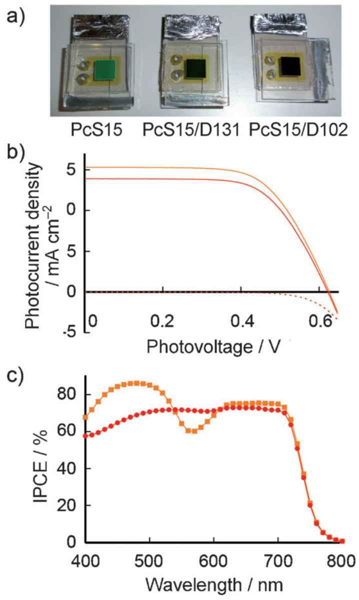


Figure 2. a) Optical images of PcS15, PcS15/D131, and PcS15/D102 cells. b) Photocurrent–voltage curve obtained with DSSCs based on PcS15/D131 (orange line: PCE = 6.2%, J_{sc} = 15.3 mA cm^{-2}, V_{oc} = 630 mV, FF = 0.64) and PcS15/D102 (red line: PCE = 5.6%, J_{sc} = 13.9 mA cm^{-2}, V_{oc} = 625 mV, FF = 0.64) under a standard global AM 1.5 solar conditions and dark currents (dotted lines). b) ICPE spectrum for DSSCs based on PcS15/D131 (orange line) and PcS15/D102 (red line).

the methoxy groups to the periphery of the molecule. The PCE value and the IPCE spectrum for the PcS13 cell were almost the same as those of the PcS6 cell, thus revealing that the introduction of methoxy groups onto the outer benzene rings of the molecule was not effective in enhancing the DSSC performance. The PcS14 cell exhibited a slight improvement in the PCE value compared to that of the PcS6 cell. Judging from the Hammett sigma constants of methyl and methoxy groups (σ_{-CH_3}: -0.170 and σ_{-OCH_3}: -0.268),[18] the electron-pushing ability is on the order of -OCH$_3$ > -CH$_3$ > H, which coincides with the overall performance of the device.

The PcS15-adsorbed TiO$_2$ electrode showed a vivid green color (Figure 2a, left). The green coloration of the PcS15 cell resulted in a lack of light harvesting in the $\lambda = 480$–600 nm region. The IPCE spectrum of the PcS15 cell showed a dip in the IPCE response at around $\lambda = 530$ nm, where the IPCE value decreased to 30% (Figure 1b). To compensate for the low IPCE around $\lambda = 500$ nm, co-sensitization of PcS15 with either the red or orange dyes D102 and D131, respectively (Mitsubishi Paper Mill),[19] was attempted. The absorption maxima of D102 and D131 in solution are $\lambda = 491$ and 425 nm, respectively. The surface of the TiO$_2$ electrode was initially covered with PcS15 by immersing the TiO$_2$ electrode into a solution of PcS15 for 48 hours, followed by immersion into the solution of either D102 or D131 for 2 hours. The color of the resulting cells covered with the mixed dyes became darkened as shown in Figure 2a (middle and left). The DSSC performance of the cocktail-type PcS15/D102 and PcS15/D131 cells were significantly enhanced in comparison to that of the PcS15 cell. Figure 2b shows the photocurrent density-voltage curve of the cocktail-type DSSCs adsorbed TiO$_2$ electrodes. The cocktail-type PcS15/D102 and PcS15/D131 cells showed 17 and 28% increase, respectively, in the J_{sc} values, compared to that of the PcS15 cell. Furthermore, the V_{oc} values of cocktail-type DSSCs were slightly increased.

The IPCE spectra of the PcS15/D102 and PcS15/D131 cells were a summation of the IPCE response for each of the dyes and the valley of IPCE response for the PcS15 cell filled with the IPCE responses of D102 and D131 (Figure 2c). The IPCE values at the near-IR region were not decreased by the co-sensitization, thus indicating that PcS15 did not interact with the organic dyes on the TiO$_2$ surface. More than 80% IPCE for the PcS15/D102 cell also suggests that there was no effect on the injection efficiency of the organic dyes by the co-sensitization. The bulky moieties attached to the phthalocyanine ring were to prevent the aggregation among the Pc dyes but the moieties were also effective in preventing the interaction with other dyes. Probably the key point of the design is that the nonconjugated bond between the Pc core and the bulky outer moiety. This is basically the same idea for reducing the intermolecular forces as a result of the induced dipole in the molecules, that is, the insertion of the bulky moiety increases the distance between the conjugated frameworks of the two molecules.[13]

Yella et al. reported the highest efficiency (above 12%) for the porphyrin-sensitized DSSCs by using cobalt (II/III) redox electrolytes.[20] The PcS15 cell showed a low efficiency, less than 1 % with cobalt redox electrolytes, because of the lack of a barrier to the approach of the redox species on the TiO_2 surface. We are now investigating the ZnPc-based sensitizers having an effective barrier to obtain higher V_{oc} values in DSSCs. In addition, since the absorption range of phthalocyanines can shift to near $\lambda = 900$ nm by the expansion of π conjugation of the phthalocyanine rings, the expansion of spectral response up to $\lambda = 900$ nm in the cocktail-type DSSCs is underway by using highly efficient naphthalocyanine derivatives.[21]

In conclusion, the photovoltaic performance of DSSCs based on near-IR-absorbing ZnPcs is enhanced by tuning of electron-pushing abilities of the peripheral substituents around the ZnPc core and the sterically isolated ZnPc PcS15 exhibited a 5.3 % efficiency when used as a light-harvesting dye on a TiO_2 electrode under standard solar conditions. The dye was then used for co-sensitization with other organic dyes that have a complementary spectral response. The sensitization process involved immersion in one dye bath after another. Without the coadsorbant, the two dyes on the TiO_2 showed high IPCE, thus suggesting that the bulky peripheral moiety attached to the framework of the dyes through a nonconjugated bond was effective in preventing intermolecular interactions between the different dyes. Such a molecular design provides a simple sensitization process for co-sensitized solar cells.

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