

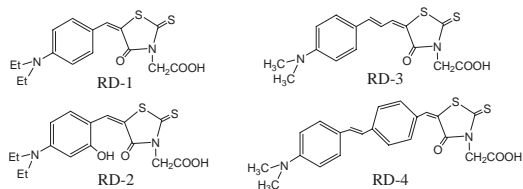
Greatly Enhanced Photovoltaic Performance by Introducing Hydroxyl or Benzene Ring into D- π -A Dye Framework: Dye Sensitized Solar Cells Based on Rhodanine Dyes

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The introduction of hydroxyl group into aniline moiety (electron donor, D) or benzene ring into the conjugation chain (π bridge) of D- π -A dye framework with rhodanine-3-acetic acid as electron acceptor (A) improved remarkably the monochromatic incident photon-to-current conversion efficiencies (IPCEs) and overall power conversion efficiencies (η), fully demonstrating the potential of molecular design in developing efficient D- π -A dyes for dye-sensitized solar cell applications.

Dye-sensitized solar cells (DSSCs) based on Ru(II) polypyridyl complexes have been actively investigated since Grätzel and coworkers reported highly efficient photoelectric conversion efficiencies of up to 10%.¹ Compared with Ru(II) polypyridyl complexes, organic dyes not only exhibit higher molar extinction coefficients, but also can be prepared and purified in easier procedures at lower cost, and therefore are attracting more and more interest. Most of the organic dyes applied in DSSCs,² such as merocyanine dyes, coumarin dyes, polyene dyes, and hemicyanine dyes, belong to typical D- π -A structures with both electron donor (D) and electron acceptor (A) linked by a π -conjugation bridge, which can effectively produce a charge-separation excited state upon photoinduced intramolecular charge transfer (ICT). The ICT processes in D- π -A structures strongly depend on the electron-donating ability of D, electron-withdrawing ability of A, as well as the electronic characteristics of the π bridge. Thus, the photoelectrochemical properties of D- π -A dyes in DSSCs may be finely tuned through chemical modification on each construction unit (D, A, or π bridge). Besides, the same chemical modification e.g. group substitution may lead to the same effect in different types of D- π -A dyes due to their similarities in ICT processes, therefore, some general guidelines may be achieved for designing more efficient sensitizer dyes. In this study we designed and synthesized four D- π -A type dye molecules (RD-1–RD-4 in Scheme 1), using rhodanine-3-acetic acid as A, *N,N*-dialkylaniline as D, and focused the effect of chemical structures of D and π bridge in these dyes on their photovoltaic behaviors in DSSCs. Several rhodanine-based D- π -A dyes had been successfully applied in DSSCs, with indoline or



Scheme 1. Molecular structures of the rhodanine dyes.

benzothiazole fraction as D.^{2a,4} Compared to these dyes, aniline type donors in RD-1 to RD-4 are structurally more simple, chemically more versatile, and commercially more available, facilitating the “structure-property relationship” studies.

As shown in Supporting Information (SI), the four rhodanine-based dyes were synthesized by condensation of rhodanine-3-acetic acid with corresponding aldehydes,^{2c,3} and characterized by ¹H NMR and EI-MS. Dye-sensitized nanocrystalline TiO₂ electrodes (3 or 9 μ m thick) were prepared following the reported methods.¹ TiO₂ paste (Ti-Nanoxide T, Solaronix SA) were spread onto fluorine-doped tin oxide conducting glass and sintered at 450 °C for 30 min. Then TiO₂ electrodes were soaked in CHCl₃ solutions of rhodanine dyes (0.5 mM) with the presence of 1.0 mM deoxycholic acid (DCA) at room temperature for 8 h. After rinsed with CHCl₃, the electrodes were dried under a stream of dry air. The sandwich-type cells consisted of a dye-sensitized nanocrystalline TiO₂ electrode as photoanode, a Pt-loaded conducting glass as cathode, and an electrolyte solution of 0.1 M of LiI, 0.05 M of I₂, 0–0.3 M of *t*-butylpyridine (TBP), and 0.3 M of 1,2-dimethyl-3-propylimidazolium iodide (DMPIImI) in methoxypropionitrile.

The absorption spectra of the rhodanine dyes in methanol solutions and on TiO₂ films are shown in SI (Figure A), and related photophysical and electrochemical data are collected in Table 1. Introduction of a hydroxyl group into aniline moiety leads to a bathochromic shift of the absorption peak and cathodic

Table 1. Photophysical and electrochemical properties of the rhodanine dyes in solutions and adsorbed on nanocrystalline TiO₂ films

Dye	RD-1	RD-2	RD-3	RD-4
$\lambda_{\max}^{\text{ab}}$ (MeOH, nm) ^a	468	478	485	483
ϵ (MeOH, 10 ⁴ M ⁻¹ cm ⁻¹) ^b	4.5	4.8	3.8	2.6
$\lambda_{\max}^{\text{fl}}$ (MeOH, nm) ^c	553	548	635	613
E_{0-0} (eV) ^d	2.43	2.44	2.17	2.28
E_{ox} (V, vs SCE) ^e	0.98	0.64	0.82	0.83
E_{ox}^* (V, vs SCE) ^f	-1.45	-1.80	-1.35	-1.45
FWHM (MeOH, nm) ^g	65	66	99	96
FWHM (TiO ₂ , nm) ^g	91	103	155	130
N (10 ⁻⁷ mol/cm ²) ^h	1.2	2.5	2.1	2.7

^aAbsorption maximum. ^bMolar extinction coefficient at $\lambda_{\max}^{\text{ab}}$. ^cFluorescence maximum. ^d0-0 transition energy calculated from the wavelength where the normalized absorption and fluorescence spectra intersect. ^eGround state oxidation potential in DMSO. ^fExcited state oxidation potential calculated by subtracting E_{0-0} from E_{ox} . ^gFull width of the absorption spectrum at half absorption maximum. ^hAdsorption amount per unit area of TiO₂ film.

shifts of the ground and excited state oxidation potentials of RD-2 vs RD-1, both due to the strong electron-donating feature of the hydroxyl group. The extension of π bridge from one double bond to two double bonds also results in a bathochromic shift in the absorption and a cathodic shift in the ground state oxidation potential, but an anodic shift in the excited state oxidation potential of RD-3 vs RD-1, in line with the general effect of conjugation length on energy levels of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO).^{4,5} Interestingly, the further extension of π bridge by insertion of a phenyl group between the two double bonds blue shifts slightly the absorption spectrum of RD-4 vs RD-3, and the excited state oxidation potential moves cathodically, demonstrating the different role of phenyl group in a conjugation system with respect to double bond, probably associated with the aromatic stabilization energy involved in phenyl group. These changes in absorption and redox potentials due to the structure variations of donor part and π bridge part influence greatly their photoelectrochemical properties of these rhodanine dyes in DSSCs (see below). Upon adsorption on TiO₂, the spectra of the rhodanine dyes broadened noticeably (see FWHM comparisons in Table 1), suggesting strong electronic couplings between these dyes and TiO₂.⁶

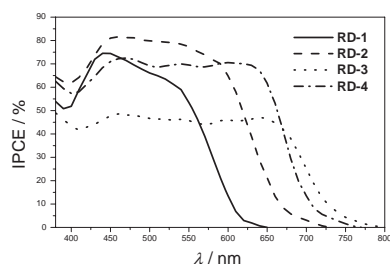


Figure 1. Photocurrent action spectra of the DSSCs based on the rhodanine dyes. The electrolyte was a solution of 0.1 M of LiI, 0.05 M of I₂, and 0.3 M of DMPIImI in methoxypropionitrile.

Figure 1 shows the action spectra of monochromatic incident photon-to-current conversion efficiencies (IPCEs) for the DSSCs based on these rhodanine dyes. What being more noteworthy than the broadening to the longer wavelengths of the photocurrent action spectrum of RD-2 vs RD-1, which is obviously the result of the absorption red shift, is that the IPCEs were improved significantly in the RD-2 sensitized cell. The improvement in IPCEs may result from cathodic movement of the excited state oxidation potential upon the introduction of hydroxyl group, leading to a larger driving force for electron injection from the excited dye to the conduction band of TiO₂, and/or enhanced dye adsorption on TiO₂ surface by using hydroxyl as an ancillary anchoring group, leading to better electronic coupling between the excited dye and TiO₂ conduction band.⁷ The increased adsorbing amount of RD-2 than RD-1 (Table 1) seems to support the latter assumption. Remarkable IPCE increase was also observed recently in hemicyanine dyes⁸ upon introduction of hydroxyl group onto the corresponding donor moieties, suggesting that this “hydroxyl effect” may be applied in other D- π -A dyes to improve their sensitizing abilities in DSSCs.

Similarly, the absorption spectrum red shifts in RD-3 and RD-4 with respect to RD-1 and RD-2 extended their photocurrent action spectra to longer wavelengths. However, the IPCEs

of RD-4 were much higher than those of RD-3, demonstrating the merit of phenyl group inserted in the π bridge. The singlet excited state lifetime of RD-3 (135 ps) in CH₃CN solution, measured with time-resolved fluorescence technique, is longer than that of RD-4 (25 ps), which precludes the intrinsic excited state decay of RD-3 as the main reason of its poor IPCEs, meanwhile indicates that the electron injection rate is fast enough for RD-4 to compete its intrinsic fast excited state decay efficiently. The inefficient IPCEs for RD-3 may originate from its less negative excited oxidation potential (Table 1). RD-3 underwent the most significant spectrum broadening (Table 1), and the line-shape over its absorption maximum varied obviously on TiO₂ than in solution (Figure A in SI). Thus, the aggregate of RD-3 formed on TiO₂ may take some negative effect on its IPCEs. Many organic dyes with double bonds as π bridges suffered IPCE decline with increasing double bond number, though photocurrent spectra got broadened.^{2b,5} Insertion of a phenyl group between the double bonds probably produces some good effects.

Due to the higher IPCEs over the wider spectrum regions, RD-2 and RD-4 exhibited more efficient sensitizing capabilities than RD-1 and RD-3 (see Table A in SI). By introducing TBP (*t*-butylpyridine) to promote open-circuit photovoltage (V_{oc}) and fill factor (ff), at slight expense in short-circuit photocurrent density (J_{sc}),⁹ the overall power conversion efficiencies (η) up to 5.5% and 5.8% (AM1.5 Global simulated light, 100 mW cm⁻²) were achieved in RD-2 and RD-4 sensitized solar cells, respectively.

In summary, the introduction of hydroxyl onto the electron donor moiety or insertion of benzene ring in π bridge improved the photoelectrochemical properties of rhodanine based D- π -A dyes in DSSCs. The “hydroxyl effect” and “phenyl effect” are worth to be investigated in other type D- π -A dyes for reaching more efficient sensitizers in DSSC applications.

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