An Improved Perylene Sensitizer for Solar Cell Applications

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Published in:
Chemsuschem

DOI:
10.1002/cssc.200800068

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
2008

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):
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Dye-sensitized solar cells (DSSCs) based on nanocrystalline semiconductors have been the subject of intense investigation owing to their potential low cost, easy processing and good performance.[1] In these cells, a dye monolayer is adsorbed on a mesoporous film of titania. Upon light absorption, the dye injects electrons into the TiO₂ conduction band, where they are transported to the anode. The neutral dye is regenerated by electron transfer either from an electrolyte containing a redox system or from a solid-state hole conductor. With a closed external circuit and under illumination, the device then constitutes a photovoltaic energy-conversion system, which is regenerative and stable. In this technology, ruthenium complexes maintained a clear lead in performance amongst the thousands of dyes tested, yielding power conversion efficiencies of 10–11%.[2] However, in view of the cost and availability of 4d metals as well as their environmental non-compatibility, many metal-free organic dyes have been developed.[3]

As metal-free dyes, perylene derivatives have been widely applied in various optical devices owing to their outstanding chemical, thermal and photochemical stability and non-toxicity.[4] Several perylene dyes have been used as sensitizers in DSSCs, however, they exhibited very low overall power conversion efficiencies (η = 1–2%).[5] Recently, we reported diphenylamino-substituted perylene monoanhydrides as sensitizers which show an improved efficiency of up to 3.9%.[6] Herein, we present a novel perylene molecule 5 that bears two thiophenol groups in the 1 and 6 positions (see Scheme 1 and Experimental Section). Substituents at the 1 and 6 positions in perylene tune the HOMO and LUMO energies and thereby the absorption wavelength of the molecule. Another aspect of introducing (bulky) side groups is their ability to suppress dye aggregation on TiO₂ resulting in more efficient electron injection.[7] In this type of molecule, light absorption is associated with an intramolecular charge transfer (ICT) excitation from the donor to the acceptor moiety of the dye, which is anchored to the surface of the TiO₂, resulting in efficient electron transfer from the excited dye into the TiO₂ conduction band.

Figure 1 shows the UV/Vis absorption spectra of 5 measured in CH₂Cl₂ solution and adsorbed on a TiO₂ electrode. The solution absorption spectrum of 5 shows two peaks at λ = 620 nm (ε = 22 727 M⁻¹ cm⁻¹) and at 462 nm (ε = 13 704 M⁻¹ cm⁻¹). From time-dependent density functional theory (DFT) calculations[8] at the B3LYP/TZVP level,[9,10] the first excitation (predicted at λ = 639 nm) corresponds to the ICT from the HOMO located mainly on the diphenylamino group to the LUMO (π*) located.

Scheme 1. Synthesis of 5. 1) Br₂, chloroform, reflux, 6 h, 86%; 2) thiophenol, K₂CO₃, NMP, RT, 3 h, 56%; 3) dip(tert-octylphenyl)amine, [Pd₂(ACTU NGL)₃], P(tBu)₃, tBuONa, overnight, 83%; 4) KOH, isopropanol, overnight, 80%. (dba = dibenzylideneacetone.)

Figure 1. Normalized UV/Vis absorption spectra of 5 in dichloromethane (solid line) and adsorbed on a noncrystalline 6-μm transparent TiO₂ film (dashed line).
mainly on the perylene. The second band (predicted at $\lambda = 473$ nm) is a transition from a mixed thiophenyl-perylene π orbital to the LUMO. When absorbed onto TiO$_2$, compound 5 shows a blue-shifted absorption ($\lambda_{\text{max}} = 506$ nm). This effect is attributed to the ring opening of the anhydride group on the perylene to form two carboxylates, which provide strong chemical interactions with the oxide surface. This phenomenon is well known for perylene anhydride sensitizers.$^{[5,6]}$

Figure 2 shows the cyclic voltammogram$^{[11]}$ of 5 which exhibits reversible waves both in the oxidation and reduction regions, indicating the electrochemical stability of 5, a vital parameter for the durability of solar cells. The HOMO and LUMO are observed at 0.48 V and $-1.08$ V (vs Fc/Fc$^+$), respectively. When the dye adsorbs to TiO$_2$, it undergoes a transition to the dicarboxylate, that is, a ring-opened structure, which results in a negative shift in the HOMO potential. From DFT calculations of the anhydride and the dicarboxylate, we obtain a shift of 0.5 eV in the ionization potential. Also, the optical gap is increased upon ring opening to the dicarboxylate, resulting in an additional negative shift to the injecting excited-state energy level (see above). Hence, the energetic alignment of the HOMO and LUMO of the dye is well suited for electron injection into the TiO$_2$ conduction band as well as regeneration of the oxidized dye.$^{[12]}$

We fabricated complete solid-state dye-sensitized solar cells, where 2,2',7,7'-tetakis(N,N-di-p-methoxyphenylamine)-9,9'-spirobirofluorene (Spiro-MeOTAD) as an organic hole-transporting material replaces the liquid electrolyte. In this setup, interfacial hole transfer from the perylene sensitizer 5 to Spiro-MeOTAD takes place and regenerates the oxidized dye.$^{[12]}$ Figure 4 shows the solid-state solar cell J–V characteristics measured under AM 1.5 solar conditions. At 100 mWcm$^{-2}$, $J_{\text{sc}} = 2.83$ mAcm$^{-2}$, $V_{\text{oc}} = 838$ mV and $FF = 0.75$ and the corresponding power conversion efficiency is 1.78%. The cell demonstrated an almost linear behavior under different light intensities ranging from 9.2 to 99% sun with a slightly higher efficiency (~1.84%) at low intensity.

In summary, we have molecularly engineered a highly efficient novel perylene sensitizer, which yields 87% IPCE and
6.8% power conversion efficiency under standard AM 1.5 solar conditions. We have also demonstrated the possibility to utilize perylenes for solid-state solar cells yielding 1.8% power conversion efficiency under standard illumination conditions. Comparing these results with other perylene sensitizers,[6] we conclude that the thiophenol groups in \( \text{5} \) contribute strongly to the obtained high efficiencies. Work to extend the spectral response of these sensitizers further into the red and near-IR spectral region is in progress.

### Experimental Section

\( \text{N}-(2,6\text{-Diisopropophenyl})\text{-perylen}-3,4\text{-dicarboximide (1)} \) was supplied by BASF-SE (Ludwigshafen). \( \text{Diisoprop-tert-octylyphenylamine} \) was purchased from MP Biomedicals Inc. All other starting materials and catalysts were purchased from Aldrich, Acros or ABCR and used as received.[1]

Synthesis of \( \text{5} \): Compound \( \text{2} \) (1 g, 1.4 mmol), thiophenol (153 mg, 1.4 mmol) and potassium carbonate (128 mg, 1.4 mmol) were stirred in \( \text{N} \)-methylpyrrolidone (NMP, 80 mL) at room temperature. After 1.5 h, additional thiophenol (76 mg, 0.6 mmol) and potassium carbonate (128 mg, 1.4 mmol) were added to the reaction mixture, which was stirred at the same temperature for another 1.5 h. After cooling to room temperature, the reaction mixture was precipitated and washed with water and dried. The product was purified by column chromatography on silica gel using dichloromethane and pentane (1:4) as eluent to give a dark red solid (600 mg, 56%).

Synthesis of \( \text{5} \): A mixture of \( \text{1} \) (300 mg, 0.28 mmol), potassium hydroxide (500 mg, 9 mmol) and isopropanol (50 mL) was refluxed under stirring overnight. The reaction mixture was cooled down to room temperature and then poured into acetic acid, and the solution was stirred at \( \text{40}^\circ \text{C} \) for \( \text{4} \) h. The solvent was removed in vacuum. The crude product was washed with water. Column chromatography using toluene as eluent on silica yielded \( \text{5} \) as a green solid (0.3 g, 80%).

Electrochemical experiments were carried out with an EG&G Princeton Applied Research potentiostat model 273. The working electrode consisted of an inlaid platinum disk (1.5-mm diameter) that was polished on a felt pad with alumina (0.05 \( \mu \)m) and sonicated in milli-Q water for 5 min before each experiment. A platinum wire was used as the counter electrode, and an Ag wire was used as the reference electrode internally calibrated with ferrocene/ferroenium (Fc/Fc+) in the measurement.

Dye-sensitized solar cells: The photoanodes composed of nanocrystalline \( \text{TiO}_2 \) were prepared using a previously reported procedure.[16] A paste composed of 20-nm anatase \( \text{TiO}_2 \) particles for the...
transparent nanocrystalline layer was coated on FTO glass plates (Nippon Sheet Glass, 4 mm thickness) pretreated with TiCl4 (40 mm) by repetitive screen printing to obtain a thickness of 6 μm. Then, a paste for the scattering layer containing 400-nm-sized anatase particles (CCIC, HPW-400) was deposited onto the transparent nanocrystalline layer. The resulting layer had a thickness of around 4 μm. The TiO2 electrodes were gradually sintered under a programmed flow: at 325 °C for 5 min, at 375 °C for 5 min, at 450 °C for 15 min and finally at 500 °C for 15 min. The TiO2 electrodes were treated again by TiCl4 under 70 °C for 30 min and sintered again at 500 °C for 30 min before they were dipped into dye solution. The TiO2 electrodes were immersed into the solutions of 5 (150 μm) in chlorobenzene and kept at room temperature for 16–18 h. The dye-adsorbed TiO2 electrode and thermally platinized counter electrode were assembled into a sealed sandwich-type cell with a gap of a hot-melt ionomer film (Surlyn, thickness 1702. 25 μm, DuPont). An electrolyte solution (0.6 μL 1-butyl-3-methylimidazolium iodide, 0.05 μL iodine, 0.1 μL LiI and 0.5 μL tert-butylpyridine in 15:85 (v/v) valeronitrile/acetonitrile) was used for the redox electrolyte. The resulting layer had a thickness of around 4 μm.

We gratefully acknowledge financial support from the German Science Foundation SFB 625, Korean–German IRTG and Korean–Swiss GBL.

Acknowledgements

We gratefully acknowledge financial support from the German Science Foundation SFB 625, Korean–German IRTG and Korean–Swiss GBL.

Keywords: dye-sensitized solar cells · fused-ring systems · photoelectrochemical cells · sensitizers


[11] a) The cyclic voltammograms (CVs) were measured in a solution of Bu4NPF6, (0.1 M) in dry dichloromethane with a scan rate of 50 mV/s. at room temperature under argon.


Received: March 3, 2008
Revised: April 16, 2008
Published online on June 6, 2008