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Simple Oligothiophene-Based Dyes for Dye-Sensitized Solar Cells (DSSCs): Anchoring Group Effects on Molecular Properties and Solar Cell Performance

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Simple oligothiophene-based dyes with a cyanoacrylic acid anchor were synthesized and evaluated as a photosensitizer for dye-sensitized solar cells (DSSCs). Although the molecular properties of the dyes at a glance are quite similar to those of related oligothiophene dyes with a carboxylic acid anchor, the DSSC performance of the former (up to $\eta = 4.8\%$) is fairly improved over the latter (≈1.2%). Absorption spectra of the oligothiophene dyes with the cyanoacrylic acid are red-shifted compared to those with the carboxylic acid, resulting in the improved photocurrent conversion efficiency at above 600 nm in the DSSCs. With the aid of theoretical calculations, electronic properties of the oligothiophene dyes were investigated, and it turned out that the excited states of the dyes are significantly affected by the anchoring groups. The cyanoacrylic acid anchor brings about a stabilized LUMO with localized electron density on the cyanoacrylic acid moiety, whereas the carboxylic acid dye has relatively a high-lying LUMO with delocalized electron density over the oligothiophene moiety. Thus, the difference in the DSSC performance is rationalized by the different electronic structure at the excited states caused by the anchoring groups on the oligothiophene cores.

Dye-sensitized solar cells (DSSCs) have attracted much attention in the last two decades owing to their low production cost and relatively high solar energy-to-electricity conversion efficiency (η).[1] Ruthenium (Ru) complex-based dyes, such as N3,[1a,2] N719,[3] and black dye,[4] have been widely investigated as prototypical photosensitizers achieving high performance with η of up to 11% under AM 1.5 irradiation.[5] On the other hand, because of limited resources and high production costs associated with Ru metal itself, Ru-free organic dyes have been considered to be a potential alternative for realizing low-cost DSSCs. In addition, flexibility and versatility in the molecular structure of organic dyes allow tuning of their properties, such as absorption spectrum and electron-transfer rate, that affect the performance of DSSCs. In fact, versatile organic dyes including coumarin-,[6] indoline-,[7] cyanine-,[8] arylamine-,[9] and thiophene-based dyes,[10] have been examined, and recent improvement of performance in organic dye-based DSSCs is quite impressive. Among them, DSSCs with organic dyes consisting of a donor/acceptor dyad (Figure 1) have been widely investigated and achieved good performance with η as high as 9%.[7,10m,11] Representative dyes of this class have an arylamine as an electron-donating part and a cyanoacrylic acid as an electron-accepting part, between which an oligothiophene is employed as a spacer group.

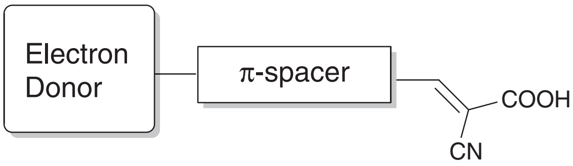

Figure 1. Schematic structure of donor/acceptor dyes.

Oligo- and polythiophenes are promising materials for optoelectronic applications[12] and actually have played a key role in thin film bulk heterojunction solar cells[13] or polymer-based organic thin-film transistors (OTFTs).[14] However, simple oligothiophene-based dyes for DSSCs have been scarcely studied, although they absorb visible light effectively. We previously reported simple oligothiophene-based dyes **1a**–**1c** consisting of quaterthiophene (4T), octithiophene (8T), or dodecithiophene (12T) and a carboxylic acid moiety for DSSCs (Figure 2).[15] With extension of the oligothiophene length, the dyes absorb visible light more effectively with the extinction coefficient (ε/M^{-1} cm^{-1}) of 3.1×10^4 for **1a**, 6.1×10^4 for **1b**, and 9.0×10^4 for **1c** (Table 1). In accordance with the effective absorption of light, the performance of the DSSCs improved; $\eta = 0.92\%$ for **1a**, 1.29% for **1b**. However, **1c**-based DSSCs

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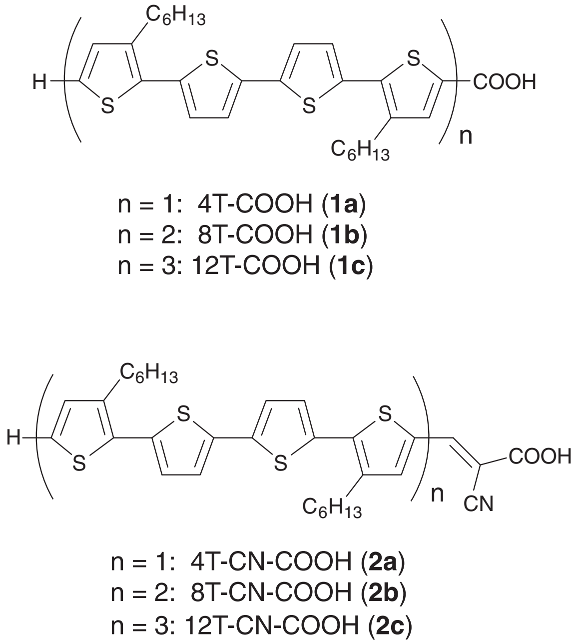


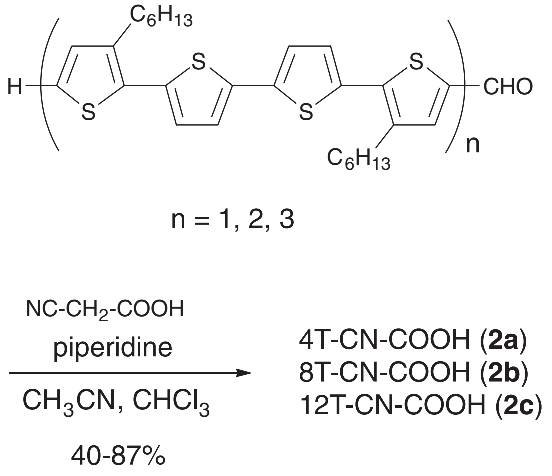
Figure 2. Molecular structures of simple oligothiophene-based dyes.

Table 1. Electrochemical[a] and Optical Properties of Oligothiophene-Based Dyes **1** and **2**

	E_{ox}[b]/V vs. Ag/AgCl	λ_{max}[c] /nm ($\varepsilon/10^4$ $\mathrm{M^{-1}\,cm^{-1}}$)	λ_{onset}[c] /nm	λ_{em}[c] /nm	HOMO[d] /V vs. NHE	LUMO[e] /V vs. NHE
1a	0.95	387 (3.1)	488	475	1.15	−1.39
1b	0.68	442 (6.1)	557	554	0.88	−1.34
1c	0.45	456 (9.0)	571	567	0.65	−1.52
2a	0.93	472 (3.5)	590	617	1.13	−0.97
2b	0.73	465 (6.3)	625	617	0.93	−1.05
2c	0.48	467 (10.0)	630	630	0.68	−1.29

a) Observed no reduction wave within the potential window between −1.0 and +1.5 V. b) Oxidation onsets. The standard Fc/Fc$^+$ redox couple showed $E_{1/2} = +0.42$ V. c) Measured in chloroform. d) Calibrated according to Ag/AgCl = −0.20 V vs. NHE. e) Estimated from optical energy gap (λ_{onset}) and HOMO. I$^-$/I$_3^-$ cycle (+0.20 V vs. Ag/AgCl, +0.4 V vs. NHE).

showed poor performance with $\eta = 0.55\%$. The decrease in performance for **1c** is mainly ascribed to its low oxidation potential (+0.45 V vs. Ag/AgCl, +0.65 V vs. NHE) approaching the redox potential of the I$^-$/I$_3^-$ cycle (+0.20 V vs. Ag/AgCl, +0.4 V vs. NHE), which leads to difficult electron supply from the electrolyte.[16] In order to make use of the highly efficient light absorption ability of the long oligothiophenes, we focused on the aforementioned cyanoacrylic acid moiety as the anchoring group, because it includes an electron-withdrawing cyano group, which could compensate the low oxidation potential of the long oligothiophene unit. We here report the synthesis, properties, and DSSC performance of new simple oligothiophene-based dyes **2a**–**2c** with cyanoacrylic acid moiety (Figure 2).



Scheme 1. Synthesis of **2a**–**2c**.

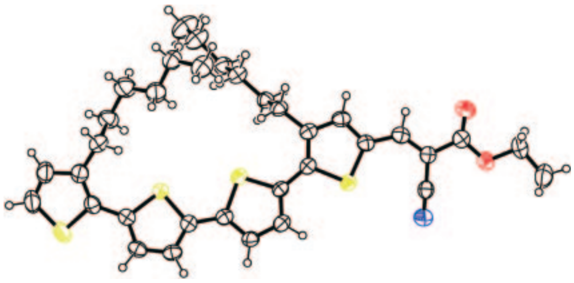


Figure 3. ORTEP drawing of ethyl ester of **2a**.

Results and Discussion

Synthesis. The synthesis of **2a**–**2c** was easily done by the Knoevenagel condensation of the corresponding oligothiophene aldehyde[17] and cyanoacetic acid in the presence of piperidine as a base (Scheme 1).[10] All new oligothiophene–cyanoacrylic acid dyes **2a**–**2c** were well characterized with spectroscopic and combustion elemental analysis. In addition, connectivity of the acrylic acid moiety to the thiophene part was unambiguously determined as *E*-form by single-crystal X-ray analysis of the ethyl ester derived from **2a** (Figure 3). Crystallographic data have been deposited with The Cambridge Crystallographic Data Centre: Deposition number CCDC-795162 for compound **2a**. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif (or from The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; e-mail: data_request@ccdc.cam.ac.uk).

Table 1 summarizes the electrochemical and optical properties of **2** in comparison with those of **1**, together with estimated HOMO and LUMO energy levels from the oxidation potentials and energy gap expected from absorption onset in chloroform solution. Contrary to our expectation, oxidation potentials of **2a**–**2c** do not positively shift so much compared to those of **1a**–**1c**, indicating that the HOMO energy levels of **2** are more or less similar to those of **1**. This implies that **2c** with low oxidation potential, i.e., highly lying HOMO has a similar problem to that of **1c** when fabricated into DSSCs as the photosensitizer; problematic electron supply to oxidized **2c** from the counter electrode via the I$^-$/I$_3^-$ redox cycle may result in poor performance for **2c**-based DSSCs.[15,16]

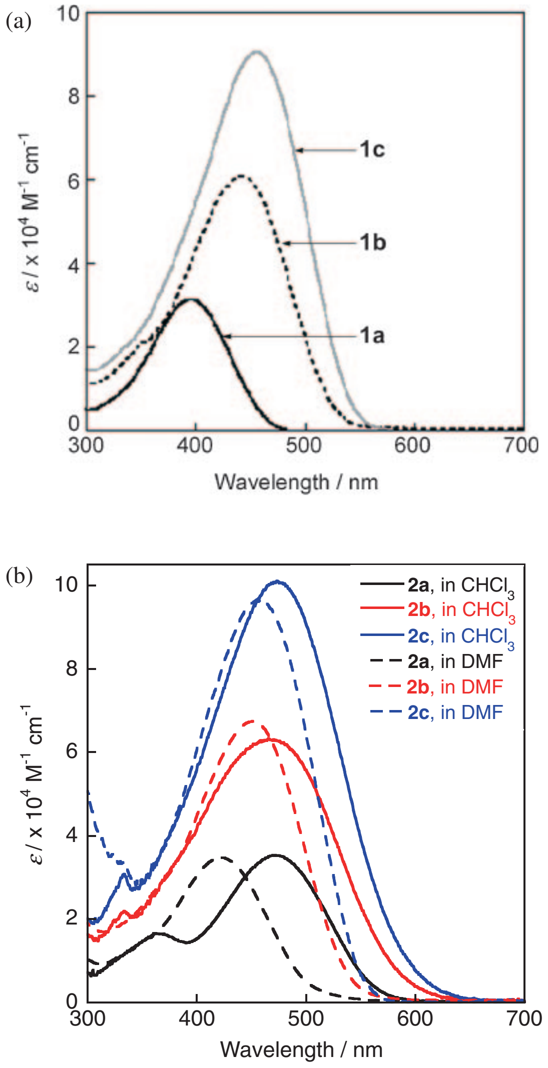


Figure 4. Absorption spectra of (a) **1a**–**1c** in chloroform and (b) **2a**–**2c** in chloroform (solid line) and in DMF (dotted line).

In contrast to similar oxidation potentials between **1** and **2**, absorption spectra of **2** are much influenced by substitution of the anchoring group from the carboxylic acid to the cyanoacrylic acid; significant bathochromic shifts are observed for all oligothiophenes (Figure 4). This can be explained by distinct effects of the more electron-negative cyanoacrylic acid moiety to the LUMO, but not to the HOMO. As was observed for the less influenced oxidation potential of **2**, the HOMO is not greatly stabilized energetically by introduction of the cyanoacrylic acid moiety, whereas the LUMO energy level is lowered significantly, resulting in similar oxidation potentials of **1** and **2** but large bathochromic shifts in absorption spectra for **2**. This consideration is supported by theoretical calculations using DFT/TD-DFT (vide infra).

It should be also noted that the λ_{max} values of the cyanoacrylic acid dyes **2** are not influenced by the length of oligothiophene moiety (Table 1 and Figure 4b), whereas the λ_{max} values shift bathochromically with extension of the oligothiophene length for the carboxylic acid dyes **1**. In the emission spectra, larger Stokes shifts are observed for **2** than for **1**, indicating that **2** with the cyanoacrylic acid moiety has different molecular structures in the ground and excited states originating from the relatively flexible molecular structures of **2**.

Table 2. DSSCs Performance Parameters for **1**-[a)] and **2**-Based DSSCs[b)]

Dye	V_{OC}/mV	J_{SC}/mA cm^{-2}	η/%	*FF*
1a	496	3.38	0.92	0.55
1b	596	3.74	1.29	0.58
1c	408	2.98	0.55	0.45
2a	605	8.34	2.93	0.54
2b	710	11.9	4.86	0.58
2c	668	12.8	4.89	0.57
N719	724	14.68	6.15	0.58

a) Ref. 13. b) Performance of the cells using TiO_2 electrode with approximately 8 µm thickness was measured with 0.25 cm^2 active area using a metal mask.

Oligothiophene-length independent λ_{max} values observed for **2** can be partially rationalized by negative solvatochromism, that is, hypsochromic shift of λ_{max} values in polar solvents (Figure 4b). In DMF as a solvent, larger hypsochromic shifts are observed for the shorter oligothiophene case; for 4T (**2a**), 26 nm; 8T (**2b**), 14 nm; 12T (**2c**), 12 nm (Figure 4b). It should be emphasized that such solvatochromism was not observed for the carboxylic acid dyes **1**, indicating that dipolar characters of **1** both in the ground and the excited states are significantly different from those of **2**, which can affect the performance of DSSCs.

As a summary of physicochemical evaluation of the new oligothiophene dyes **2**, the HOMO energy levels are not significantly lower than those of **1**, but bathochromic shifts caused by substitution of the carboxylic acid with the cyanoacrylic acid result in broad and strong absorption of visible light, which will be suitable as the photosensitizer in DSSCs.

Dye-Sensitized Solar Cells. DSSCs with an active area of 0.5 × 0.5 cm^2 square on a fluorine-doped tin oxide (FTO) substrate were fabricated using **2a**–**2c** as the photosensitizer, TiO_2 nanoparticles, and electrolyte solution consisting of 0.05 M iodine, 0.05 M lithium iodide, 0.6 M 1-propyl-2,3-dimethylimidazolium iodide (DMPII), and 0.5 M 4-*t*-butylpyridine in dry acetonitrile. The **2a**–**2c**-based DSSCs were evaluated under AM 1.5 illumination, and the performance parameters are listed in Table 2. For comparison, a standard DSSC with N719 as the photosensitizer was also fabricated and evaluated (see Supporting Information). The photocurrent–voltage (*J*–*V*) curves and the incident photocurrent conversion efficiencies (IPCEs) of the **2a**–**2c**-based cells are shown in Figure 5.

Compared with the **1**-based cells, the performance of **2**-based cells is apparently improved for all oligothiophene lengths, not only for the open-circuit voltage (V_{OC}) but also the short-circuit current density (J_{SC}), indicating that the anchoring group on the oligothiophene moiety is crucially important. As in the case of **1**, elongation of the oligothiophene length is beneficial for improving the performance of the DSSCs based on **2**; from 4T (**2a**) to 8T (**2b**) the conversion efficiency (η) is raised from 2.93% to 4.86%, owing to improvement of both J_{SC}

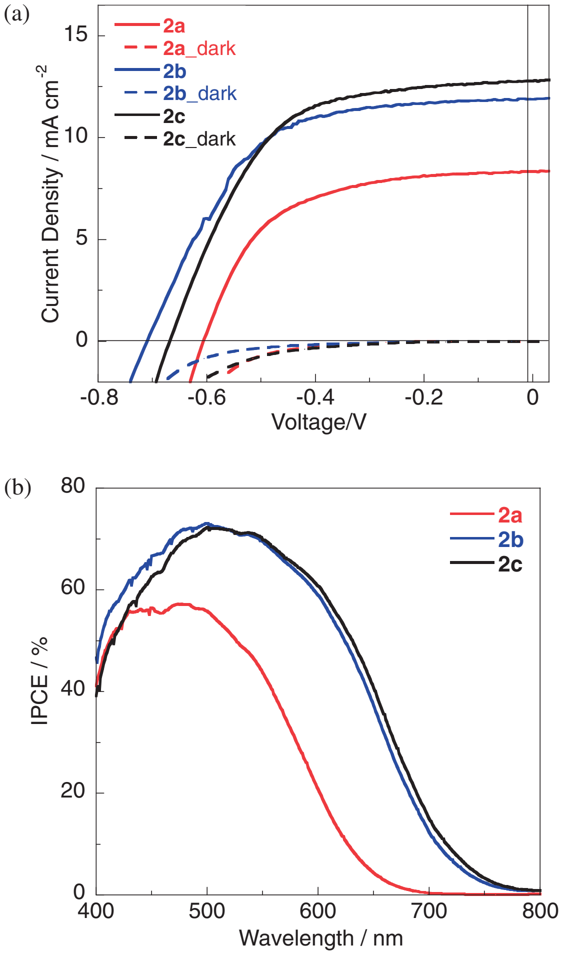


Figure 5. *J–V* curves (a) and IPCE plots (b) of **2**-based DSSCs.

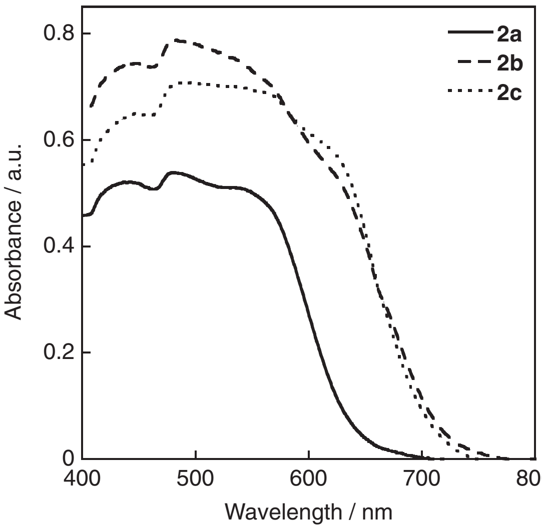


Figure 6. Absorption spectra of **2a**–**2c** on the TiO_2 film.

and V_{OC}. The increase in J_{SC} for **2b** is consistent with the IPCE, where higher efficiency and broader light conversion in the visible range is observed for the **2b**-based cell than for the **2a**-based one. Such improvements are consistent with the superior light absorption of **2b** than **2a** in the visible range (Figure 4b). Furthermore, pronounced red-shifted absorption up to 750 nm for **2b**–TiO_2 is observed, whereas the absorption of **2a**–TiO_2 film is less intensive and not red-shifted as much (Figure 6).

On the other hand, 12T-based dyes showed quite different behaviors between the carboxylic acid dye **1c** and the cyanoacrylic acid dye **2c**. In the case of **1c**, significant decrease in the performance compared to **1b** was observed. In sharp contrast, the **2c**-based cell shows almost comparable performance with the 8T-based **2b**. In order to understand the different behaviors, we carefully inspected **2b**– and **2c**–TiO_2 films. First, absorption spectra of the films are compared (Figure 6). Very interestingly, the spectra are similar to each other, indicating similar light absorption in the TiO_2 films. This indicates that **2c** does not make use of its excellent light absorption ability ($\varepsilon \approx 10^5\,M^{-1}\,cm^{-1}$) in the actual DSSCs. The comparable absorption specta of **2c**–TiO_2 is rationalized by a reduced amount of **2c** molecules absorbed on the TiO_2 film by ca. 20% than that of **2b**, implying that **2c** is too bulky to absorb densely on the film (see Supporting Information). Second, cyclic voltammograms of **2b**– and **2c**–TiO_2 films are compared to get insight into their oxidation behaviors on the TiO_2 films. Although the oxidation waves were rather broad, oxidation onsets extracted from the voltammograms are +0.64, +0.45, and +0.34 V (vs. Ag/AgCl) for **2a**, **2b**, and **2c**, respectively, the order of which is consistent with that in the solution potentials (Table 1). However, the degree of oxidation shift (ΔE) by the extension of oligothiophene chain is rather different. In the solution voltammograms, ΔE is in the range of 0.2–0.25 V, whereas ΔE for **2b** to **2c** in the TiO_2 film is only ca. 0.1 V. These results imply that elevation of the HOMO of **2c** does not significantly affect in the actual DSSC process, giving rationale for comparable DSSC performance between **2b**- and **2c**-based DSSCs in combination with similar light absorption spectra in the TiO_2 films as discussed above. Although the reasons for this effect is not clear, we speculated that the effective conjugation length of 12T units is limited in the film because of the steric bulk of the long oligothiophene moiety as well as the hexyl groups attached, rendering less planar molecular structure, which elevates the oxidation potential.

Theoretical Calculation. It is interesting to discuss the similarities and differences in physicochemical properties of the carboxylic acid dyes **1** and cyanoacrylic acid dyes **2** including oxidation potentials, absorption spectra, and solvatochromism. In order to get insight into the electronic structure of these systems, theoretical calculations using DFT/TD-DFT[18] for quaterthiophene carboxylic acid **3** and quaterthiophene cyanoacrylic acid **4** were carried out as model compounds for **1a** and **2a**, respectively. Figure 7 shows the calculated HOMO and LUMO of **3** and **4** together with the energy level of each molecular orbital. As expected from the similar oxidation potentials of **1** and **2**, the calculated HOMO energy level of **4** (5.41 eV below the vacuum level) is only slightly reduced compared with that of **3** (5.22 eV). In contrast, the LUMO level of **4** is considerably stabilized (≈0.8 eV), qualitatively agreeing with bathochromic shift in the absorption spectra. In addition, the TD-DFT calculations help us to understand the difference between the absorption spectra of **1a** and **2a**. The calculations gave two electronic transitions with large oscillator strengths

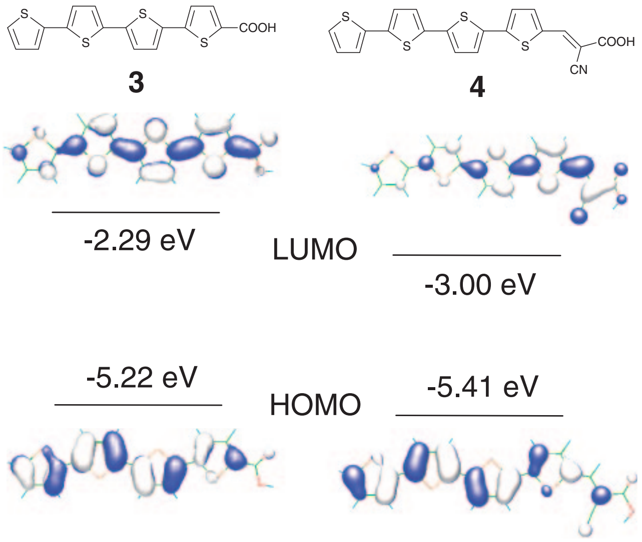


Figure 7. Calculated HOMO and LUMO of model compounds for **1a** and **2a**.

Table 3. Calculated Excitation Energies for **3** and **4**[a)]

State	Excitation	Energy/eV	f[b)]
3			
S_1	HOMO → LUMO	2.72 (455 nm)	1.26
S_2	HOMO−1 → LUMO HOMO → LUMO+1	3.39 (366 nm)	0.12
4			
S_1	HOMO → LUMO	2.27 (547 nm)	1.22
S_2	HOMO−1 → LUMO HOMO → LUMO+1	2.98 (415 nm)	0.49

a) The excitation energies were calculated by using TD-DFT at the B3LYP/6-31G(d) level. b) Oscillator strength.

(f) for **3** and **4** (Table 3) in the visible range; the energies of the intense transitions (S_1) of HOMO to LUMO are 2.72 (455 nm) and 2.27 eV (547 nm) with $f = 1.26$ and 1.22 for **3** and **4**, respectively. In addition, combined transitions (S_2) originating from HOMO−1 to LUMO and HOMO to LUMO+1 are at 3.39 (366 nm) and 2.98 eV (415 nm) with $f = 0.12$ and 0.49 for **3** and **4**, respectively. Considering these results, we summarized the band at 387 nm in the experimental spectra (Figure 4b) is the S_1 transition. On the other hand, the bands at 472 and 380 nm in the spectra of **2a** (Figure 4b) correspond to the S_1 and S_2 transitions. This indicates that the S_2 transition in **2a** plays an important role in absorbing visible light effectively.

It is also interesting to note the electron density on the HOMO and LUMO. Distribution of electron density in the HOMO for both compounds are quite similar, where the electron density delocalizes over the entire oligothiophene moiety, indicating that the anchoring group affects only through the inductive effect. By contrast, the delocalized LUMO over the oligothiophene moiety is characteristic for **3**, whereas the LUMO of **4** is much localized on the cyanoacrylic acid moiety and neighboring two thiophene rings. This means qualitatively that both inductive and resonance effects of the cyanoacrylic acid work on the LUMO of **4**, resulting in favorable electron transfer from HOMO to LUMO upon photoexcitation, which is consistent with the better DSSC performance observed for **2** than **1**.

Another interesting point that should be addressed is the pronounced negative solvatochromism for **2a**, whereas solvatochromism is negligible for **1a**. Similar negative solvatochromism has already been pointed out for related organic dyes with molecular structures of donor–oligothiophene spacer–cyanoacrylic acid,[10e,10n] where the negative solvatochromism is rationalized by decreased electron-withdrawing nature of the carboxylic acid due to partial deprotonation in polar solvents, which destabilize the excited state. For **2a** a similar mechanism is highly likely, because the LUMO localizes on the cyanoacrylic acid moiety, whereas the HOMO delocalizes on the whole molecule; destabilization caused by the deprotonation is much pronounced for LUMO. In contrast, for the carboxylic acid dye **1a** or **3**, both the HOMO and LUMO delocalize over the whole molecule, indicating that destabilization caused by deprotonation is more or less equal for both frontier orbitals, resulting in almost negligible solvatochromism. Additional rationale for negligible solvatochromisms for **1a** may lie in the different acidity of the carboxylic acid moiety of **1a** and the cyanoacrylic acid moiety of **2a**. Higher acidity of the latter can result in higher probability of deprotonation in polar solvents, which can enhance the solvent effect in the absorption spectra.

Conclusion

In summary, new simple long oligothiophene-based dyes with a cyanoacrylic acid moiety **2a**–**2c** were successfully synthesized, evaluated by means of electrochemical and optical measurements and applied to DSSCs. In comparison with related oligothiophene dyes **1a**–**1c** with a carboxylic acid anchor, the performance of **2**-based DSSCs was significantly improved. In particular the 8T-based dye **2b** and 12T-based dye **2c** showed η as high as 4.8%. The absorption spectra of **2** in solution were red-shifted compared with those of **1**, which effectively contributes to the improvement of the IPCE of the **2**-based cells at above 600 nm.

To understand the difference in the DSSC performance of the oligothiophene dyes, we investigated their electronic properties with the aid of theoretical calculations, and it turned out that the excited states of the dyes are significantly affected by the anchoring groups. The cyanoacrylic acid anchor brings about localized LUMO on the cyanoacrylic moiety, whereas the carboxylic acid anchor gives delocalized LUMO over the oligothiophene moiety. The localized LUMO on the anchoring group could facilitate electron transfer from the dye to the conduction band of TiO_2, which likely contributes to better performance for **2**-based DSSCs than **1**-based units.

The present performance of DSSCs based on the simple oligothiophene dyes, in particular the 8T-based compound **2b** and 12T-based compound **2c**, although not among the best for recently developed donor/acceptor dyes with oligothiophene spacers, are moderately good for organic dye-based DSSCs, which indicates that simple oligothiophene dyes are also promising candidates for high-performance organic dyes for

DSSC application. For realizing better performance by taking advantage of the high light absorbing ability of oligothiophene chromophore, effective molecular modification that enables harvesting near infrared light could be the next issue. Further studies in this direction are now under way in our group.

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Supporting Information

Experimental, ^{1}H and ^{13}C NMR spectra of **2a–2c**, *J–V* curve of N719-based DSSCs, adsorption measurement of **2**-loaded TiO_2 film, and cyclic voltammograms of **2**–TiO_2 film. This material is available free of charge on the web at http://www.csj.jp/journals/bcsj/.

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