

Enhancement of Overall Photovoltaic Efficiency by Changing the Position of the Attaching Group $-RSO_3^-$ on the Hemicyanine Dye Molecules

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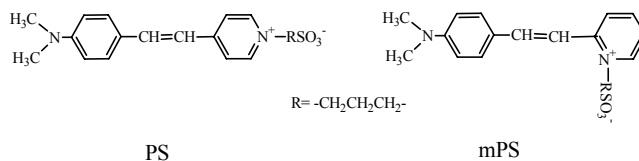
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Abstract: A new photoresponsive D- π -A dye, mPS, has been designed and synthesized. Compared to the parent dye PS, IPCE values in the region from 400 nm to 560 nm was greatly improved upon changing the attaching group from the *p*- position to the *o*- position of the π -conjugation bridge. A solar cell based on mPS generated a remarkably high overall yield η of 5.4% under irradiation of 80.0 mW cm⁻² white light from a Xe lamp. Compared with PS, the overall yield η increased by 64%.

Keywords: D- π -A dye, nanocrystalline TiO₂ electrode, photoelectric conversion property.

Dye-sensitized nanocrystalline semiconductor solar cells (DSSC) have been extensively investigated since Gratzel and coworkers reported a highly efficient solar cell with conversion efficiency over 10%¹. Recently, as attractive sensitizers, pure organic dyes were introduced into DSSC³⁻⁸, owing to their small size, large extinction coefficient and much lower cost. In our previous publications^{9,10}, using Langmuir-Blodgett(LB) technology we have systematically investigated the structure-function effects of hemicyanine dyes through varying donors and acceptors. Recently, we introduced $-RSO_3^-$ as attaching group into hemicyanine dye molecules, and found that they can adsorb onto the surface of TiO₂ successfully and show good charge-transfer properties⁷. Here, a new hemicyanine dye, (E)-N-(3-sulfopropyl)-2-[2-(4-dimethylaminophenyl)ethenyl]pyridinium (mPS), was synthesized by changing the attaching site of the $-RSO_3^-$ group to the dye

Figure 1 Chemical structures of PS and mPS



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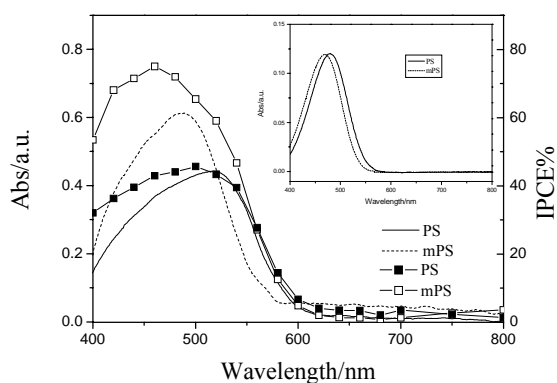
molecules. The new dye compared with the parent dye, (E)-N-(3-sulfopropyl)-4-[2-(4-dimethylaminophenyl)ethenyl]pyridinium (PS), shows more remarkably efficient charge-transfer properties. mPS-sensitized solar cell generated 5.4% of overall photoelectric conversion yield, which is 1.6 times of that produced by PS system. The structures for PS and mPS are shown in **Figure 1**.

The synthesis and characterization of PS referred to literature⁷, mPS was prepared according to the same method of PS. N-3-sulfopropyl-2-methylpyridinium was used as starting material instead of N-3-sulfopropyl-4-methylpyridinium.

mPS: mp > 300 °C. Anal. calcd. for C₁₈H₂₂N₂O₃S: C, 62.40; H, 6.40; N, 8.09. Found: C, 62.12; H, 6.28; N, 8.13. δ_{H} (500MHz, DMSO): 2.11-2.22 (m, 2H), 2.60 (t, 2H, J=6.19 Hz), 3.04 (s, 6H), 4.86 (t, 2H, J=7.34 Hz), 6.78 (d, 2H, J=8.59 Hz), 7.50 (d, 1H, J=15.68 Hz), 7.69-7.73 (m, 1H), 7.85 (d, 2H, J=8.56 Hz), 7.97 (d, 1H, J=15.55 Hz), 8.31-8.34 (m, 1H), 8.49 (d, 1H, J=8.41 Hz), 8.76 (d, 1H, J=6.00 Hz).

The absorption spectra of PS and mPS were measured in methanol solutions. The absorption peaks in the visible region are at 480 nm for PS and 468 nm for mPS (cf. the inset of **Figure 2**), with molar extinction coefficients of 4.0×10^4 (mol/L)⁻¹ cm⁻¹ and 3.9×10^4 (mol/L)⁻¹ cm⁻¹ for PS and mPS, respectively. A 5- μm thick nanocrystalline TiO₂ film, coated onto conducting glass (fluorine doped SnO₂ sheet, resistance 20 Ω per cm²), was colored with the dye by immersing for 12 h in a 3×10^{-4} mol/L solution of the dye in chloroform. The absorption peaks (514 nm for PS and 488 nm for mPS in **Figure 2**) for the dyes on TiO₂ films, comparing with their corresponding absorption peaks in methanol

Figure 2 Absorption spectra of PS and mPS on TiO₂ film (line) and IPCE% values of the corresponding solar cell (line + symbol).



The light absorbed and reflected by conducting glass was not corrected. Upper right inset: absorption spectra of PS and mPS in methanol solutions (3×10^{-6} mol/L).

solutions, are red-shifted by 34 and 20 nm for PS and mPS, respectively. The structure of PS molecules is in linear, which is of favor for PS molecules adsorbing onto the surface of the TiO₂, while with a sickle-like structure, the number of adsorbed molecules of mPS would decrease owing to steric effect. In fact, the number of adsorbed mPS is

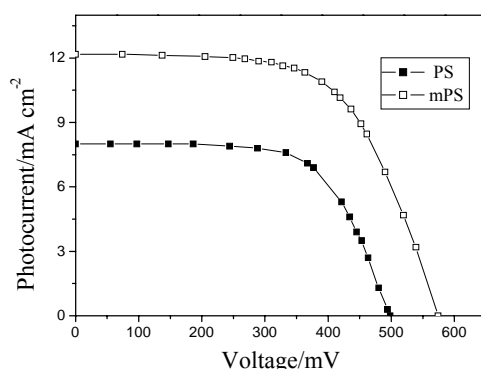
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$1.12 \times 10^{-7} \text{ mol cm}^{-2}$, which is only 44.1 per cent of that for PS. Having less steric effect and with more adsorbed molecules, the interaction between neighboring PS molecules on TiO_2 film may be more intense than that of mPS, the absorption spectrum of PS on TiO_2 film is broader than that of mPS.

The ground and excited-state energy levels for PS are assumed to be -5.46 eV and -3.05 eV on the absolute scale, respectively, with reference to the oxidation potential 0.76 V (vs. Ag/AgCl)⁷ and the band gap 2.41 eV (514 nm). We believe that change of the position of the $-\text{RSO}_3^-$ group will have only a very weak effect on the ground state of the two dyes. So it is reasonable to consider that the two dyes have the same ground-state energy level. Then, the excited-state energy level of -2.92 eV for mPS is then deduced combining the band gap 2.54 eV (488 nm). Obviously, the excited-state energy levels of the two dyes both lie above the conduction band (CB) edge of TiO_2 (-4.41 eV)². Therefore, one can conclude that electron injection from the excited-state dye molecules of PS and mPS to the CB of TiO_2 is thermodynamically possible.

The photoelectrochemical experiments were carried out in a standard two-electrode system^{2,7}. A 500W xenon lamp (Ushio Electric, Tokyo, Japan) served as a white light source in conjugation with an IRA-25S filter (Schott, USA) and a GG400 cutoff filter (Toshiba, Japan). Monochromatic light in the range of 400 nm to 800 nm was produced by setting an IRA-25S filter and a suitable band-pass filter (Schott, USA) in the path of the light beam. The photocurrent action spectra are also shown in **Figure 2** where IPCE is plotted as a function of wavelength. For mPS, IPCE values are greatly increased in the region from 400 nm to 560 nm comparing with PS. The maximum IPCE value of mPS is

Figure 3 I-V curves of solar cells sensitized with PS and mPS.



The electrolyte: 0.5 mol/L LiI + 0.05 mol/L I_2 + 0.6 mol/L 4-methylpyridinium iodide in propylene carbonate (PC). Effective area: 0.188 cm^2 . The light absorbed and reflected by conducting glass was corrected.

75%, and in the region from 400 nm to 540 nm, its IPCE values exceeded 40%. While the maximum IPCE value for PS-sensitized TiO_2 solar cell is only 45%. Improved IPCE values for mPS-sensitized solar cell can be attributed to the changed position of $-\text{RSO}_3^-$ onto the dye molecule. After the fact that less mPS molecules adsorbed onto the TiO_2

surface was taken into account, this change mainly originated two main advantageous effects for photosensitizer mPS. The first is that the excited-state energy level of mPS is positively shifted 0.13 eV, which increased the driving force for electron injection from excited-state dye molecules to the CB of the TiO₂ electrode. Secondly, owing to the sickle-like molecular structure, the distance between mPS conjugated molecules and the TiO₂ particles shortened compared with the linear structure of PS. Illumination with 80.0 mW cm⁻² white light from a Xe lamp (Ushio Electric, Japan), a sandwich-type solar cell, in conjugation with an electrolyte composed of 0.5 mol/L LiI, 0.05 mol/L I₂ and 0.6 mol/L 4-methylpyridinium iodide in propylene carbonate (PC), generated 8.0 mA cm⁻², 498 mV and 0.662 of short-circuit photocurrent (I_{sc}), open-circuit photovoltage (V_{oc}), and the fill factor (FF), respectively, with an overall yield (η) of 3.3% for the PS-sensitized nanocrystalline TiO₂ film, while 12.2 mA cm⁻² I_{sc} , 574 mV V_{oc} , 0.612 FF and 5.4% η were obtained from the solar cell sensitized with mPS (see **Figure 3**). It is interesting that the overall yield η increased by 64% with I_{sc} and V_{oc} increased by 53% and 15%, respectively, upon changing the position of the attaching group from the *p*- position to the *o*- position of the π -conjugation bridge. From the above experiments, we believe that the excited dye molecules might inject electrons from the whole π -conjugated system to the conduction band of TiO₂ and not just along the σ -alkyl group. Detailed research including electron injection mechanism and longer-time test about mPS-sensitized solar cell is under progress.

Acknowledgments

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