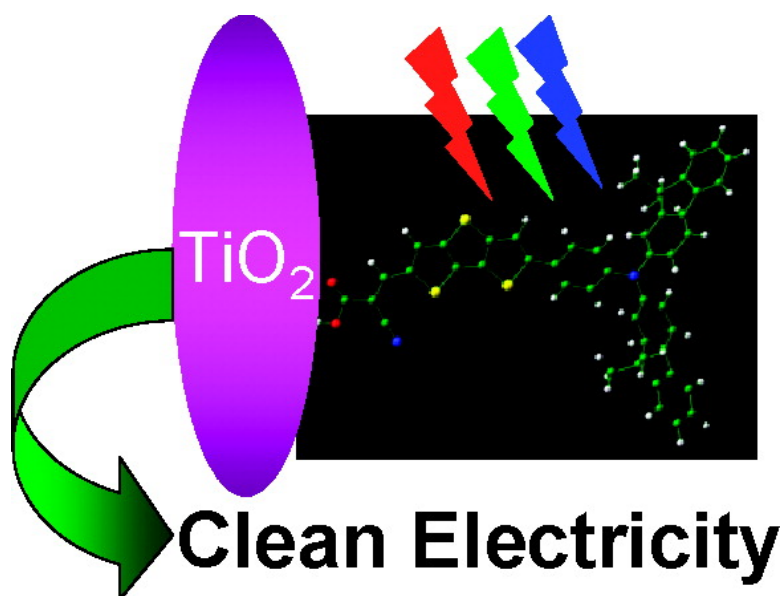## Communication

An Organic Sensitizer with a Fused Dithienothiophene Unit for Efficient and Stable Dye-Sensitized Solar Cells

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An Organic Sensitizer with a Fused Dithienothiophene Unit for Efficient and Stable Dye-Sensitized Solar Cells

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A sensitizer, as the light-harvesting component in a dye-sensitized solar cell (DSC), is of paramount importance to photovoltaic performance. The sensitizer is attached to the surface of a mesoporous wide band-gap semiconductor serving as electron transporter.[1] Until now the record efficiency of the DSC is kept by a polypyridyl ruthenium sensitizer in combination with a highly volatile electrolyte.[2] For commercial applications it is necessary to employ nonvolatile or even solvent-free electrolytes. However, with a low fluidity electrolyte the charge collection yield becomes low because of the shortened electron diffusion length. Enhancing the optical absorptivity of a stained mesoporous film can counter this effect. Thus, the development of a high molar extinction coefficient organic dye seems to be an ideal choice.[3] In this context, an impressive device efficiency up to 9% has been reached by employing an indoline dye along with an acetonitrile-based electrolyte.[4] Unfortunately, our preliminary testing shows that it is hard to make a long-term stable device mainly due to a desorption of the indoline dye from TiO$_2$ nanocrystals even in combination with several state-of-the art stable electrolytes. Inspiringly, a stable device showing ~6% efficiency has been achieved with a fluorene[5] or coumarin[6] dye.

With a motivation to eliminate the dye desorption during the long-term device operation, here we design and synthesize a novel organic sensitizer coded C203 and shown in Figure 1. Because of the fused dithienothiophene unit it has a low free energy of solvation in the high polarity electrolytes normally used by DSC. This sensitizer was synthesized in three steps as depicted in the Supporting Information. The Suzuki coupling of *N,N*-bis(9,9-dimethylfluoren-2-yl)-4-bromoaniline and (dithieno[3,2-*b*;2′,3′-*d*]thiophen-2-yl)boronic acid produced 6-[*N,N*-bis(9,9-dimethylfluoren-2-yl)phenyl]dithieno[3,2-*b*;2′,3′-*d*]thiophene, which was converted into its corresponding carbaldehyde via the Vilsmeier–Haack reaction. The aldehyde was condensed with cyanoacetic acid by means of the Knoevenagel reaction in the presence of piperidine to form the target compound.

Square-wave voltammetry in combination with the ultramicro-electrode technique was employed to measure the redox potentials of the sensitizer in a nitrogen-filled glovebox. The negative offset of the measured LUMO (−0.762 V) of C203 relative to the conduction band edge (−0.5 V) of TiO$_2$ provides a suitable thermodynamic driving force for electron injection even considering the typical exciton binding energy of organic dyes.

As shown in Figure S1, in the positive potential range the average value of well-defined anodic and cathodic peaks for the C203 dye
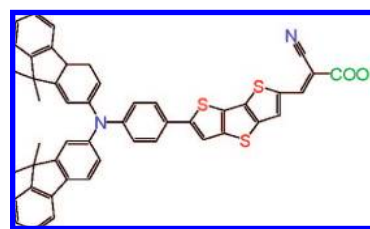

Figure 1. Molecular structure of the C203 sensitizer.

in DMF solution is 0.987 V versus normal hydrogen electrode (NHE), which is 0.451 V higher than that of the iodide/triiodide redox couple in electrolytes, guaranteeing an ample driving force for efficient dye regeneration.

The electronic absorption and emission spectra of the C203 dye in chloroform are shown in Figure S2. While the trivial ultraviolet absorption for DSC with a molar extinction coefficient (ε) of 50.0 × 10^3 M^{-1} cm^{-1} peaks at 372 nm, the ε value of its low energy band at 525 nm (mainly stemming from the intramolecular charge-transfer transition) is 44.8 × 10^3 M^{-1} cm^{-1}. As presented in the Supporting Information, the origins of these absorptions are detailed by calculating the singlet electronic transition with the ZINDO/S method in the Gaussian 03W program suite. We have further noted that in contrast to the insensitivity of the high-energy absorption band, the charge transfer absorption of the deprotonated C203 dye is ~70 nm blue-shifted owing to the weakened electron-withdrawing strength of carboxylate compared to carboxylic acid. The emission of C203 is centered at 718 nm and the excitation transition energy (E_{0-0}) was estimated to be 2.04 eV.

Some preliminary photovoltaic experiments were conducted to evaluate the performance of the C203 dye using a voltatile acetonitrile-based electrolyte and a stable solvent-free ionic liquid electrolyte, respectively. The electrolyte compositions were as follows: (device A) 1.0 M 1,3-dimethylimidazolium iodide, 0.05 M LiI, 0.1 M guanidinium thiocyanate, 0.03 M I$_2$, and 0.5 M *tert*-butylpyridine in the mixture of acetonitrile and valeronitrile (85/15, *v*/*v*); (device B) 1,3-dimethylimidazolium iodide/1-ethyl-3-methylimidazolium iodide/1-ethyl-3-methylimidazolium tetracyanoborate/iodine/*N*-butylbenzoimidazole/guannidinium thiocyanate (molar ratio, 12/12/16/1.67/3.33/0.67). The standard mesoporous double-layer titania film[7] was employed. A 7 μm thick film of 20-nm-sized TiO$_2$ particles was first screen-printed on a fluorine-doped SnO$_2$ (FTO) conducting glass electrode, and a 4 μm thick second layer of 400-nm-sized light scattering anatase particles was subsequently coated onto the first one. The TiO$_2$ electrode was derivatized by immersing it into a dye solution containing 300 μM C203 and saturated 3α,7α-dihyroxy-5β-cholanic acid in chloroben-
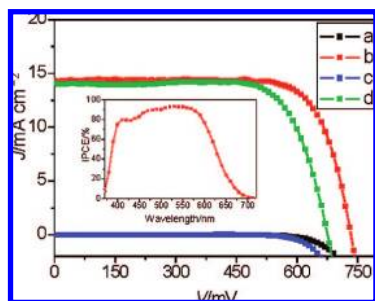
Figure 2. $J-V$ characteristics measured in the dark and under the illumination of AM 1.5G full sunlight (100 mW cm^{-2}): (a) device A in the dark; (b) device A under light; (c) device B in the dark; (d) device B under light. The inset is the photocurrent action spectrum of device A. Cells were tested using a metal mask with an aperture area of 0.159 cm^2.

zene at room temperature for ~5 h. A platinized FTO conducting glass was used as counter electrode. The two electrodes were separated by a 25 μm thick Surlyn hot-melt gasket and sealed up by heating. The internal space was filled with the above-mentioned electrolytes using a vacuum back filling system. The electrolyte-injecting hole made by an ultrafine sandblaster on the counterelectrode glass substrate was sealed with a Bynel sheet and a thin glass cover by heating.

The photocurrent action spectrum of device A with C203 as sensitizer is shown in the inset of Figure 2. The incident photon-to-collected electron conversion efficiency (IPCE) exceeds 80% from 410 to 590 nm, reaching the maximum of 93% at 530 nm. Considering the light absorption and scattering loss by the conducting glass, the maximum efficiency for absorbed photon-to-collected electron conversion efficiency (APCE) is unity over a broad spectral range. As shown in Figure 2, the short-circuit photocurrent density (J_{sc}), open-circuit photovoltage (V_{oc}), and fill factor (FF) of device A with an acetonitrile-based electrolyte under an irradiance of AM 1.5G full sunlight are 14.33 mA cm^{-2}, 734 mV, and 0.76, respectively, yielding an overall conversion efficiency (η) of 8.0%. More importantly, the photovoltaic parameters (J_{sc}, V_{oc}, FF, and η) of device B with a solvent-free ionic liquid electrolyte are 14.06 mA cm^{-2}, 676 mV, 0.74, and 7.0%, respectively. It is encouring that there is a negligible photocurrent difference between these two devices, proving for the first time that the dilemma between optical absorption and charge diffusion lengths can be overcome via the rational molecular engineering of a high molar extinction coefficient organic sensitizer. The positive-shifted conduction band-edge of the sensitized titania film[8] and the calculated 17 mV negative-shifted equilibrium potential of the electrolyte in device B together explain its measured lower V_{oc} in contrast to that of device A. We are now systematically optimizing the compositions of ionic liquid electrolytes to target this issue for the further enhancement of device efficiency.

To lower the cost of photovoltaic power production, a substantial improvement in the DSC efficiency is still necessary. Nevertheless, stable, low-cost, flexible, and lightweight solar cells based on plastic matrix are attractive even if their solar conversion efficiencies are moderate, that is, in the 5 to 9% range. However for these devices, the use of organic solvents is undesirable, as they would permeate across polymeric cell walls. As shown in Figure 3, device B with a solvent-free ionic liquid electrolyte has an excellent light soaking
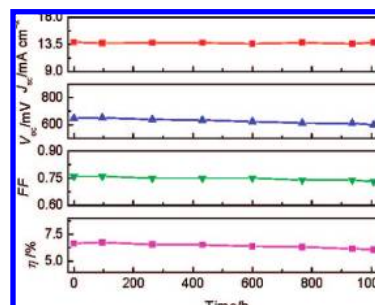

Figure 3. Detailed photovoltaic parameters of device B with a solvent-free ionic liquid electrolyte measured under the irradiance of AM 1.5 G sunlight during successive one sun visible-light soaking at 60 °C.

stability at 60 °C. After a 1000 h aging test, device efficiency only changed from 6.7 to 6.1% due to a 47 mV drop of V_{oc} while there was no change of J_{sc}. Apart from the intrinsic stability of the electrolyte, such an impressively stable performance implies the robustness of C203 itself and the titania/dye/electrolyte interface.

In summary, we have synthesized a high molar extinction coefficient organic sensitizer for high performance dye-sensitized solar cells. In combination with a solvent-free ionic liquid electrolyte, we have demonstrated a ~7% cell with an organic dye showing an excellent stability measured under the thermal and light-soaking dual stress. This work has also proved that enhancing the optical absorption length of stained mesoscopic TiO$_2$ film is a feasible strategy to realize a high efficiency DSC with a solvent-free ionic liquid electrolyte.

Supporting Information Available: Details on synthesis, characterization, and calculation. This material is free of charge via the Internet at http://pubs.acs.org.

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