# Dye Sensitization of Nanocrystalline Tin Oxide by Perylene Derivatives

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A new sensitizing dye−semiconductor system comprised of perylene derivatives on $SnO_2$ has been characterized. The tetracarboxylic acid form ("PTCA") of the commercially available dye perylene-3,4,9,-10-tetracarboxylic dianhydride and the novel compound perylene-3,4-dicarboxylic acid-9,10-(5-phenanthroline)-carboximide ("PPDCA") adsorb strongly to the surface of colloidal films of $SnO_2$ and inject electrons into the semiconductor film upon absorption of light. A film of PPDCA on $SnO_2$ yields a short circuit photocurrent density of 3.26 mA/cm$^2$, a photovoltage of −0.45 V, and an overall cell efficiency of 0.89% at one sun light intensity. Estimates of the oxidation potential of adsorbed PPDCA indicate that it may also be useful in a water-splitting configuration. The results presented here indicate that the perylene−$SnO_2$ system is a promising dye−semiconductor combination and warrants further study.

## Introduction

Dye sensitization of wide band gap semiconductors is a rapidly expanding field which is beginning to realize applications in solar cell technology. The recent growth is primarily due to the significant advancement made by Grätzel and co-workers with high surface area titanium dioxide ($TiO_2$) nanocrystalline particles sensitized by ruthenium bipyridyl complexes.[1] The complex [Ru(4,4′-dicarboxylic acid-2,2′-bipyridine)$_2$ (NCS)$_2$] or "[Ru(L)$_2$(NCS)$_2$]" has thus far given the most promising results; conversion efficiencies of 10% were reported several years ago.[2] Since then, although other systems have been explored, their efficiencies were comparably low. Consequently, most research continues to focus on derivatives of ruthenium bipyridine and $TiO_2$ as the dye−semiconductor combination.[3] However, the investigation and development of other dye−semiconductor systems are essential to furthering our fundamental understanding of the electron injection process, exploring specialized and long term applications of dye-sensitized solar cells, and quite possibly, to fully realizing their potential as solar cells.

From a fundamental standpoint, the unusually high efficiency with which [Ru(L)$_2$(NCS)$_2$] sensitizes $TiO_2$ is difficult to rationalize. Compared to other chromophores, its photophysics in solution are quite poor. The extinction coefficient for absorption of visible light is relatively low (~14 000 M$^{-1}$ cm$^{-1}$), and the complex luminesces very weakly from a triplet state, with a quantum yield of ~0.40% (125 K).[2] Furthermore, the stability of a coordination complex such as [Ru(L)$_2$(NCS)$_2$] over long term operation in a liquid cell is unknown; ligand substitution reactions with solvent or electrolyte are likely to occur over time. In addition, although the [Ru(L)$_2$(NCS)$_2$]−$TiO_2$ system produces a substantial power output, specialty applications of dye-sensitized cells, which might include fuel production, detoxification, or photoelectrochromics,[4] may require conditions that optimize parameters other than electrical power.

Dyes based on perylene-3,4,9,10-tetracarboxylic acid (Figure 1b) offer both fundamental and practical advantages for use as sensitizers. They are highly absorbing in the visible ($\epsilon \sim 10^5$ M$^{-1}$cm$^{-1}$) and emit from a singlet state with quantum yields near unity.[5] Electron injection from dye singlet states into the conduction band of a semiconductor is, in general, faster than
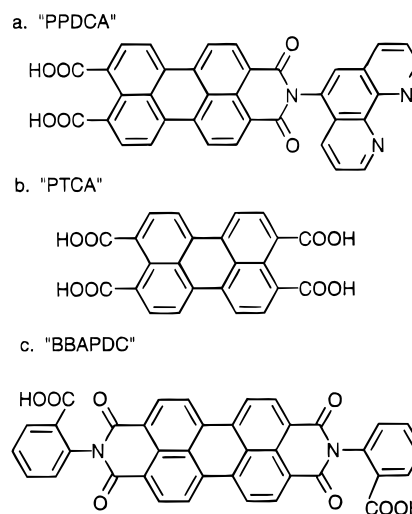


**Figure 1.** Structures of perylene chromophores: (a) perylene-3,4-dicarboxylic acid-9,10-(5-phenanthroline)carboximide, (b) perylene-3,4,9,10-tetracarboxylic acid, and (c) *N,N′*-bis(2-benzoic acid)-3,4,9,10-perylenebis(dicarboximide).

from triplet states[6] and conserves more potential from the light captured. *N,N′*-substituted perylene-3,4,9,10-tetracarboxylic diimides (example, Figure 1c) have been used commercially as red pigments for almost 50 years because of their chemical stability and lightfastness.[7] Furthermore, there are many examples of perylenes in organic solid state photovoltaic devices.[8]

Perylene derivatives might also prove versatile in answering mechanistic questions regarding injection: since they are highly emitting, the time-correlated emission experiments employed to measure injection rates are facilitated. Their synthetic chemistry, while not as extensive in the literature as it is for ruthenium−bipyridine-based complexes, has a potentially wide range of flexibility for altering properties such as color and redox potential. Additionally, an adsorbing moiety such as −CO$_2$H or −PO$_3$H can be attached to the perylene ring system at one of four edges. This would allow the investigation of two different orientations of the dye−semiconductor linkage: one oriented parallel to the excited state dipole moment and one oriented perpendicular.

Willig and co-workers recently reported an electron injection rate of 190 fs for 2,5-bis(*tert*-butyl)-9-methylphosphonic acid−

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perylene adsorbed on nanocrystalline $TiO_2$.[9] Otherwise, perylene derivatives remain unexplored in the dye sensitization literature. For the reasons detailed above we have begun investigating several perylene derivatives as sensitizing dyes. Although numerous studies of dye injection into colloidal $SnO_2$ have been published, the sensitizing dyes are usually ruthenium bipyridine complexes.[10] Here we report on the excellent adsorption properties and sensitization yields obtained for two perylene derivatives adsorbed onto colloidal $SnO_2$ films.

## Experimental Section

**Materials and Measurements.** Fifteen percent tin(IV) oxide, as a colloidal dispersion of 15 nm particles in water, was obtained from Alfa/Aesar. Acetonitrile (Burdick & Jackson) was dried and distilled over calcium hydride. All other commercial reagents were used without further purification. Nanocrystalline $TiO_2$ films were prepared as previously described.[11] Absorbance spectra were measured on a Hewlett Packard 8452A diode array spectrophotometer. Current−voltage measurements were made at white light intensity approximating AM 1.5 solar emission for the wavelength region between 300 and 800 nm from a Xenon arc lamp (PTI, model A 1010) and monitored by a Keithley 236 source measure unit. Current−voltage curves and IPCE spectra were generated using programs written in LabVIEW Version 4.0.

**Preparation of Dyes.** *Perylene-3,4-dicarboxylic acid-9,10-(5-phenanthroline) Carboximide ("PPDCA", Figure 1a).* The dye was obtained via two different methods; both approaches are modifications of a procedure by Tröster for preparing monoimide perylenedicarboxylic acids.[12]

*Procedure 1.* To a 500 mL flask was added 1.00 g of 3,4,9,-10-perylenetetracarboxylic dianhydride (2.55 mmol), 200 mL of water, and 170 mg of KOH (solid, pellets). After the solution was warmed for 1 h, 1.00 g of 5-amino-1,10-phenanthroline (5.13 mmol) and 25 mL of methanol were added and the reaction refluxed for 2 days. The product was then isolated according to Tröster[12] and vacuum dried at room temperature.

*Procedure 2.* To a 100 mL flask, 575 mg (2.95 mmol) of 5-amino-1,10-phenanthroline, 45 mL of distilled water, and 10 mL of *N,N′*-dimethylformamide were added. The suspension was stirred at room temperature. Subsequently 300 mg (0.669 mmol) of monopotassium 3,4:9,10-perylenetetracarboxylate[12] were added, and the reaction mixture was stirred at room temperature for 2.5 h. The reaction was heated at 90 °C for approximately 16 h. The product was isolated via Tröster[12] and vacuum dried at room temperature.

Typical yields for both procedure 1 and 2 were 40 mg of PPDCA (~10%).

*Perylene-3,4,9,10-tetracarboxylic Acid ("PTCA", Figure 1b).* 3,4:9,10-Perylenetetracarboxylate was prepared by dissolution of 3,4:9,10-perylenetetracarboxylic dianhydride (Aldrich) into a dilute solution of KOH. Then, 1 M HCl was added dropwise until a precipitate formed, which was collected, kept from heat, and vacuum dried at room temperature.

*N,N′-Bis(2-benzoic acid)-3,4,9,10-perylenebis(dicarboximide) ("BBAPDC", Figure 1c)* was prepared from 3,4:9,10-perylenetetracarboxylic dianhydride and anthranilic acid using a standard literature procedure.[13]

**Preparation of $SnO_2$ Electrodes.** The 15% $SnO_2$ colloidal solution was used without dilution. However, 1g/L "Carbowax" (poly(ethylene glycol), compound with 2,2′-[(1-methylethylidene)bis(4,1-pheneleneoxymethylene)]bisoxirane) was added to aid adherence to the glass and the deposition of multilayers. F-doped $SnO_2$ (Libby Owens Ford, 8 Ω/square) glass was soaked in saturated KOH in isopropanol overnight. Precut 1
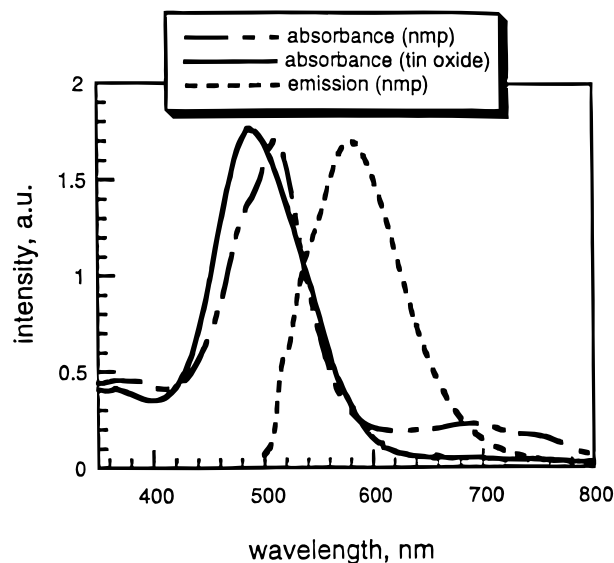
**Figure 2.** Absorbance spectra of PPDCA in nmp and adsorbed on a 2 $\mu$m thick colloidal film of $SnO_2$, and emission spectrum in nmp. Excitation was at 514 nm.

× 1.5 cm pieces were then cleaned with soap, ethyl alcohol, acetone, and 2-propanol, respectively. A 75 $\mu$L aliquot of the $SnO_2$ colloidal solution was spin coated onto each electrode at 2000 rpm. For multilayer electrodes, each layer application was followed by heating the film at 400 °C in a Thermolyne 48000 Furnace for approximately 15 min. The final films were cured at 400 °C for 1 h. The cooled electrodes were dipped into a solution of, typically, 15 mg of dye in 25 mL of 1-methyl-2-pyrrolidinone (nmp) overnight. The dye BBAPDC (Figure 1c) was adsorbed onto the colloidal films from *N,N′*-dimethylformamide (DMF). The electrodes, which were stained dark red, were removed from dye solution and placed into fresh nmp until use to desorb any aggregated or unbound dye.

**Cell Characterization.** In order to measure cell operation, the dye-stained $SnO_2$ films were employed in a sandwich type cell, similar to the configuration described for dye-sensitized $TiO_2$ solar cells.[2] A cell holder containing clamps for positioning and contacting the electrodes was used to gently press together the film electrode and the counter electrode, which was a platinum-coated piece of F-$SnO_2$ glass. A drop of electrolyte solution was placed in the space between the electrodes, and then the two electrodes were pressed together more forcefully.

## Results and Discussion

Both PPDCA and PTCA adsorb to the $SnO_2$ films, as apparent to the eye, within seconds of immersion into dye solution. By analogy to ruthenium dyes based on 4,4′-dicarboxylic acid-2,2′-bipyridine, we presume that the dyes adsorb via the carboxylic acid groups, either bonding electrostatically or forming an ester linkage by a hydrolysis reaction with an Sn−OH functionality.[1] The optical density of a dyed film was determined by the film thickness: a film with a thickness of ~400 nm had a dye absorbance peak of ~0.5; a ~2 $\mu$m thick film had an absorbance of ~2. The absorbance spectrum of a $SnO_2$ film dyed with PPDCA and the absorbance and emission of the same dye in 1-methyl-2-pyrrolidinone (nmp) is shown in Figure 2. The dye absorbance maximum, 510 nm in solution, is blue shifted by approximately 25 nm when adsorbed onto the $SnO_2$ film.

A current−voltage curve for a typical PPDCA-sensitized $SnO_2$ film is presented in Figure 3. In $Br^-/Br_2$ in acetonitrile containing 4-*tert*-butylpyridine[2], the short-circuit photocurrent density is 3.26 mA/cm$^2$, and the open-circuit photovoltage is
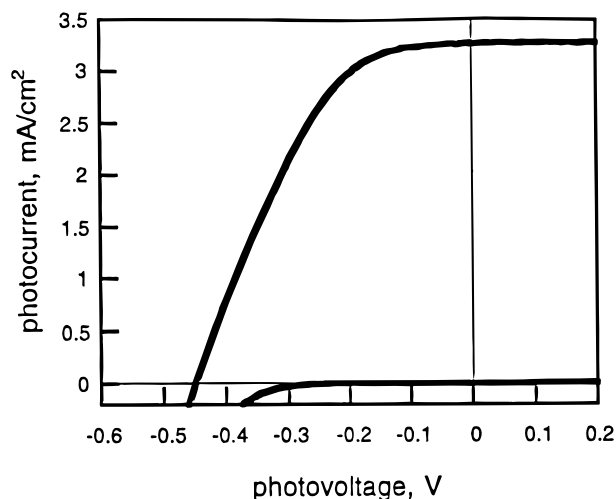
**Figure 3.** Current−voltage curves in the dark (lower curve) and under white light illumination (simulated AM 1.5) for a 1.2 $\mu$m thick film of SnO$_2$ dyed with PPDCA. The electrolyte solution is 0.5 M LiBr, 0.05 M Br$_2$, and 0.2 M 4-*tert*-butylpyridine[2] in acetonitrile.
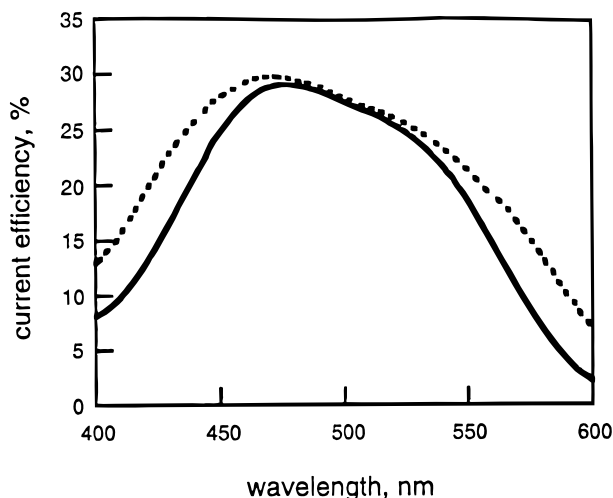


**Figure 4.** Incident and absorbed photon-to-current efficiency of PPDCA adsorbed on a SnO$_2$ film. Solid line is IPCE; dashed line is APCE. The data were obtained for a 2.5 $\mu$m thick film employing an electrolyte solution of 0.5 M LiBr, 0.05 M Br$_2$, and 0.2 M 4-*tert*-butylpyridine[2] in 80/20 v/v ethylene carbonate/propylene carbonate.

−0.45 V; the fill factor is 45.5, and the overall cell efficiency is 0.89%. Comparable photocurrents are also obtained in I$^-$/I$_3^-$ solution; however, the open-circuit photovoltage obtained with I$^-$/I$_3^-$ is only −0.20 V. The difference in photovoltages is presumably caused by the difference between Br$^-$/Br$_2$ and I$^-$/I$_3^-$ solution potentials, which we measured to be +0.535 and +0.115 V vs SCE, respectively. Films dyed with PTCA exhibited short-circuit photocurrents comparable to those shown in Figure 3; however, the open-circuit photovoltages in Br$^-$/Br$_2$ were, on average, −0.40 V. Also, PTCA was not as strongly bound to the SnO$_2$ as the PPDCA and desorption occurred after repeated cyclings.

An incident photon-to-current efficiency (IPCE) plot for PPDCA on SnO$_2$ is shown in Figure 4; also indicated is the absorbed photon-to-current efficiency (APCE), or quantum yield for the dye, calculated by dividing the IPCE by the absolute absorbance of the PPDCA. The data were obtained using the Br$^-$/Br$_2$ couple in 80/20 ethylene carbonate/propylene carbonate; this solvent was chosen since more volatile solvents tended to evaporate during the time necessary to obtain data. The maximum quantum yield of the dye in this solvent system is approximately 30% for the wavelength region 458−488 nm.

Although the IPCE confirms that the wavelength dependence of the collected current traces out the absorbance features of the dye, both the IPCE and the APCE underestimate the efficiencies obtained in acetonitrile. In fact, a single-point APCE measured at 460 nm in acetonitrile containing Br$^-$/Br$_2$ is 60%. Incorporation of the transmission loss due to the glass substrate ($\sim$25% at 460 nm) makes the actual quantum efficiency at this wavelength closer to 80%.

PPDCA and PTCA also adsorb to colloidal TiO$_2$ and Al$_2$O$_3$ films. TiO$_2$ is a semiconductor with a conduction band edge approximately 0.5 V more negative than SnO$_2$,[14] whereas Al$_2$O$_3$ is an insulator. While PPDCA emits strongly when adsorbed to either TiO$_2$ or Al$_2$O$_3$, the dye emission is strongly quenched on SnO$_2$. Furthermore, the photocurrent density obtained on nanocrystalline TiO$_2$ for the PPDCA dye is on the order of 100 $\mu$A/cm$^2$ at short circuit, about 30 times less than that obtained on SnO$_2$. The excited state oxidation potential of the dye was estimated from electrochemical and spectroscopic data to be between −0.60 and −0.85 V vs SCE. The conduction band edge of single-crystal TiO$_2$ is approximately −0.6 V vs SCE (pH 7), compared to −0.1 V for SnO$_2$.[14] However, the conduction band edge of TiO$_2$ in nonaqueous solvents is more negative than in aqueous solution and depends on the electrolyte; for colloidal particles in acetonitrile containing 0.1 M LiBr and 0.2 M tetrabutylammonium bromide, it is $\sim$−0.85 V vs SCE.[15] Therefore, the lower photocurrent on TiO$_2$ compared to SnO$_2$ is likely caused by the smaller driving force for electron injection.

We also investigated the adsorption properties and photosensitization yields for *N,N'*-bis(2-benzoic acid)-3,4,9,10-perylenebis(dicarboximide) (Figure 1c) on SnO$_2$ films. Because of steric constraints, the carboxylic acid groups on the phenyl ring are oriented perpendicular to the perylene ring system. The dye adsorbed strongly to the SnO$_2$ surface, presumably through the carboxy groups, and has similar spectral properties to PTCA but exhibited a small short-circuit photocurrent density ($\sim$100 $\mu$A/cm$^2$ for a dyed film with conditions similar to those indicated in Figure 3). The poor photosensitization obtained for this dye may be related to its orientation on the surface of the SnO$_2$ particles.

The amount of dye adsorbed on the SnO$_2$ films did not scale linearly with increasing film thickness. Furthermore, the film integrity broke down (with appearance of bubbles, uneven film boundaries, etc.) for very thick films. Likewise, cells made from increasingly thicker films exhibited decreasing fill factors and limiting photocurrent behavior at high light intensities, perhaps caused by transport limitations through the cell. The poorer behavior of thicker films may be caused by the film inhomogeneity resulting from multilayer film applications. Although the size of the colloids is initially 15 nm, multiple sinterings may shrink or compact the particles, and this effect would be unevenly distributed throughout a multilayer film. A decrease in particle size and correspondingly smaller pore sizes may limit the ability of the dye to diffuse deep into the film during the adsorption process and may limit the transport of redox species during cell operation. Additionally, the occurrence of bubbles and seams in the film indicates areas of electrical discontinuity which may prevent the collection of injected electrons. While we are encouraged by such promising findings using a commercially available colloid, the system described here has not been optimized. We anticipate that the development of a method to make thick films with a single application of SnO$_2$ colloids would improve the cell characteristics.

We are currently attempting to design a dye-sensitized solar cell capable of splitting water into oxygen and hydrogen. Our

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initial interest in perylene derivatives was due to their very positive oxidation potential, which is thermodynamically capable of driving the water oxidation reaction at appropriate pH's.[16] For example, the oxidation potential of a commercially available diimide derivative, *N,N′*-bis(2,5 di-*tert*-butylphenyl)-3,4,9,10-perylenedicarboximide, is +1.66 V vs SCE in $CH_2Cl_2$. Because of the poor solubility of the perylene chromophores in Figure 1a−c in electrochemical solvents, we have been unable to obtain solution electrochemical data for them. However, assuming their oxidation potentials are similar to the commercial derivative and only minimally solvent dependent, there should be a substantial overpotential for water oxidation (+0.63 V vs SCE at pH 7).

Because of the aforementioned solubility limitations, we have instead estimated the oxidation potential of PPDCA on a dyed $SnO_2$ film, in both acetonitrile and acidic water. This approach may be more appropriate than solution electrochemistry for predicting the energetics of a sensitizing dye, since adsorption might alter the dye's redox potentials.[11] On a film of Sb-doped $SnO_2$, a reversible reduction occurs at −0.88 V vs SCE in acetonitrile containing 0.1 M $TBAPF_6$. We are unable to do oxidative electrochemistry on the film because of the semiconducting nature of the $SnO_2$; however, the oxidation potential estimated from the reduction potential and the energy of emission is +1.2 V vs SCE. We also estimated the oxidation potential of the adsorbed dye in aqueous solution by immersing the film into a solution of $Ce^{IV}$ ($E_0$, $Ce^{IV/III}$ = +1.20 V vs SCE in 1 M $H_2SO_4$[17]) and monitoring the spectral changes of the adsorbed dye. Immersion of a dyed film of PPDCA into $Ce^{IV}$ in 0.5 M $H_2SO_4$ resulted in ~10% oxidation of the dye. Subsequent immersion into water (deionized, pH 6) resulted in recovery of the spectrum, indicating re-reduction of the dye presumably via the oxidation of water. The resistance of the dye to complete oxidation by $Ce^{IV}$ indicates that its oxidation potential is more positive than ~+1.2 V vs SCE in 0.5 M $H_2SO_4$. Its re-reduction by immersion in deionized water suggests that its oxidized form is indeed capable of oxidizing water at pH 6. However, there were complications from desorption of the PPDCA that limited our ability to quantify these findings. We are continuing these experiments with other perylene dyes which exhibit stronger adsorption properties.

## Conclusions

Perylene derivatives containing carboxylic acid groups adsorb to and efficiently photosensitize colloidal $SnO_2$ films. This is the first detailed account of the dye sensitization of a wide band gap semiconductor by perylene derivatives. Furthermore, the perylene dyes presented here may be useful in water-splitting dye-sensitized solar cells.

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