Enhancement of Incident Photon-to-Current Conversion Efficiency for Phthalocyanine-Sensitized Solar Cells by 3D Molecular Structuralization

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Dye-sensitized solar cells (DSSCs) have attracted increasing attention as low-cost, lightweight, and flexible devices.[1] To date, the highest conversion efficiencies ($\eta > 11\%$) have been achieved with red-colored polypyridylruthenium complex sensitizers.[2] However, an issue with respect to these dyes is their weak absorption coefficient above 650 nm. In contrast, metallophthalocyanines (MPcs) possess strong absorption bands in the near-IR region, but the efficiencies of DSSCs employing MPcs have not been impressive.[3] This is mainly due to their strong tendency to aggregate on the TiO_2 surface and the lack of directionality of electron transfer in the excited state.[4] Recently, Torres and co-workers[5] reported a high conversion efficiency ($\eta = 3.5\%$) for DSSCs using the unsymmetrical amphiphilic zinc phthalocyanine (ZnPc) dye **TT1** having three *tert*-butyl groups and a carboxylic acid group (its structure is shown in Figure S1 in the Supporting Information). However, the dye needed a coadsorbent to prevent its aggregation on the TiO_2 surface,[6] showing that the bulkiness of the *tert*-butyl groups was not sufficient. We also synthesized various ZnPcs, including **PcS2** (Chart 1), but could not prevent the aggregation well by enlarging **PcS2** planarly (dye no. 4; Figure S2).[7] Recently, McKeown et al.[8] succeeded in preparing crystalline nanoporous materials by using steric crowding of 2,6-diisopropylphenoxy groups on the phthalocyanine ring, and the substituents prevented the formation of $\pi-\pi$ stacks among ZnPcs within the crystal. In this communication, we report the synthesis of highly sterically hindered ZnPcs having three or six 2,6-diphenylphenoxy groups and show that the three-dimensional (3D) enlargement of the molecular structure prevents the aggregation almost completely. With the dye, the incident photon-to-current conversion efficiency (IPCE) was increased substantially not only for the Q band but also for the Soret band and shoulder peak, giving the highest energy conversion efficiency of 4.6% among DSSCs using Pcs.

A series of unsymmetrical ZnPcs (**PcS2**, **PcS5**, and **PcS6**; Chart 1) were synthesized by combining four phthalonitriles possessing different substituents (see the Supporting Information). It should be noted that the ^{1}H NMR spectra of **PcS2** and **PcS5** indicate the presence of some isomers, and Chart 1 shows only one regioisomer.

Figure 1 shows the absorption spectra of **PcS2** and **PcS6** in solution and on nanoporous TiO_2 films without $3\alpha,7\alpha$-dihydroxy-5β-cholonic acid (CDCA) as a coadsorbent. **PcS2** on TiO_2 shows a broader absorption spectrum around 600 nm, suggesting the formation of aggregation on the surface. This result is similar to that for **TT3**,[5c] which has the same structure as **PcS2**. On the other hand, **PcS6** showed a sharp Q band both in solution and on TiO_2, indicating a significant decrease in aggregation. **PcS5** also showed a reduction in aggregation (Figure S3), but to a lesser extent than **PcS6**.

Table 1 summarizes the $I-V$ characteristics [short-circuit currents (J_{sc}), open-circuit voltages (V_{oc}), fill factors (FF), and conversion efficiencies (η)] of the DSSCs under one-sun conditions, and Figure 2 shows the IPCEs of the DSSCs.
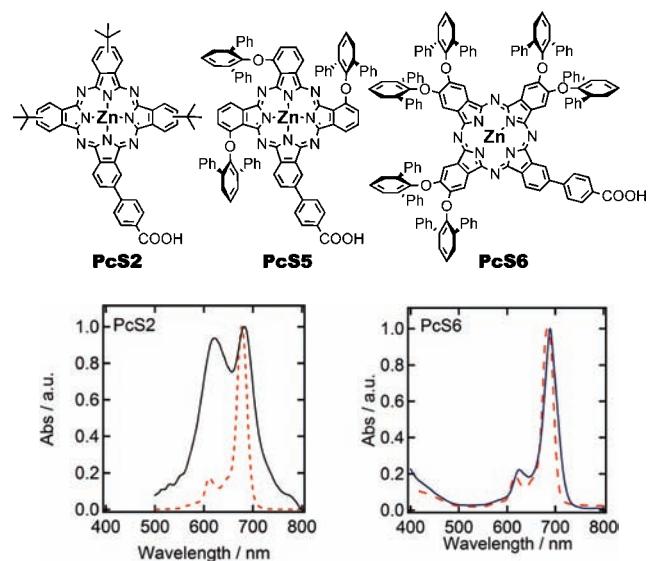
Chart 1. Structures of ZnPcs

PcS2 **PcS5** **PcS6**

Figure 1. Visible absorption spectra of (left) **PcS2** and (right) **PcS6** in THF solution (dashed lines) and adsorbed on a nanocrystalline 2 μm thick TiO_2 film (solid lines). The wavelengths of the Q-band absorption maxima, their absorption coefficients [log(ε/M^{-1} cm^{-1})], and the emission wavelengths were 675 nm, 5.35, and 698 nm for **PcS2** and 684 nm, 4.91, and 699 nm for **PcS6**, respectively.

Table 1. $I-V$ Characteristics of DSSCs[a] with Various Dyes under One-Sun Conditions and Values of Maximum IPCE

dye	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF	η (%)	IPCE$_{max}$ (%)
PcS2[b]	5.3	0.58	0.74	2.3	30
PcS5[b]	4.8	0.58	0.77	2.1	52
PcS6[c]	10.4	0.63	0.70	4.6	78
N719[c,d]	14.4	0.71	0.67	6.9	86

[a] The TiO_2 electrode consisted of a 7−8 μm thick nanoporous layer with a 5−6 μm scattering layer, with $TiCl_4$ treatment. The electrolyte was 0.1 M LiI, 0.6 M DMPImI, 0.05 M I_2, and 0.5 M tBP in acetonitrile. The measurements used an aperture mask with area of 0.17 cm^2. The area of TiO_2 was ∼0.14 cm^2. [b] With 10 mM CDCA in the dye solution. [c] Without CDCA. [d] **N719** is a Ru complex dye (see ref 9).

The highest IPCE value for **PcS2** (i.e., 30%) is much lower than that observed with **TT1** (80%).[5b] The lower efficiency of **PcS2** may result because the additional phenyl ring, which acts as a

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spacer, reduces the charge injection yield. The same J_{sc} but different IPCE values of **PcS2** in comparison to those of **TT3** may be due to different conditions of aggregation caused, for example, by different TiO$_2$ surface and adsorption conditions.
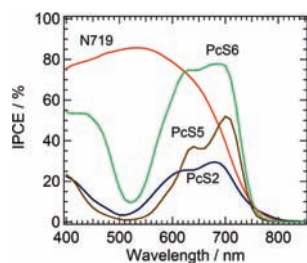

Figure 2. IPCEs of dye-sensitized solar cells with four different dyes. The cells were the same as those in Table 1.

In contrast to **PcS2**, **PcS6** showed high performance, with $\eta =$ 4.6%. To the best of our knowledge, this η value is the highest efficiency reported to date for DSSCs using ZnPcs. DSSCs with **PcS5** and **PcS6** were also prepared with various amounts of CDCA, and **PcS5** showed the highest η with 10 mM CDCA, while **PcS6** showed the highest without it. The 2,6-diphenylphenoxy substituent lies out of the plane of the phthalocyanine rings, but the results imply that two substituents are needed to have the angle to form a large enough 3D structure.

With **PcS6**, the IPCE at the maximum absorption of the Q band reached 78%. For the case of **TT1**, the addition of CDCA resulted in an increase in IPCE at the Q band but a decrease at the shoulder peak and Soret band.[6] For **PcS6**, the high IPCE values were observed not only for the Q band but also for the shoulder peak and Soret band. Such a remarkable result is probably due to the increased directional electron-transfer property (pushing ability) of the substituents as well as the prevention of aggregation. This is especially highlighted because the estimated potential of the LUMO for **PcS6** (-0.83 V vs NHE) was more positive than that of **PcS2** (-0.90 V vs NHE), and compared with **TT1**, **PcS6** has an additional phenyl ring between the Pc ring and the adsorption site, which was assigned to reduce J_{sc}.[5c]

In order to examine the origin of the lower V_{oc} for **PcS6** than for **N719**, electron lifetimes and densities were measured with various amounts of adsorbed dyes (Figure 3). Little difference was seen in the V_{oc}-versus-electron density plot, suggesting a negligible shift of the conduction band edge position among the cells. Thus, the low V_{oc} was due to the shorter electron lifetime. When the amount of adsorbed dye was reduced, the lifetimes of **PcS6** and **N719** became comparable. There are at least two reasons for the reduced electron lifetime in DSSCs: (1) a smaller blocking effect (less compact dye layer) and (2) the enhancement of recombination by adsorbed dye.[10] When the amount of adsorbed dye was reduced, a smaller blocking effect is expected, making it easy to distinguish the effect of the enhancement. Under these conditions, some dyes showed lifetimes shorter than that for the cell using bare TiO$_2$.[10a,c] The lifetime in DSSCs/**PcS6** was not shorter than DSSCs/**N719**, indicating little recombination enhancement by **PcS6**. The dark-current onset potentials of **PcS6** and **N719** cells were higher than that of the cell without dyes (Figure S4), also supporting this. Thus, the lower V_{oc} of DSSCs/**PcS6** was mostly due to the smaller blocking effect against the approach of acceptor species in the electrolyte. This may be related to the nonspherical large structure of the dyes, which makes it difficult to cover the whole TiO$_2$ surface.

In view of the mechanism of recombination enhancement, we suppose that the dispersion force is the origin.[10c] From this view, the small enhancement by **PcS6** can be interpreted in terms of blocking of the interaction between the π-conjugated ring and I$_3^-$ by the nonconjugated bulky substituents. In other words, the short electron lifetimes of Pc dyes are probably not intrinsic, and this encourages us to modify these dye structures further by adding the blocking function.
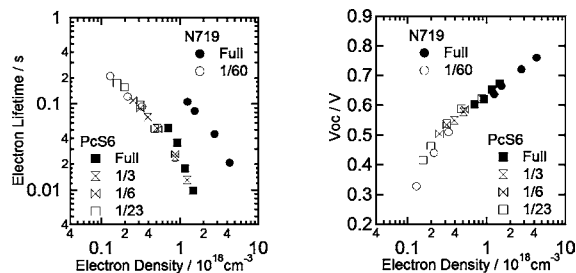

Figure 3. (left) Electron lifetime and (right) V_{oc} for DSSCs as a function of electron density in the DSSCs. Full denotes 4 h of dye adsorption, the same as used in Table 1; the fractions denote the amount of dye adsorption relative to the full amount.

Supporting Information Available: Experimental procedures including synthesis, electrochemical analyses, previously published dye structures, absorption spectra of **PcS5**, and dark $I-V$ curves. This material is available free of charge via the Internet at http://pubs.acs.org.

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