

Novel organic dyes for efficient dye-sensitized solar cells†

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Two novel metal-free organic dyes containing thienothiophene and thiophene segments have been synthesized. Nano-crystalline TiO₂ dye-sensitized solar cells were fabricated using these dyes as light-harvesting sensitizers, and a high solar energy-to-electricity conversion efficiency of 6.23% was achieved.

Dye-sensitized solar cells (DSSCs) have received wide attention due to their high performance and low-cost of production. DSSCs based on Ru-complex photosensitizers such as N3 and black dyes can provide efficient solar energy-to-electricity conversion efficiencies (η) of up to 10%.^{1–6} Compared to Ru-complexes, the advantages of sheer organic dyes are that not only can they exhibit high molar extinction coefficients, but that they can also be prepared and purified easily at lower cost. Metal-free dyes such as perylene dyes,^{7,8} cyanine dyes,^{9,10} xanthene dyes,¹¹ merocyanine dyes,^{12–14} coumarin dyes,^{15–17} hemicyanine dyes,^{18,19} and indoline dyes^{20,21} have been investigated as sensitizers in DSSCs, and great progress has been made in this field. To date the highest overall photoelectric conversion efficiency of organic dye-sensitized solar cells already can reach a considerable level of 8%.²¹ Therefore, development of new organic dyes with photo-response in the broad solar spectrum is promising for the improvement of the light-to-electricity conversion in DSSCs. Generally, organic dyes should contain a structure of donor-to-acceptor bridged by a π -conjugation system, and possess a broad and intense spectral absorption. A usual approach to extend the absorption region of dyes is to increase the methine unit ($-\text{CH}=\text{CH}-$) to enlarge the π -conjugation system, leading to a red-shift of dye absorption. However, such a measure also often result in instability of dye molecules due to the possibility of isomer formation. To obtain organic dyes with both red-shift absorption and high stability, introduction of new π -conjugation segments into dye molecules is necessary, and much research has been done along this line.^{22–25} Here, we report two new dyes containing thienothiophene or thiophene segments as π -conjugation system (coded as D-ST and D-SS, respectively, Fig. 1). To the best of our knowledge there has been no report on the application of a dye containing a thienothiophene moiety in DSSCs.

The dyes D-ST and D-SS were constructed by a stepwise synthetic protocol illustrated in the ESI.†‡ For the preparation of DSSC, an FTO glass plate (Nippon Sheet Glass, 10 Ω sq⁻¹) was cleaned with detergent solvents, water and ethanol, respectively. After treatment in a UV-O₃ system for 18 min, the glass was

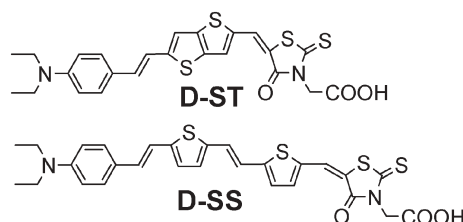


Fig. 1 Molecular structure of the dyes.

treated with 40 mM TiCl₄ aqueous solution as reported by the Grätzel group.²⁶ The double layer of TiO₂ was prepared by the screen-printing mode. The first TiO₂ layer of 10 μm thickness was coated with paste (PST 18 NR, CCI in Japan, TiO₂ particle size: 18 nm), and the second TiO₂ layer of 4 μm thickness was printed with a different paste (PST 400 C, CCI, TiO₂ particle size: 400 nm) for the improvement of light harvesting by the photo-scattering

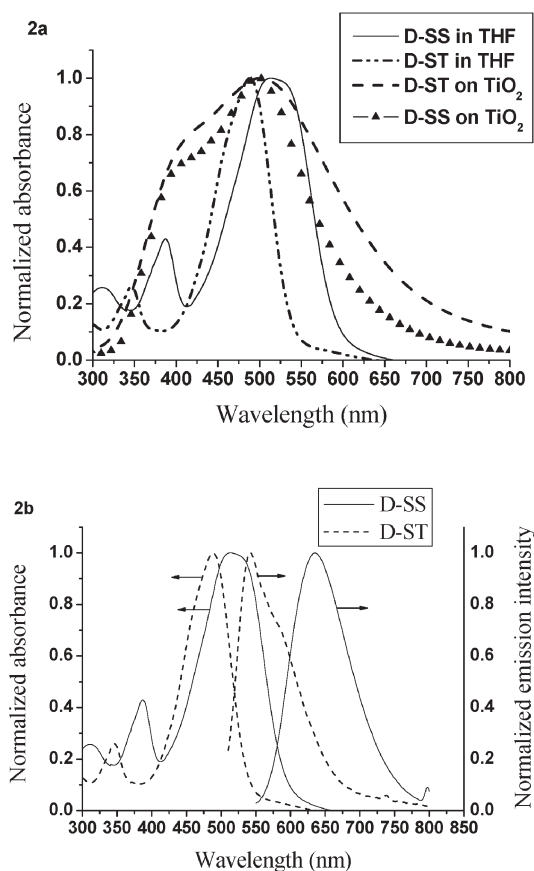


Fig. 2 (a) Absorption spectra of the dyes in THF and on the TiO₂ film. (b) Absorption and emission spectra of the dyes recorded in THF.

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Table 1 Optical, redox and DSSC performance parameters of the dyes

Dye	$\lambda_{\text{abs}}^a/\text{nm}$ ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$)	$\lambda_{\text{em}}^a/\text{nm}$	$E_{\text{ox}}(\Delta E_p)^b/\text{V}$ (vs Ag/Ag ⁺)	E_{0-0}^c/eV	E_{ox}^*/V (vs Ag/Ag ⁺)	V_{oc}	J_{sc}	FF	η (%)
D-SS	513 (38400)	636	0.40 (0.10)	2.13	-1.73	0.52	10.64	0.70	3.87
D-ST	488 (50100)	542	0.29 (0.05), 0.48 (0.07)	2.39	-2.10, -1.91	0.56	15.23	0.73	6.23

^a Absorption and electrochemical data were recorded in THF solution. ^b Redox potentials were measured in 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile. Scanning rate: 20 mV s⁻¹; ΔE_p is the separation between the anodic and cathodic peaks. ^c Determined from the intersection point of absorption and emission spectra.

property of large TiO₂ particles. The detailed procedure for sintering TiO₂ was similar to that described in literature.²⁷ After being sintered, the TiO₂ film was re-treated with 40 mM TiCl₄,²⁶ and then heated at 400 °C for 20 min. After cooling to 80 °C, the film was immersed in a THF solution of 0.3 mM dye at room temperature for 24 h. In order to prevent aggregation of dye molecules on the TiO₂ surface, 20 mM of chenodeoxycholic acid was added to the dye solution.²⁸

For the photovoltaic measurement, the dye-coated TiO₂ film was sandwiched with a Pt-sputtered FTO glass, and an organic electrolyte was introduced between electrodes by the capillary force. The electrolyte composed of 0.05 M I₂, 0.1 M LiI, 0.6 M 1-propyl-3-methylimidazolium iodide and 0.5 M 4-*tert*-butylpyridine in a mixed solvent of acetonitrile and valeronitrile (1 : 1, v/v). The photovoltaic performance was recorded under the simulated AM 1.5 irradiation (100 mW cm⁻²).

The absorption and emission spectra of the dyes are displayed in Fig. 2, and the data are collected in Table 1. In THF solution, both dyes give narrow absorption bands, and the dye D-SS has a slight red-shift absorption in comparison to D-ST. This may arise from larger π -conjugation system of D-SS than D-ST. On the other hand, the absorption spectra of the two dyes on TiO₂ film are broadened. D-SS produces a slight blue-shift due to the formation of H-aggregate on the TiO₂ electrode and D-ST has a red-shift due to J-aggregation. As a result, the dye D-ST has a broader absorption spectrum than the dye D-SS. The broadening of absorption is favorable for harvesting solar light and leading to a large photocurrent.

The action spectra of monochromatic incident photo-to-current conversion efficiencies (IPCEs) for the DSSCs based on the two dyes are presented in Fig. 3. The IPCE spectrum of the DSSC based on D-ST is red shifted compared to that based on D-SS,

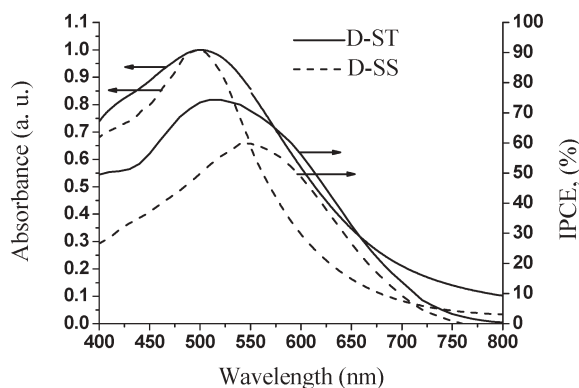


Fig. 3 Absorption spectrum of the dyes absorbed on nanocrystalline TiO₂ and the action spectra for DSSCs constructed using D-SS and D-ST.

which is in good agreement with the absorption behavior of the dyes on TiO₂ film. The onset of the IPCE spectrum of the DSSC based on D-ST is 790 nm, and a high IPCE (>70%) was observed in the range from 470 nm to 580 nm with a maximum value of 82% at 515 nm. In contrast, the DSSC based on D-SS shows a relatively low IPCE with the maximum of 66% at 540 nm.

To judge the possibility of electron transfer from the excited dye molecule to the conductive band of TiO₂, cyclic voltammograms were performed to determine redox potentials of the two dyes. Both dyes are reversible at a moderately high oxidation potential. The oxidation peak potential of cathodic current and the reduction potential calculated from the oxidation potential and the energy at the crossing section of absorption and emission spectra observed under low-concentration conditions are listed in Table 1. As shown in Table 1, the excited state oxidation potential (E_{ox}^*) of the dyes (D-SS: -1.73 vs Ag/Ag⁺, -0.93 vs NHE; D-ST: -2.10, -1.91 vs Ag/Ag⁺, -1.30, -1.11 vs NHE) are far more negative than the band edge energy of the nanocrystalline TiO₂ electrode (-0.5 vs NHE), indicating that the electron injection process from the excited dye molecule to TiO₂ conduction band is energetically permitted.

The performance statistics of the devices are also listed in Table 1. An overall conversion efficiency (η) of 6.23% was achieved from the DSSC based on the dye D-ST (short-circuit photocurrent density, $J_{\text{sc}} = 15.23 \text{ mA cm}^{-2}$; open-circuit photovoltage, $V_{\text{oc}} = 0.56 \text{ V}$; fill factor, $ff = 0.73$). This efficiency is much higher than the efficiency of 3.87% obtained from the DSSC based on the dye D-SS, although D-SS possesses a larger π -conjugation system.

In summary, we have designed and synthesized two novel organic dyes featuring thienothiophene- and thiophene-bridging structures. Both dyes show good performance for DSSCs. Especially the conversion efficiency of the DSSC based on the dye D-ST can reach 6.23%, a considerably high level for organic dyes. This result strongly suggests that thienothiophene could be an excellent π -conjugation system for organic dyes to harvest the solar spectrum.

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Notes and references

‡ D-SS: ¹H NMR (DMSO-*d*₆): δ 1.10 (6H, t, $J = 6.98 \text{ Hz}$), 3.34 (4H, q, $J = 6.96 \text{ Hz}$), 4.46 (2H, s), 6.64 (2H, d, $J = 8.76 \text{ Hz}$), 6.82 (1H, d, $J = 15.77 \text{ Hz}$), 7.03 (1H, d, $J = 3.49 \text{ Hz}$), 7.11 (1H, d, $J = 16.15 \text{ Hz}$), 7.13 (1H, d, $J = 15.82 \text{ Hz}$), 7.22 (1H, d, $J = 3.77 \text{ Hz}$), 7.36–7.39 (3H, m), 7.43 (1H, d, $J = 15.89 \text{ Hz}$), 7.71 (1H, d, $J = 3.86 \text{ Hz}$), 8.04 (1H, s). MALDI-TOF m/z : 566.1 [M⁺]. HRMS-SIMS (m/z): [M⁺] calcd for C₂₈H₂₆N₂O₃S₄, 566.0826, found, 566.0837 (100%); [M - COOH]⁻ calcd for C₂₇H₂₅N₂O₁S₄, 521.0850, found, 521.0851 (100%).

D-ST: ¹H NMR (DMSO-*d*₆): δ 1.10 (6H, t, *J* = 6.98 Hz), 3.38 (4H, q, *J* = 7.02 Hz), 4.49 (2H, s), 6.67 (2H, d, *J* = 8.02 Hz), 6.99 (1H, d, *J* = 16.11 Hz), 7.26 (1H, d, *J* = 15.98 Hz), 7.44 (2H, d, *J* = 8.13 Hz), 7.52 (1H, s), 8.08 (1H, s), 8.20 (1H, s). MALDI-TOF *m/z*: 514.4 [M⁺]. HRMS-SIMS (*m/z*): [M⁺] calcd for C₂₄H₂₂N₂O₃S₄, 514.0513, found, 514.0525 (100%); [M - COOH]⁻ calcd for C₂₃H₂₁N₂O₁S₄, 469.0537, found, 469.0549 (78%).

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