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Efficient Sensitization of Nanocrystalline TiO_2 Films by a Near-IR-Absorbing Unsymmetrical Zinc Phthalocyanine**

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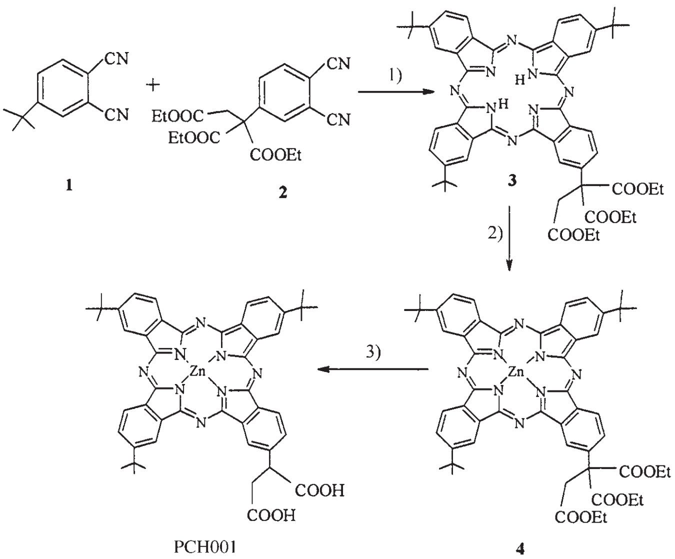
Dye-sensitized solar cells (DSSCs) have attracted significant attention as low-cost alternatives to conventional solid-state photovoltaic devices.[1–12] The most successful charge-transfer sensitizers employed in these cells are polypyridylruthenium complexes, which yield solar-to-electric power conversion efficiencies of 10–11 % with simulated sunlight.[13] In spite of this, the main drawback of ruthenium-based sensitizers is their lack of absorption in the red region of the visible spectrum. Phthalocyanines (Pc) are well known for their intense absorption in the red/near-IR (Q band) regions, therefore they are an excellent alternative for solar-cell applications.[14–17] As well as providing good absorption in the red/near-IR region of the solar spectrum, phthalocyanines can be tuned to be transparent over a large region of the visible spectrum, thereby enabling the possibility of using them as "photovoltaic windows": a red/near-IR absorbing photovoltaic cell, in place of a window, will allow visible light to enter a building whilst harvesting the solar power from the red/near-IR part of the spectrum. In addition to directly generating power, this also reduces the solar heating of buildings, thereby reducing the demand for, and power consumption of, air-conditioning units.

Several groups have tested phthalocyanines as sensitizers for wide-bandgap oxide semiconductors, although they have all reported unimpressive power conversion efficiencies.[15,16,18–20] The low efficiency of cells incorporating phthalocyanines appears to be due to aggregation and lack of directionality in the excited state.[21] One of the essential requirements for the light-harvesting system of a molecular/semiconductor junction is that the sensitizer possesses directionality of its electronic orbitals in the excited state. This directionality should be arranged to provide an efficient electron transfer from the excited dye to the TiO_2 conduction band by good electronic coupling between the lowest unoccupied molecular orbital (LUMO) of the dye and the Ti 3d orbital.

In order to incorporate these essential properties we have designed and developed a novel unsymmetrical zinc phthalocyanine (PCH001) sensitizer that contains three *tert*-butyl and two carboxylic acid groups that act as "push" and "pull" groups, respectively. The function of the two carboxylic acid groups is to graft the sensitizer onto the semiconductor surface and to provide intimate electronic coupling between its excited-state wave function and the conduction-band manifold of the semiconductor. The purpose of the three *tert*-butyl groups is to enhance the solubility, to minimize the aggregation, and to tune the LUMO level of the phthalocyanine that provides directionality in the excited state. We report herein the synthesis and electronic, electrochemical, and photovoltaic properties of this sensitizer in liquid-electrolyte and solid-state cells.

Scheme 1 shows the synthetic strategy used to obtain the sensitizer PCH001 (see also *Experimental Section*). The UV/



Scheme 1. Synthesis of PCH001. 1) DBU, pentanol, reflux 20 h; 2) $Zn(OAc)_2$/DMF; 3) Na/ethanol 7 d. DBU = 2,3,4,6,7,8,9,10-octahydropyrimidol[1,2-*a*]azepine.

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Vis absorption spectrum of PCH001 in ethanol (Figure 1) shows a maximum at 692 nm ($\varepsilon = 191\,000\ \text{M}^{-1}\,\text{cm}^{-1}$). When PCH001 is excited at 298 K within the charge-transfer (CT) absorption band in an air-equilibrated ethanol solution it exhibits luminescence maxima at 698 and 750 nm (Figure 2).

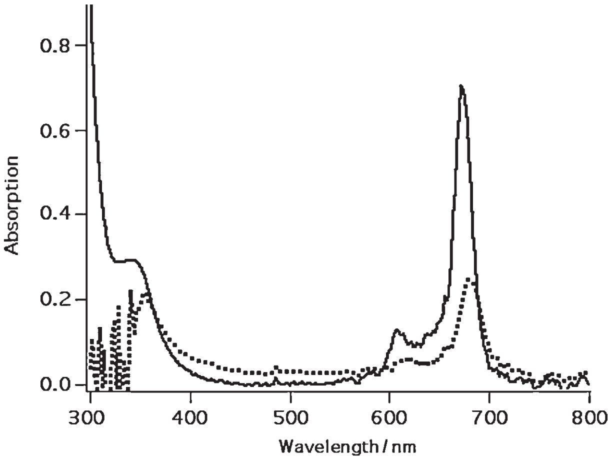

Figure 1. UV/Vis absorption spectra of PCH001 in ethanol (3.5×10^{-6} M; solid line) and adsorbed on a nanocrystalline 2-µm transparent TiO_2 film (dotted line). An identical TiO_2 nanocrystalline film was used as reference.

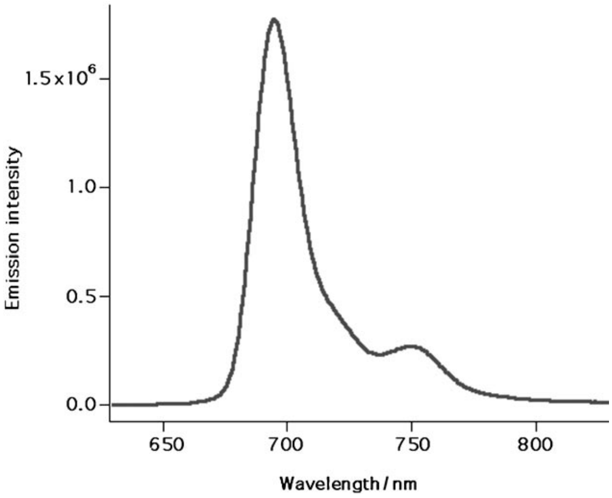

Figure 2. Emission spectrum of PCH001 measured at 298 K in an air-equilibrated ethanol solution.

The spectral profile of the emission decays as a single exponential with a lifetime of 10 ns in degassed solution. The absorption spectrum of PCH001 adsorbed on a 2-µm TiO_2 film shows features similar to those seen in the corresponding solution spectra but with a slight red-shift due to interaction of the anchoring groups with the surface (Figure 1). The excitation spectrum obtained by exciting at the luminescence maximum at 750 nm shows a maximum at 698 nm, and the $E_{0\text{-}0}$ energy of PCH001 estimated from the excitation and emission spectra is 1.78 eV. PCH001 exhibits a quasireversible oxidation at $E_{1/2} = 0.65$ V and a reduction at $E_{1/2} = -1.31$ V versus ferrocene (Fc).

For solar-cell fabrication, screen-printed, double-layer films consisting of a 6-µm transparent layer and a 4-µm scattering layer were prepared and treated with a 0.05 M titanium tetrachloride solution using a previously reported procedure.[13,22] The films were heated to 500 °C in air and calcined for 20 min before use. Dye solutions were prepared in the concentration range $2\text{–}3 \times 10^{-5}$ M as a solution in ethanol containing 60 mM of 3α,7α-dihydroxy-5β-cholanic acid (chenodeoxycholic acid). The electrodes were dipped into the dye solution for 4 h at 22 °C and the dye-coated electrodes were then rinsed quickly with ethanol and used as such for photovoltaic measurements. The liquid-electrolyte and the solid-state solar cells were fabricated as described previously.[13,23]

Figure 3 shows the photocurrent action spectrum obtained with a sandwich cell using an electrolyte containing 0.6 M 1-butyl-3-methylimidazolium iodide, 0.05 M iodine, 0.05 M LiI, and 0.5 M *tert*-butylpyridine in a 50:50 (v/v) mixture of valeronitrile and acetonitrile (1376). The incident monochromatic photon-to-current conversion efficiency (IPCE) plotted as a function of excitation wavelength reaches 75 %. From the overlap integral of this curve with the solar

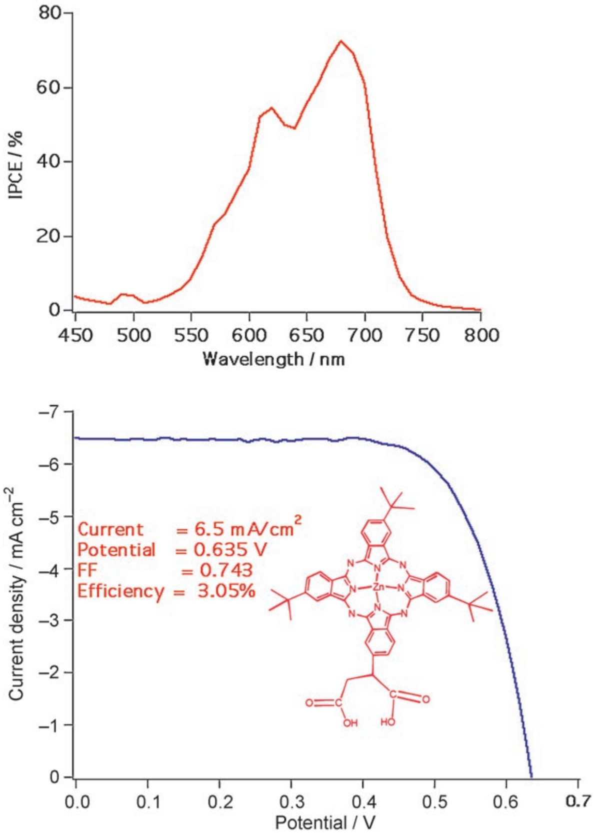

Figure 3. Photocurrent action spectrum (top) and current–voltage characteristics (bottom) of PCH001 obtained for a nanocrystalline TiO_2 film support on a conducting glass sheet and derivatized with a monolayer of PCH001 in the presence of chenodeoxycholic acid. A sandwich-type cell configuration was used to measure this spectrum. The redox electrolyte was 1376 and the cell's active area 0.158 cm².

spectrum one can calculate a short-circuit photocurrent density (i_{sc}) of 6.2 mA cm^{-2}. In agreement with this measurement, the PCH001-sensitized cell gave an i_{sc} of (6.50 ± 0.20) mA cm^{-2}, an open-circuit voltage of (635 ± 30) mV, and a fill factor (FF) of 0.74 ± 0.03, corresponding to an overall conversion efficiency (η) of 3.05 % under standard global air mass (AM) 1.5 solar conditions (Figure 3).

Under similar conditions zinc tetracarboxyphthalocyanine yields an efficiency of only 1 %.[21] The high efficiency of PCH001 is likely to be due to the three bulky *tert*-butyl groups, which not only enhance the solubility but also create directionality in the excited state, thus providing an efficient electron-injection pathway into the TiO_2 conduction band. The presence of two carboxy groups on one ring immobilizes the sensitizer on nanocrystalline titanium dioxide and also acts as an electron-withdrawing (pull) group. The significant effect asserted by the "push" and "pull" groups on PCH001 is evident from the IPCE spectrum and the current–voltage characteristics compared to zinc tetracarboxyphthalocyanine.

As an alternative to liquid-electrolyte cells, a solid-state organic hole-transporter can be used in place of the liquid electrolyte.[24] These cells typically exhibit lower efficiencies than the original liquid-electrolyte version, primarily due to the electron diffusion length being much shorter as a consequence of faster charge recombination. However, they are attracting great interest, both academically and industrially, as their solid-state nature potentially allows concerns of solvent leakage and toxicity to be overcome.

In Figure 4 we present the short-circuit photocurrent action spectrum for a solid-state cell incorporating PCH001 as the sensitizer and 2,2′,7,7′-tetrakis(*N*,*N*-di-*p*-methoxyphenylamine)-9,9′-spirobifluorene (spiro-MeOTAD)[24] as the hole-transporting component. We observe a phenomenal response in the red part of the spectrum, with a peak IPCE close to 45 %. This peak IPCE is comparable to solid-state cells incorporating the best-performing ruthenium dyes, which absorb in the visible part of the spectrum.[25] Integrating the IPCE over the solar spectrum gives a calculated short-circuit current of approximately 2.4 mA cm^{-2} under 100 mW cm^{-2} AM 1.5 illumination. The inset to Figure 4 shows the current–voltage curve measured for the same cell as in the main Figure under AM 1.5 simulated sunlight at an intensity of 90 mW cm^{-2}. The collected current is in good agreement with the IPCE measurements, with the cell exhibiting a short-circuit current, open-circuit voltage, fill factor, and power conversion efficiency of 2.1 mA cm^{-2}, 0.72 V, 0.52, and 0.87 % respectively.

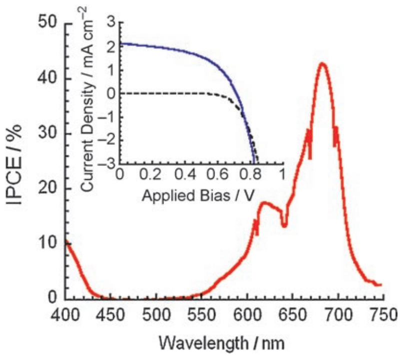

Figure 4. Photocurrent action spectrum, and current–voltage characteristics (inset) measured in the dark (dashed line) and under simulated AM 1.5 solar illumination at 90 mW cm^{-2} (blue solid line) for a solid-state DSSC using PCH001 as the molecular sensitizer and spiro-MeOTAD as the hole-transporting material.

For the solid-state cell it is apparent that there is little response over most of the visible region of the spectrum. This is likely due to the cell being much thinner than the liquid-electrolyte cell, therefore it only performs efficiently where the dye absorption is strongest. Although this will reduce the current collected when exposed to sunlight, it makes these cells a real contender to be used as "photovoltaic windows".

To the best of our knowledge, these results represent a major breakthrough in the design and development of phthalocyanine-based sensitizers. We therefore believe that the data and findings of this study should spark a broad interest in the field of phthalocyanine-sensitized solar cells for use as photovoltaic windows that transmit part of the visible light and harvest in the red/near-IR part of the spectrum.

In conclusion, we have demonstrated the selective functionalization of a phthalocyanine sensitizer, which yields 75 % IPCE with a 3.05 % power conversion efficiency under "one sun" when incorporated in a liquid-electrolyte cell. The sensitizer also performs impressively when used in a solid-state cell, with a 43 % peak IPCE. Our findings demonstrate that creating directionality in the excited state of the sensitizer by adjusting the electron densities of the donor moieties is the key for the unprecedented efficiency of PCH001.

Experimental Section

The synthesis of 4-(1,1,2-tricarbethoxyethyl)phthalonitrile (**2**; Scheme 1) was accomplished according to the reported procedure.[26]

Synthesis of **3**: Compound **2** (1.00 g, 2.69 mmol), 4-*tert*-butylphthalonitrile (**1**; 1.484 g, 8.07 mmol), and 100 mg of DBU were dissolved in 20 mL of pentanol. The reaction mixture was refluxed for 20 h and the solvent was then removed under reduced pressure. The solid material obtained was subjected to silica gel column chromatography with $CHCl_3$ as eluent. The second band, a greenish-blue one, contained the desired phthalocyanine **3**. The phthalocyanine was recrystallized twice from 50:50 (v/v) $CHCl_3$/hexane (yield: 10 %). IR (KBr pellet): $\tilde{\nu} = 3423$, 2957, 2923, 2857, 1713, 1612, 1396, 920, 525 cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} ($\log \varepsilon$) = 674 (5.21), 611 (4.81).

Synthesis of **4**: Zinc metalation of the free-base phthalocyanine **3** was achieved by treatment with zinc acetate in DMF.

Synthesis of PCH001: This compound was synthesized by hydrolysis of **4** with Na/ethanol. Thus, 100 mg of **4** was dissolved in 25 mL of ethanol and 1 g of Na was added. The resulting reaction mixture was stirred at room temperature for 7 d and the solvent was then evaporated under reduced pressure. The obtained solid material was redissolved in ethanol and the pH value was adjusted to 3 by addition of dilute HCl. The precipitate was filtered and dried under reduced pressure. This phthalocyanine was characterized by ^{1}H NMR and UV/Vis spectroscopy, matrix-assisted laser desorption/ionization (MALDI) time-of-flight (TOF) mass spectrometry, and elemental analysis. Elemental analysis calcd for $C_{48}H_{44}N_8O_4Zn$ (863): C 66.86, H 5.14, N 12.99; found: C 66.74, H 5.30, N 13.00. IR (KBr): $\tilde{\nu} = 3423$, 2957, 2923, 2857, 1713, 1612, 1488, 1396, 1365, 1325, 1281, 1256, 1193, 1089, 920, 746, 671 cm^{-1}. ^{1}H NMR ([D$_6$]DMSO): $\delta = 9.75$ (m, 8H), 8.60 (d, $J = 5.2$ Hz, 4H), 5.35 (s, 2H), 4.60 (s, 1H), 1.65 ppm (s, 27H).

MALDI-TOF: m/z (%): 863 (5), 689 (30). UV/Vis (ethanol): $\lambda_{\max}$ ($\log\varepsilon$) = 692 (5.28), 347 (4.85).

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