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A Novel Organic Sensitizer Combined with a Cobalt Complex Redox Shuttle for Dye-Sensitized Solar Cells

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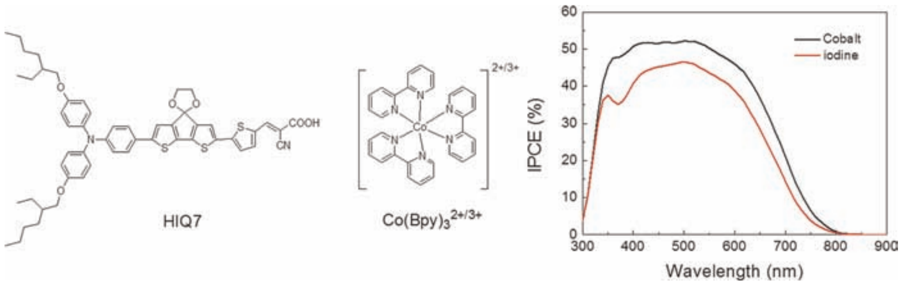
ABSTRACT



A novel donor-π-acceptor organic dye (HIQ7) was used in dye-sensitized solar cells with a cobalt redox shuttle. The cells showed broad incident monochromatic photon-to-current conversion efficiency spectra covering the entire visible range and extending into the near-infrared region.

Dye-sensitized solar cells (DSCs) have been the subject of much academic and industrial research, owing to their potential use for low-cost production of renewable energy and in large-area, flexible, colorful, lightweight devices.[1] Recently, a certified energy conversion efficiency (η) of 11.4% was achieved under standard AM 1.5 conditions with DSCs based on ruthenium sensitizers.[2] Because of the limited availability of ruthenium, ruthenium-free organic dyes based on the donor-π-bridge-acceptor (D-π-A) configuration have attracted attention over the past decade.[3]

Almost all reported high-efficiency DSCs (η > 10%) have used a iodide/triiodide redox shuttle to regenerate the oxidized dye.[4] However, the cells generate only a limited open-circuit voltage (V_{oc}) of 0.7–0.8 V because the redox potential of iodide ions is too low for most sensitizing dyes, even though the dyes have a relatively large energy gap. Energy loss during the regeneration process is large. Moreover, the iodide/triiodide system is limited by the corrosiveness of iodide/triiodide and by competitive absorption of light by triiodide. To overcome these limitations and increase conversion efficiency, researchers have recently explored new redox species possessing higher redox potentials than iodide ions, such as iron-, cobalt-, and copper-based complexes.[5] Among them, divalent/trivalent cobalt bipyridine complexes exhibit impressive performance in

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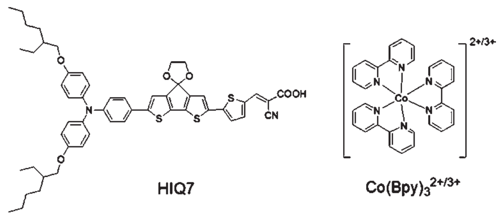
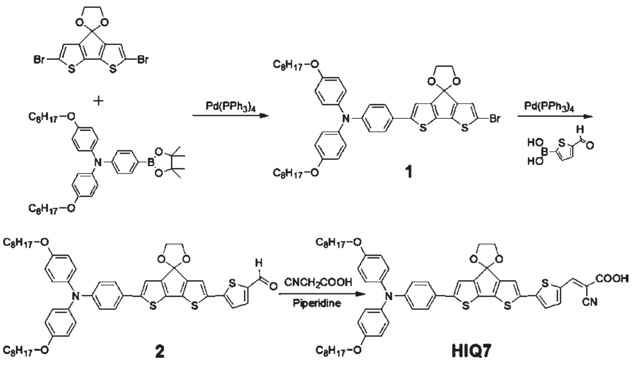


Figure 1. Chemical structures of dye **HIQ7** and cobalt complex.

DSCs sensitized with organic D-π-A dyes.[6] A state-of-the art DSC that combines a porphyrin dye and a cobalt electrolyte and exhibits conversion efficiencies exceeding 12% was reported in late 2011.[7] However, the absorption spectra and the incident monochromatic photon-to-current conversion efficiency (IPCE) spectra of the DSC did not extend into the near-infrared (NIR) region. Thus, the development of new sensitizers with broad absorption spectra and energy levels matched with the cobalt complex redox system is necessary for higher efficiency. Herein, we report a novel D-π-A sensitizer (**HIQ7**, Figure 1) based on 4,4-ethylenedioxy-4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophen, which exhibited broad absorption (extending into the NIR region) on a TiO_2 film and was employed successfully in combination with a cobalt complex redox shuttle for DSCs.

Feldt and co-workers reported that the key to making efficient cells is modifying the periphery of the sensitizing dyes and the cobalt complexes with electrically inactive groups with just enough bulk to slow down recombination without blocking the necessary electron transfer processes.[5b] Thus, we designed a dye with the following features: (1) the electron-rich 4,4-ethylenedioxy-4*H*-cyclopenta-[2,1-*b*:3,4-*b*′]dithiophen group to tune the band gap for harvesting a broad spectrum of the sun's radiation, (2) bulky groups on the donor moiety to suppress charge recombination between the injected electron and the redox couple and thus increase V_{oc}, and (3) an electron-donating alkyloxy group to elevate the energy level of the HOMO, which facilitated dye regeneration by the redox shuttle and reduced energy loss during the regeneration process.

Scheme 1. Synthesis Routes of **HIQ7**



HIQ7 was synthesized as follows (Scheme 1). The dye precursor was obtained from two sequential asymmetrical Suzuki coupling reactions[8] of 2,6-dibromo-4,4-ethylene-dioxy-4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophen with 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-*N,N*-bis(4-(ethylhexyloxy)phenyl)aniline and 5-formylthiophen-2-boronic acid, respectively. The resulting precursor was subjected to a Knoevenagel condensation[9] with cyanoacetic acid to afford **HIQ7**, which was characterized by ^1H and ^{13}C NMR, elemental analysis, and HRMS. The obtained dye was a black-red solid that dissolved readily in common organic solvents, such as chloroform, DMF, and methanol.

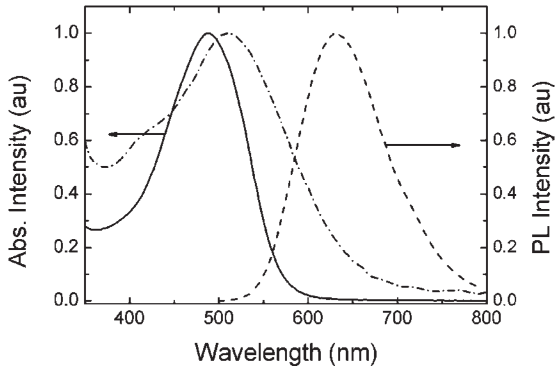


Figure 2. Absorption spectra of **HIQ7** in DMF (line), on TiO_2 (dash dot line) and fluorescence emission spectrum (dash line).

In a DMF solution, **HIQ7** absorbed strongly over the entire visible region (Figure 2), with a peak at 488 nm ($\varepsilon = 4.7 \times 10^4$ M^{-1} cm^{-1}) due to intramolecular charge transfer from the donor moiety to the acceptor moiety. In solution, **HIQ7** exhibited a strong red fluorescence emission around 631 nm. When adsorbed on a transparent TiO_2 electrode, **HIQ7** showed a broadened absorption spectrum, with an absorption peak (at 510 nm) that was strongly red-shifted compared to the corresponding peak in the solution spectrum. The shift was attributed to interaction of the anchoring group with surface titanium anions and the formation of J-aggregates.[10] Moreover, the onset of absorption occurred at about 750 nm, making **HIQ7** a good candidate for an NIR sensitizer for DSCs.

To investigate the thermodynamics of electron injection from the excited state of the dye to the conduction band of the TiO_2 electrode and the thermodynamics of dye regeneration via electron donation from cobalt complex redox couples, we obtained a cyclic voltammogram in a typical three-electrode electrochemical cell with dye-sensitized

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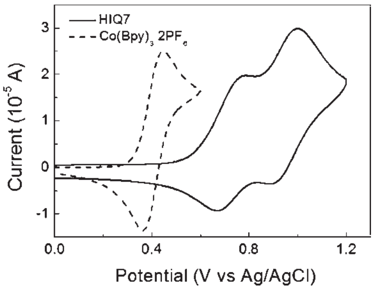

Figure 3. Cyclic voltammograms of the **HIQ7** absorbed on TiO_2 film and $Co(Bpy)_3 \cdot 2PF_6$ in acetone nitrile.

TiO_2 films as the working electrodes and 0.1 M tetra-*n*-butylammonium hexafluorophosphate as the supporting electrolyte (Figure 3). The reference electrode was Ag/AgCl calibrated with ferrocene as an internal reference. **HIQ7** on TiO_2 exhibited two reversible oxidative waves. The ground-state oxidation potential corresponding to the HOMO of **HIQ7** was measured to be 0.95 V (vs Normal Hydrogen Electrode (NHE)), and this value was low enough for efficient regeneration of the oxidized dyes by means of reaction with the redox couples (0.4 V for I^-, 0.56 V for $Co(Bpy)_3 \cdot 2PF_6$ vs NHE).[11] The zero–zero transition energy, which is related to the band gap energy, was determined from the intercept of the normalized absorption and emission spectra (Figure 2). The calculated excited-state oxidation potential (referred to as the LUMO level) was −1.26 V and was much more negative than the conduction band level of TiO_2 (approximately −0.5 V vs NHE), ensuring efficient electron injection from the excited state of the dye to the TiO_2 conduction band. Thus, our 4,4-ethylenedioxy-4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophen-based sensitizer possessed ideal energy levels for use in a cobalt redox system.

To investigate the molecular orbitals and molecular geometries of the dye, we carried out time-dependent density functional theory calculations on **HIQ7** (Figure 4).

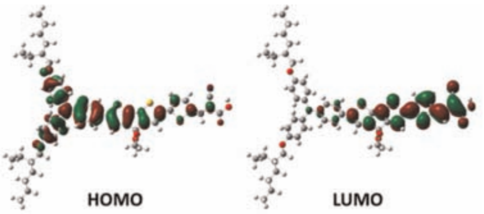

Figure 4. Frontier molecular orbital profiles of **HIQ7** at the B3LYP/6-31G* level.

Molecular orbital calculations demonstrated that the HOMO was largely delocalized over the triphenylamino unit and a portion of the 4,4-ethylenedioxy-4*H*-cyclo-penta-[2,1-*b*:3,4-*b*′]dithiophen moiety. These results suggest that delocalization of the HOMO over the donor moiety may have facilitated reduction of the oxidized dye by reaction with the redox shuttle, making the dye suitable for highly efficient solar cells. The LUMO was located predominantly on the cyanoacrylic unit and extended to the 4,4-ethylenedioxy-4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophen moiety, facilitating electron injection from the photoexcited sensitizer to the TiO_2 semiconductor. HOMO–LUMO excitation moves the electron from the donor moiety to the cyanoacrylic acid moiety via a π-space group. Such electron density distributions are beneficial for efficient charge separation and electron injection.

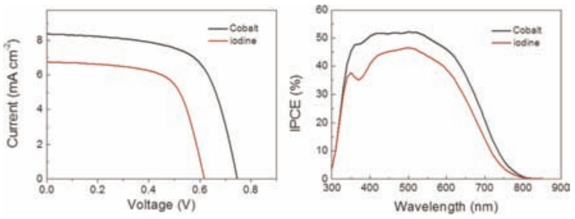

Figure 5. $J-V$ and IPCE curves of DSCs sensitized with **HIQ7** with iodine and cobalt as a redox couple, respectively.

We performed preliminary photovoltaic experiments to evaluate the potential of **HIQ7** as a sensitizer for DSCs. A double-layer TiO_2 photoelectrode (thickness 10 μm; area 0.25 cm^2) was used as a working electrode. A 5 μm main transparent layer with titania particles (~25 nm) and a 5 μm scattering layer with titania particles (~400 nm) were screen-printed on a fluorine-doped tin oxide conducting glass substrate. The TiO_2 film was stained with **HIQ7** by immersion in a 0.3 mM dye solution in *tert*-butanol/acetonitrile (1:1 v/v) for 12 h. The photovoltaic performance of DSCs sensitized with **HIQ7** was studied with two redox shuttles under standard AM 1.5 irradiation (100 mW cm^{-2}). During the measurements, a black metal mask and an edge attached to the active area of the cells were used to avoid inflated photocurrents due to stray light.[12] We used the following electrolyte solutions: 0.6 M dimethylpropylimidazolium iodide, 0.05 M I_2, 0.1 M LiI, and 0.5 M *tert*-butylpyridine (TBP) in acetonitrile; 0.22 M $Co(Bpy)_3 \cdot 2PF_6$, 0.05 M $Co(Bpy)_3 \cdot 3PF_6$, 0.5 M TBP, and 0.1 M $LiClO_4$ in acetonitrile.

The V_{oc} of the **HIQ7** cell with a cobalt redox shuttle was 131 mV higher than that of a cell with an iodine electrolyte system (Table 1), and the increase was ascribed mainly to a 160 mV negative shift of the redox potential of the cobalt complex.[6a] The short-circuit current density (J_{sc}) of the cell with the cobalt electrolyte was 34% higher than that of the

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Table 1. Current−Voltage Characteristics of DSCs Sensitized with **HIQ7** in Different Electrolytes

	J_{sc} [mA cm^{-2}]	V_{oc} [V]	FF	η [%]
cobalt	8.38	0.747	0.648	4.04
iodine	6.24	0.616	0.636	2.44

iodine-based DSC. The increase was ascribed to two factors: (1) competitive light absorption by triiodide, which lowered the IPCE of the iodine system relative to that of the cobalt system (Figure 5); (2) faster recombination between injected electrons in the photoanode and I_3^-, which is smaller than the cobalt electrolyte and thus penetrates more deeply into the TiO_2 film.[13] Consequently, changing from an iodine-based redox system to a cobalt-based system increased η from 2.44% to 4.04%. It is noteworthy that the IPCE response of the **HIQ7**-based cell extended to 820 nm, which is one of the longest-wavelength responses among all DSCs based on cobalt redox systems reported to date.

We used intensity-modulated photovoltage spectroscopy and intensity-modulated photocurrent spectroscopy to deepen our understanding of the differences between the two systems.[14] For identical cell structures, the diffusion coefficient was lower for the cobalt complex than for iodine, owing to higher mass transport (Figure S1). However, investigation of the relationship between the electron lifetime and V_{oc} for the DSCs with the iodine and cobalt redox shuttles (Figure S2) indicated that the latter electrolyte afforded a much longer electron lifetime than did the former, implying that the recombination reaction between the electrons on the TiO_2 surface and the trivalent cobalt complex in the electrolyte was considerably suppressed. This result confirms that our molecular design is ideal for cobalt-based DSCs. Although the efficiency was not impressive, owing to the relatively weak IPCE response, the use of this type of D-π-A configuration offers a simple, feasible approach to the construction of NIR dyes for cobalt-based systems. Further research on 4,4-ethylenedioxy-4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophen, including optimization of the structure, tuning of the energy levels and electron injection efficiency, and optimization of the electrolyte solution and TiO_2 paste, is likely to result in more-efficient NIR dyes.

In conclusion, we developed a novel 4,4-ethylenedioxy-4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophen-based D-π-A organic dye and introduced it into a DSC with a cobalt-based redox system. By means of systematic and rational molecular design, we fabricated a DSC that exhibited a broad IPCE response spectrum (extending to 820 nm). Intensity-modulated photovoltage and photocurrent spectroscopy indicated that the combination of **HIQ7** with a cobalt complex efficiently suppressed electron recombination between the TiO_2 surface and the redox oxide species. Finally, an **HIQ7**-sensitized DSC with a cobalt electrolyte showed an overall conversion efficiency of 4.04%, which was 1.65 times that observed with an iodine electrolyte. Our results demonstrate the great potential of compounds containing 4,4-ethylenedioxy-4*H*-cyclopenta-[2,1-*b*:3,4-*b*′]-dithiophen-based D-π-A structures as NIR sensitizers for cobalt-based DSCs.

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Supporting Information Available. Experimental details, characterization data for all new compounds, details of the DSC fabrication, intensity-modulated photovoltage, and photocurrent spectroscopy data characterizations. This material is available free of charge via the Internet at http://pubs.acs.org.

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The authors declare no competing financial interest.