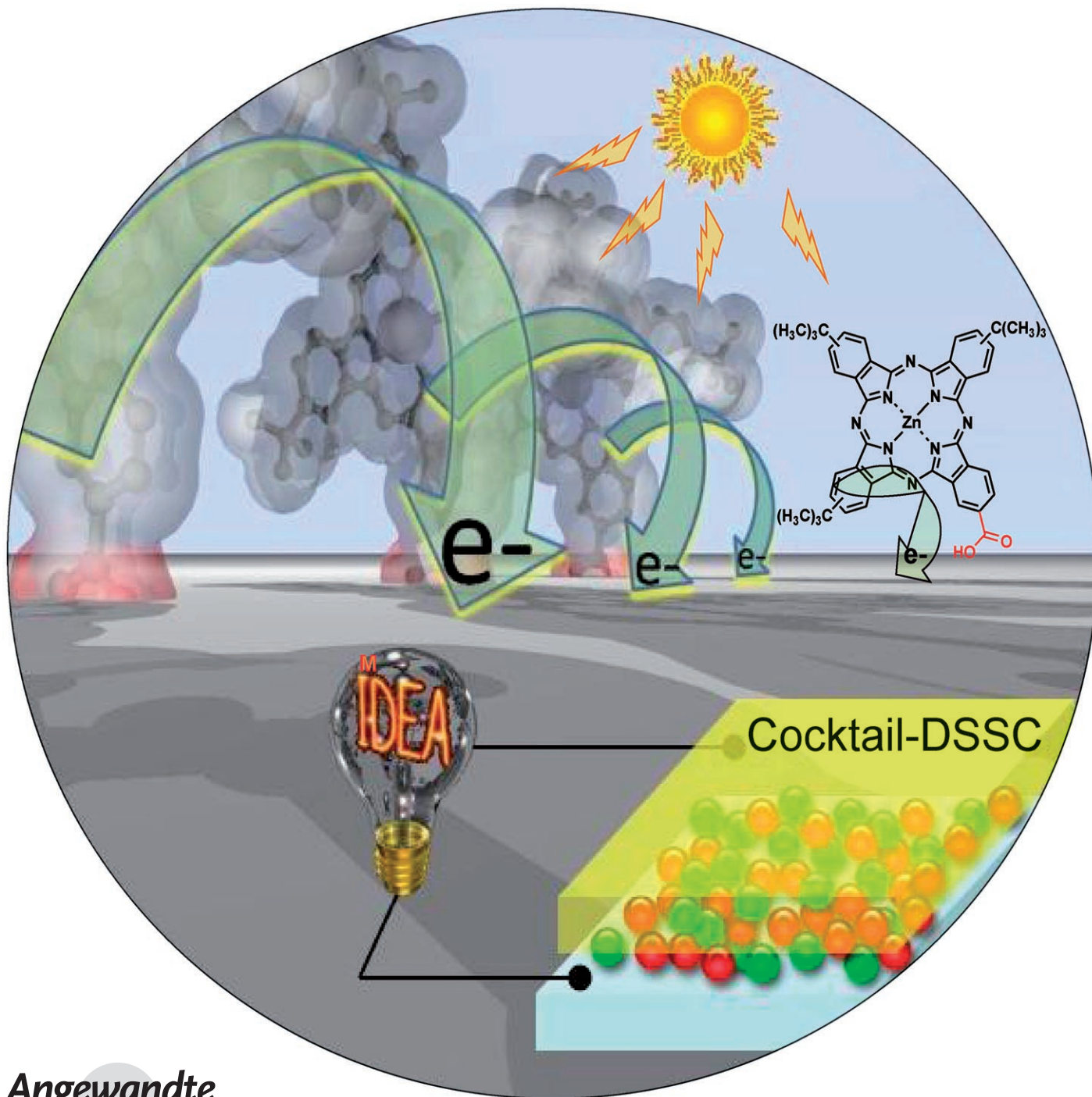


Molecular Cosensitization for Efficient Panchromatic Dye-Sensitized Solar Cells**

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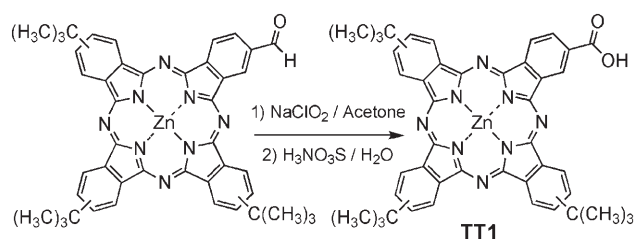
Molecular photovoltaic devices with extended absorption in the near-IR region of the spectrum are currently a hot topic in the area of solar cells. In the case of plastic (“all organic”) photovoltaic devices,^[1] the synthesis of stable low-band-gap polymers for efficient light-to-electricity conversion is a major challenge, and more efficient absorbing dyes are sought for dye-sensitized TiO₂ solar cells (DSSCs).^[2] Phthalocyanines (Pcs)^[3] exhibit very high extinction coefficients around 700 nm (where the maximum solar photon flux occurs) for efficient photon harvesting, and redox features that make them especially suitable for integration in light-energy conversion systems.^[3a,4a] During the last few years we have focused our attention on constructing multifunctional Pc-based donor–acceptor hybrids in which the complementary electroactive constituents are connected through a variety of covalent or supramolecular junctions.^[4]

Previous work on zinc phthalocyanines showed that the control over the formation of molecular aggregates onto the semiconductor nanoparticles was key to achieve moderate efficiencies. However, it was not sufficient to explain the low incident photon to current conversion efficiencies (IPCE) observed (generally no higher than 45 % at the maximum absorbance of the Q band, typically $\lambda = 700$ nm). We recently reported^[5] that the use of a tri-*tert*-butyl-substituted zinc phthalocyanine not only avoids the formation of molecular aggregates but also arranges the excited states to permit directionality of the charge transfer from the LUMO (lowest unoccupied molecular orbital) of the dye to the Ti 3d orbital

and, therefore, optimizes the photocurrent of the device with efficiencies exceeding 3 % at 1 sun.

Herein, we would like to stress another important property of phthalocyanines: as well as providing excellent absorption in the near-IR region, their UV/Vis spectra contain an optical window in the visible region that could allow their use in combination with an appropriate dye to achieve panchromatic sensitization of the mesoporous photoelectrode and increase the device efficiency. Several groups have already attempted this challenge by combining two or more dyes in “molecular cocktails” using ionic interactions, as well as supramolecular and materials chemistry.^[6] However, molecular cosensitization using phthalocyanines has often resulted in an unimpressive power conversion or, in the worse case, lower efficiency than those of single-dye devices.

To challenge this target, we synthesized a novel zinc carboxyphthalocyanine (**TT1**), which has a carboxy group linked directly to the Pc ring and incorporates all the desired properties mentioned above. This compound was prepared in 78 % yield by oxidation of the corresponding aldehyde^[4b,7] with sodium chlorite in the presence of sulfamic acid (a chlorine scavenger)^[8] (Scheme 1; for more details see the Experimental Section).^[9] Spectroscopic data are given in the Supporting Information.



Scheme 1. Synthesis of carboxyphthalocyanine **TT1**.

The presence of *tert*-butyl groups not only minimizes the formation of molecular aggregates but also increases the solubility of **TT1** in organic solvents and, owing to their push–pull character, induces directionality in the excited state of the zinc phthalocyanine. The visible absorption spectrum of **TT1**/TiO₂ shows a maximum at 680 nm, which is in good agreement with that of the sample in solution (Figure 1) and implies a low degree of molecular aggregation onto the nanoparticle surface. Time-correlated single photon counting (TCSPC) has been employed to estimate the electron-injection yield of **TT1** on the mesoporous semiconductor. The transient luminescence studies confirmed efficient electron injection for the **TT1**-sensitized TiO₂ films. As illustrated in Figure 2, the excited-state lifetime of **TT1** adsorbed onto mesoporous metal oxide films is extremely short ($\tau_1 = 1.1$ ns (81.4 %) and $\tau_2 = 2.8$ ns (18.6 %) relative to that of the solution sample ($\tau_1 = 4$ ns (40.5 %) and $\tau_2 = 2.8$ ns (59.5 %)). In fact, in our experimental setup with an instrument response time of 250 ps, it was difficult to resolve properly the kinetics for **TT1**/TiO₂. However, an injection yield of more than 80 % was measured by comparing the signal intensity between **TT1**/Al₂O₃ and **TT1**/TiO₂ for a constant acquisition time.

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[**] This work has been supported by the Spanish MEC (CTQ-2005-08933-BQU, CONSOLIDER-INGENIO NANOMOL 2010 C-07-25200), and CONSOLIDER HOPE CSD 2007-0007, the Comunidad de Madrid (S-0505/PPQ/000225), the EU (STRP 516982, HETEROMOLMAT, and the ESF-MEC (MAT2006-28180-E, SOHYDS). E.M.F. and E.P. acknowledge the Spanish MEC for the Juan de la Cierva and the Ramon y Cajal fellowship, respectively.

Supporting information for this article is available on the WWW under <http://www.angewandte.org> or from the author.

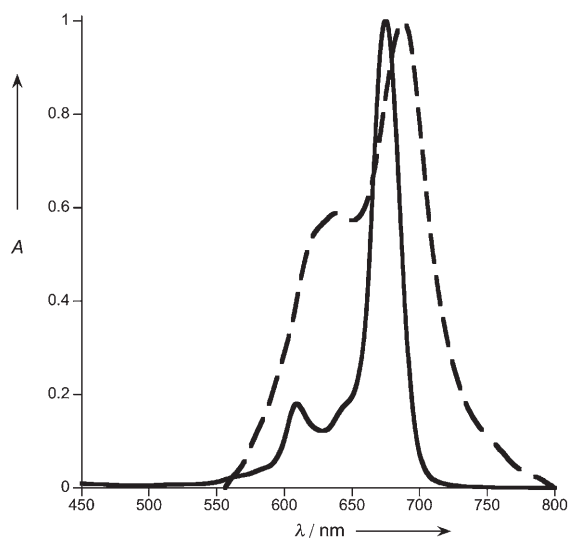


Figure 1. Visible absorption spectra of **TT1** in ethanol (1×10^{-6} M, solid line) and adsorbed on a transparent 4- μm -thick mesoporous TiO_2 film (dashed line).

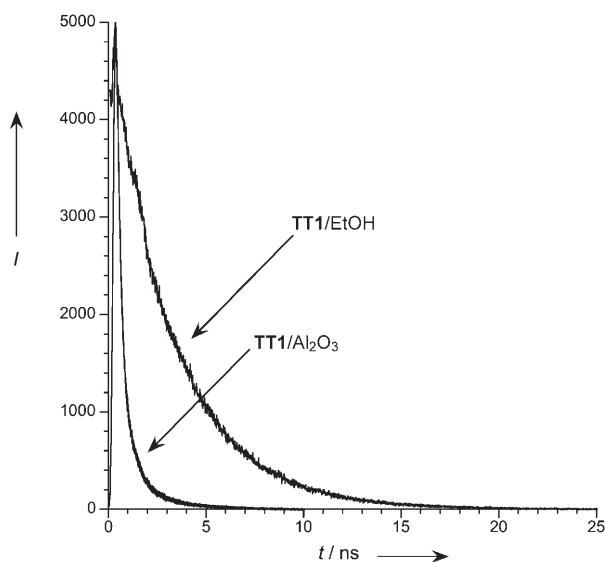


Figure 2. Time-correlated single photon counting measurements for **TT1** in EtOH (1×10^{-6} M) with chenodeoxycholic acid (2×10^{-4} M) and on an Al_2O_3 film ($\lambda_{\text{ex}} = 635$ nm, $\lambda_{\text{em}} = 695$ nm).

To investigate the electron-transfer recombination kinetics, we also carried out laser transient-absorption spectroscopy (see the Supporting Information) on the **TT1**/ TiO_2 samples. The measured recombination lifetime was $\tau_{\text{rec}} = 3.2$ ms, which is of the same order of magnitude as that of the standard ruthenium dye used for efficient DSSC devices (**N719**; see the Supporting Information).

We then turned to the efficiency of devices using **TT1**. For the cell fabrication, a 10- μm -thick layer of transparent mesoporous TiO_2 with 4- μm -thick layer of scattering mesoporous TiO_2 was prepared and treated with a 40 mM solution of titanium tetrachloride according to a previously reported procedure.^[2c] The films were heated at 500 °C in air and

calcined for 30 min before use. **TT1** solutions were prepared in ethanol at a concentration of 0.05 mM with 10 mM chenodeoxycholic acid (Cheno) (see the Supporting Information). The films were immersed into the dye solution for 4 h at room temperature, rinsed with ethanol to remove any unadsorbed dye, and then used as such for photovoltaic measurements in completely sealed devices. Figure 3 shows the IPCE and the I/V (current–voltage) curve for the **TT1**/ TiO_2 cell.

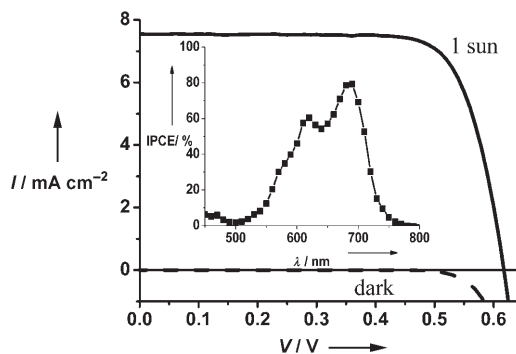


Figure 3. IPCE spectrum (inset) and I/V curve of a **TT1**/ TiO_2 DSSC with an active area of 0.2 cm^2 .

The **TT1** DSSC shows an impressive efficiency under simulated solar irradiation (1 sun = 100 mW cm^{-2} 1.5 air mass global) of 3.52% with a short-circuit current I_{sc} of $7.60 \pm 0.20 \text{ mA cm}^{-2}$, an open-circuit voltage (V_{oc}) of 617 ± 20 mV, and a fill factor (FF) of 0.75 ± 0.02 . As far as we know this is the highest efficiency ever reported for a zinc phthalocyanine TiO_2 DSSC. The IPCE at the maximum absorption of the Q band reaches 80%, and curve integration over the solar spectrum gives a short-circuit current I_{sc} of 7.4 mA cm^{-2} , which is in agreement with the measured device photocurrent.

As mentioned in the introduction, the use of phthalocyanines allows us to introduce a secondary dye that complements the absorption spectra by matching the optical window of the phthalocyanine between 400 and 550 nm. Figure 4 shows the IPCE spectrum of a cosensitized DSSC containing the previously reported organic dye **JK2** (see the Supporting Information) and **TT1**. The cell comprises a double layer of 10- μm -thick mesoporous TiO_2 and 4- μm -thick scattering TiO_2 . The film was sensitized for 1 h and 3 h with solutions

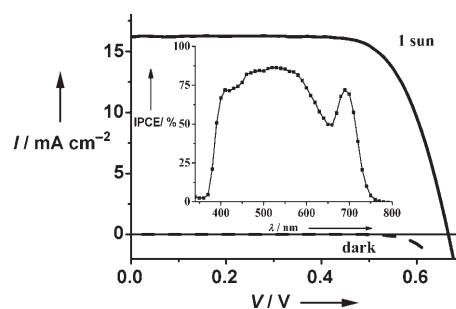


Figure 4. IPCE spectrum (inset) and I/V curve of a **JK2**/**TT1**/ TiO_2 DSSC with an active area of 0.2 cm^2 .

of **JK2** and **TT1**, respectively. The photoresponse of the “molecular cocktail” extends up to 700 nm with photon-to-electron conversion efficiencies of 72% at 690 nm, which corresponds to the Q band of **TT1**. The overall device efficiency one day after the preparation of the device was 7.74%, and values of I_{sc} of $16.20 \pm 0.20 \text{ mA cm}^{-2}$, V_{oc} of $666 \pm 30 \text{ mV}$, and FF of 0.72 ± 0.03 were obtained. Neither **JK2** nor **TT1** devices could reach such efficiencies as a single-dye solar cell. Under our experimental conditions, **JK2/TiO₂** devices showed an efficiency of 7.08%, which is in agreement with previously published results. We believe that such results represent a clear advance towards efficient cosensitized DSSCs based on systems with extended spectral response in the near IR region.

In conclusion, we have demonstrated the efficient electron injection of zinc phthalocyanine, which yields 80% IPCE at 690 nm, and a record efficiency for near-IR DSSCs of 3.52% under standard illumination conditions. Moreover, we have also illustrated the possibility of efficiently combining two dyes with complementary spectra to achieve higher efficiencies than could be achieved with each separate dye, by taking advantage of the optical properties of the zinc phthalocyanine. We hope that our findings will motivate other groups to explore the molecular cosensitization on molecular photovoltaics to achieve the desired “full-spectrum” solar cell.

Experimental Section

Chemicals were purchased from Aldrich Chemical Co. and used as received. UV/Vis spectra were recorded with a Hewlett-Packard 8453 instrument. The FTIR spectrum was recorded on a Bruker Vector 22 spectrophotometer. The MALDI-TOF mass spectrum was obtained from a BRUKER REFLEX III instrument equipped with a nitrogen laser operating at 337 nm. The NMR spectrum was recorded with a BRUKER AC-500 instrument. Elemental analysis was performed with a Perkin-Elmer 2400 CHN equipment. Column chromatography was carried out on reverse-phase silica gel (Merck, LiChroprep RP-18, 25–40 μm). Monitoring of the reaction was carried out by TLC on aluminum sheets precoated with reverse-phase silica gel (RP-18 F254S).

9(10),16(17),23(24)-Tri-*tert*-butyl-2-carboxy-5,28:14,19-diimino-7,12:21,26-dinitrilotetrabenzo[*c,h,m,r*][1,6,11,16]tetraazacycloicosinato-(2⁻)-*N*²⁹,*N*³⁰,*N*³¹,*N*³² zinc (II) (mixture of regioisomers) (**TT1**): NaClO₂ (47 mg, 0.50 mmol) was added in a few portions to a vigorously stirred solution of 9(10),16(17),23(24)-tri-*tert*-butyl-2-formyl-5,28:14,19-diimino-7,12:21,26-dinitrilotetrabenzo[*c,h,m,r*][1,6,11,16]tetraazacycloicosinato-(2⁻)-*N*²⁹,*N*³⁰,*N*³¹,*N*³² zinc (II) (mixture of regioisomers)^[7] (130 mg, 0.17 mmol) cooled to 0 °C in acetone (96 mL). Then, a solution of sulfamic acid (51 mg, 0.50 mmol) in Milli-Q-grade deionized water (12 mL) was added immediately in one portion. The reaction was allowed to proceed at room temperature for 4 h. After the starting compound disappeared, the solution was poured into aqueous HCl (0.1M, 400 mL) and a blue-greenish solid precipitated. The solid was filtered over celite and washed with water and mixtures of water/MeOH (3:1 and 2:1, 100 mL each). The solid was dried under vacuum and extracted with THF. The solvent was evaporated and the crude product was triturated in hexane, filtered, and washed with a cold solution of water/MeOH (1:1, 50 mL) and finally with MeOH (25 mL). In this way, carboxyphthalocyanine **TT1** (103 mg, 0.13 mmol) was obtained as a dark-blue solid (yield 78%). Further purification can be accomplished on a chromatographic column (reverse phase) employing water/THF (2:1) as the

carrier phase. M.p. > 250 °C; ¹H NMR (500 MHz, [D₆]DMSO, 25 °C, TMS): δ = 13.4 (brs, 1H; COOH), 9.9–8.0 (m, 12H; Pc-H), 1.8 ppm (m, 27H; C(CH₃)₃); IR (KBr): $\bar{\nu}$ = 3484 (m; ν_{str} (COO–H) free monomer), 2955–2865 (s; ν_{str} (COO–H) associated dimer), 2953, 2828 ν_{str} (C–H), 1697 (s; ν_{str} (C=O)), 1612 (s), 1484 (s), 1394 (s), 1364 (s), 1323 (s), 1281 (s), 1256 (s), 1192 (s), 1139 (s), 1081 (vs), 1046 (vs), 924 (m; ν_{s} (OC–OH)), 833 (m), 745 (s), 728 (w), 689 cm^{-1} (w); UV/Vis (THF): λ_{max} (ϵ) = 680 (160000), 668 (160000), 606 (32000), 350 nm (80000); MS (MALDI, dithranol): m/z (%): 788–796 (100) [$M+H^+$]; elemental analysis calcd (%) for C₄₅H₄₀N₈O₂Zn (790.24): C 68.40, H 5.10, N 14.18; found C 68.31, H 5.19, N 14.40.

Dye-sensitized solar cells: Photoanodes were prepared using a previously reported procedure.^[5] TiO₂ electrodes were immersed into the **TT1** solutions (50 μM in EtOH with 10 mM of chenodeoxycholic acid) and kept at room temperature for 4 h. For molecular cocktail cells, the TiO₂ electrodes were immersed into **JK2** solution (0.5 mM in THF with 1 mM chenodeoxycholic acid) and **TT1** solution for 1 and 3 h, sequentially. An electrolyte solution (0.6M 1-butyl-3-methylimidazolium iodide, 0.04M iodine, 0.025M LiI, 0.05M guanidinium thiocyanate, and 0.28M *tert*-butylpyridine in a 15:85 (v/v) mixture of valeronitrile and acetonitrile) was used for the redox couple. The photovoltaic measurements of the DSSCs were carried out as described elsewhere.^[5]

Received: July 11, 2007

Published online: October 2, 2007

Keywords: dyes/pigments · phthalocyanines · sensitizers · solar cells · zinc

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