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Organic Dyes Incorporating the Dithieno[3,2-*b*:2′,3′-*d*]thiophene Moiety for Efficient Dye-Sensitized Solar Cells

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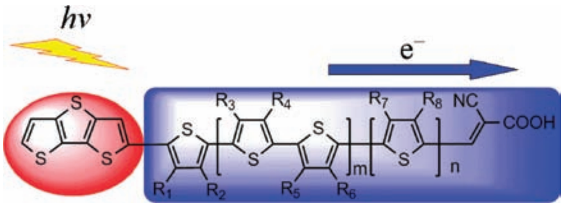
ABSTRACT



New dipolar compounds incorporating a dithieno[3,2-b:2′,3′-*d*]thiophene unit as the electron donor, an oligothiophene moiety as the conjugated spacer, and 2-cyanoacrylic acid as the electron acceptor have been synthesized. These nonarylamine type metal-free organic compounds have been successfully used as the sensitizers of dye-sensitized solar cells (DSSCs). The conversion efficiencies of the DSSCs range from 3.54 to 5.15% under AM 1.5 G irradiation. The best efficiency reached ∼70% of the ruthenium dye N719-based standard cell fabricated and measured under similar conditions.

Dye-sensitized solar cells (DSSCs) have attracted considerable attention after Grätzel's report in 1991[1] due to their easy production and design versatility of the sensitizers relative to conventional semiconductor-type solar cells. Photosensitizers certainly play a key role for highly efficient DSSCs. Ruthenium-based sensitizers, such as N3,[2] N719,[3] and black dye,[4] have achieved efficiencies of up to ∼11% under AM 1.5 G irradiation. Efficiencies surpassing the N3-based standard cells were also reported.[5] There are also increasing interests in metal-free organic sensitizers because of the rarity and high cost of the ruthenium metal. Moreover, high molar extinction coefficients of metal-free organic dyes allow the use of thinner TiO$_2$ films which is beneficial for charge separation. Efficiencies of ∼9% have been achieved for DSSCs using metal-free sensitizers.[6] Very high conversion efficiency (∼10%) and excellent stability was also reported in a recent paper of Wang.[7]

Arylamines or alkylamines are electron donors in most of the dipolar metal-free dyes,[8] and possibly the strong electron-donating ability of these donors facilitates intramolecular charge transfer between the donor and the acceptor and leads to a red shift of the absorption. In recent years, we developed

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(1) O'Reagen, B.; Grätzel, M. *Nature* **1991**, *353*, 737.

(2) Grätzel, M. *J. Photochem. Photobiol. A* **2004**, *168*, 235.

(3) Nazeeruddin, M. K.; Kay, A.; Rodicio, L.; Humphry-Baker, R.; Müller, E.; Liska, P.; Vlachopoulos, N.; Grätzel, M. *J. Am. Chem. Soc.* **1993**, *115*, 6382.

(4) Nazeeruddin, M. K.; Péchy, P.; Renouard, T.; Zakeeruddin, S. M.; Humphry-Baker, R.; Comte, P.; Liska, P.; Cevey, L.; Costa, E.; Shklover, V.; Spiccia, L.; Deacon, G. B.; Bignozzi, C. A.; Grätzel, M. *J. Am. Chem. Soc.* **2001**, *123*, 1613.

(5) (a) Chen, C.-Y.; Wu, S.-J.; Li, J.-Y.; Wu, C.-G.; Chen, J.-G.; Ho, K.-C. *Adv. Mater.* **2007**, *19*, 3888. (b) Chen, C.-Y.; Chen, J.-G.; Wu, S.-J.; Li, J.-Y.; Wu, C.-G.; Ho, K.-C. *Angew. Chem., Int. Ed.* **2008**, *47*, 7342.

(6) (a) Ito, S.; Zakeeruddin, M.; Hummphrey-Baker, R.; Liska, P.; Charvet, R.; Comte, P.; Nazeeruddin, M. K.; Péchy, P.; Takata, M.; Miura, H.; Uchida, S.; Grätzel, M. *Adv. Mater.* **2006**, *18*, 1202. (b) Choi, H.; Baik, C.; Kang, S. O.; Ko, J.; Kang, M.-S.; Nazeeruddin, M. K.; Grätzel, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 327.

(7) Zhang, G.; Bala, H.; Cheng, Y.; Shi, D.; Lv, X.; Yu, Q.; Wang, P. *Chem. Commun.* **2009**, 2198.

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some series of amine-based metal-free sensitizers for DSSCs.[9] In one report, the pyrrolyl moiety was found to be capable of electron donating upon photoexcitation.[9e] Therefore, we became interested in metal-free dyes using an electron-excessive moiety with a smaller spatial volume as a substitute for arylamines. Such sensitizers may have higher dye density on the TiO_2 surface and are also ideal for the panchromatic approach, i.e., a combination of different dyes for better light harvesting.[10] Metal-free sensitizers using nonamine donors are still rare, and DSSCs using these dyes normally have low to moderate efficiencies.[9c,11] No amine-free organic sensitizers using dithieno[3,2-*b*:2′,3′-*d*]thiophene (DTT) as the electron donor have been reported though thieno[3,2-*b*]thiophene, and DTT motifs were used in the spacer of arylamine-based dyes.[12] We therefore set out to synthesize compounds consisting of a DTT donor, a 2-cyanoacrylic acid acceptor, and an oligothiophene spacer. Use of the oligothiophene spacer is not only beneficial to high molar extinction coefficients of the absorption but also helps to suppress dark current upon appropriate incorporation of the hydrophobic hydrocarbon chain.[6b,8d,13]

Four new compounds (Figure 1) were obtained in >65% yields in several steps as illustrated in Scheme 1. Oligothiophenes without functional end groups were constructed via Kumada coupling[14] or Suzuki coupling[15] reaction. The α,*ω*-substituted oligothiophenes were synthesized according to the literature method.[16] Assembly of DTT with oligothiophene was achieved via the palladium-catalyzed Stille coupling reaction.[17] These compounds are soluble in common organic solvents.

The absorption spectra of the dyes in THF solution are displayed in Figure 2, and the corresponding data are presented in Table 1. The compounds have an intense absorption band at 426−440 nm attributable to the $\pi-\pi^*$ transition with charge-transfer character. The absorption wavelength (λ_{max}) and molar extinction coefficient of oligothiophenes normally increase with increasing effective conjugation length.[18] The order of λ_{max} values, **HY-4** ∼ **HY-3** > **HY-2** ∼ **HY-1**, is consistent with this trend. In common with many metal-free dyes, there is blue shift of the absorption peak in more polar solvents (Figure S1, see Supporting Information) or upon adsorption on TiO_2.[9d] The former may be attributed to the strong interaction of polar solvent molecules with the sensitizer, which weakens the O−H bond of the carboxylic acid and consequently decreases the electron-withdrawing nature of the COOH group. The latter may stem from deprotonation of the carboxylic acid and/or polar interaction of the dye with TiO_2. There is a very prominent red shift of the absorption band from toluene solution to the TiO_2 film for **HY-1** and **HY-2**, indicating that there is significant J-aggregation of the dye molecules (Figure S2, see Supporting Information). All the compounds emit weakly, and the large Stokes shifts observed (>2500 cm^{-1}) can be attributed to the more planar structure of the dyes at the excited state.

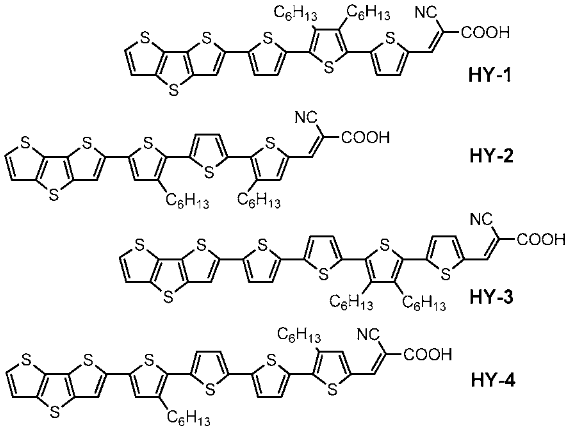

Figure 1. Structure of the dyes.

A quasi-reversible oxidation wave attributed to the oxidation of oligothiophene was found in each of the compounds, and it decreased as the number of thiophene rings

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(8) (a) Horiuchi, T.; Miura, H.; Sumioka, K.; Uchida, S. *J. Am. Chem. Soc.* **2004**, *126*, 12218. (b) Hara, K.; Sato, T.; Katoh, R.; Furube, A.; Yashihara, T.; Murai, M.; Kurashige, M.; Ito, S.; Shinpo, A.; Suga, S.; Arakawa, H. *Adv. Funct. Mater.* **2005**, *15*, 246. (c) Hagberg, D. P.; Edvinsson, T.; Marinado, T.; Boschloo, G.; Hagfeldt, A.; Sun, L. *Chem. Commun.* **2006**, 2245. (d) Koumura, N.; Wang, Z.-S.; Mori, S.; Miyashita, M.; Suzuki, E.; Hara, K. *J. Am. Chem. Soc.* **2006**, *128*, 14256. (e) Kim, S.; Lee, J. K.; Kang, S. O.; Ko, J.; Yum, J.-H.; Fantacci, S.; De Angelis, F.; D; Censo, D.; Nazeeruddin, M. K.; Grätzel, M. *J. Am. Chem. Soc.* **2006**, *128*, 16701. (f) Choi, H.; Lee, J. K.; Song, K.; Kang, S. O.; Ko, J. *Tetrahedron* **2007**, *63*, 3115. (g) Ning, Z.; Tian, H. *Chem. Commun.* **2009**, 5483. (h) Ning, Z.; Zhang, Q.; Pei, H.; Luan, J.; Lu, C.; Cui, Y.; Tian, H. *J. Phys. Chem. C* **2009**, *113*, 10307.

(9) (a) Velusamy, M.; Justin Thomas, K. R.; Lin, J. T.; Hsu, Y.-C.; Ho, K.-C. *Org. Lett.* **2005**, *7*, 1899. (b) Justin Thomas, K. R.; Lin, J. T.; Hsu, Y.-C.; Ho, K.-C. *Chem. Commun.* **2005**, 4098. (c) Tsai, M.-S.; Hsu, Y.-C.; Lin, J. T.; Chen, H.-C.; Hsu, C.-P. *J. Phys. Chem. C* **2007**, *111*, 18785. (d) Justin Thomas, K. R.; Hsu, Y.-C.; Lin, J. T.; Lee, K.-M.; Ho, K.-C.; Lai, C.-H.; Cheng, Y.-M.; Chou, P.-T. *Chem. Mater.* **2008**, *20*, 1830. (e) Yen, Y.-S.; Hsu, Y.-C.; Lin, J. T.; Chang, C.-W.; Hsu, C.-P.; Yin, D.-J. *J. Phys. Chem. C* **2008**, *112*, 12557. (f) Huang, S.-T.; Hsu, Y.-C.; Yen, Y.-S.; Chou, H.-H.; J, T; Lin, J. T.; Chang, C.-W.; Hsu, C.-P.; Tsai, C.; Yin, D.-J. *J. Phys. Chem. C* **2008**, *112*, 19739. (g) Lin, J. T.; Chen, P.-C.; Yen, Y.-S.; Hsu, Y.-C.; Chou, H.-H.; Yeh, M.-C. P. *Org. Lett.* **2009**, *11*, 97.

(10) (a) Chen, Y.; Zeng, Z.; li, C.; Wang, W.; Wang, X.; Zhang, B. *New J. Chem.* **2005**, *29*, 773. (b) Cid, J.-J.; Yum, J.-H.; Jang, S.-R.; Nazeeruddin, M. K.; Marrtínez-Ferrero, E.; Palomares, E.; Ko, J.; Grätzel, M.; Torres, T. *Angew. Chem., Int. Ed.* **2007**, *46*, 8358. (c) Robertson, N. *Angew. Chem., Int. Ed.* **2008**, *47*, 1012.

(11) Tan, S.; Zhai, J.; Fang, H.; Jiu, T.; Ge, J.; Li, Y.; Jiang, L.; Zhu, D. *Chem.—Eur. J.* **2005**, *11*, 6272.

(12) (a) Li, S.-L.; Jiang, K.-J.; Shao, K.-F.; Yang, L.-M. *Chem. Commun.* **2006**, 2792. (b) Chen, R.; Yang, X.; Tian, H.; Wang, X.; Hagfeldt, A.; Sun, L. *Chem. Mater.* **2007**, *19*, 4007. (c) Xu, M.; Li, R.; Pootrakulchote, N.; Shi, D.; Guo, J.; Yi, Z.; Zakeeruddin, S. M.; Grätzel, M.; Wang, P. *J. Phys. Chem. C* **2008**, *112*, 19770. (d) Wang, M.; Xu, M.; Shi, D.; Li, R.; Gao, F.; Zhang, G.; Yi, Z.; Humphry-Baker, R.; Wag, P.; Zakeeruddin, S. M.; Grätzel, M. *Adv. Mater.* **2008**, *20*, 4460. (e) Qin, H.; Wenger, S.; Xu, M.; Gao, F.; Jing, X.; Wang, P.; Zakeeruddin, S. M.; Grätzel, M. *J. Am. Chem. Soc.* **2008**, *130*, 9202.

(13) Hara, K.; Wang, Z.-S.; Sato, T.; Furube, A.; Katoh, R.; Sugihara, H.; Dan-oh, Y.; Kasada, C.; Shinpo, A.; Suga, S. *J. Phys. Chem. B* **2005**, *109*, 15476.

(14) Tamao, K.; Sumitani, K; Kumada, M *J. Am. Chem. Soc.* **1972**, *94*, 4374.

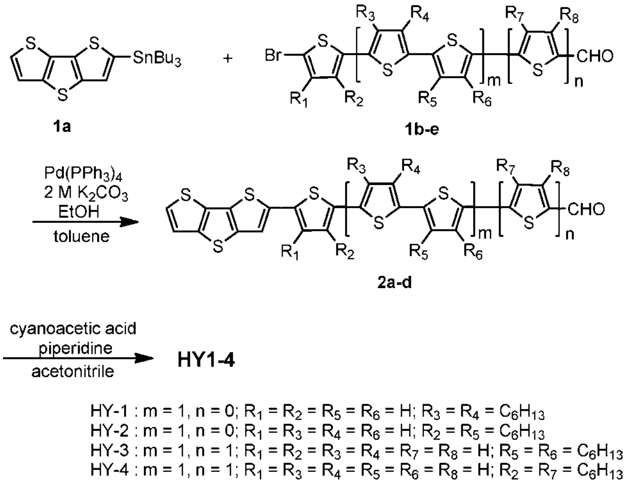
(15) (a) Miyaua, N.; Suzuki, A. *Chem. Commun* **1979**, 866. (b) Suzuki, A. *J. Organomet. Chem.* **1999**, *576*, 147.

(16) Wei, Y.; Yang, Y.; Yeh, J.-M. *Chem. Mater.* **1996**, *8*, 2659.

(17) Stille, J. K. *Angew. Chem., Int. Ed.* **1986**, *25*, 508.

(18) (a) Tour, J. M.; Wu, R. *Macromolecules* **1992**, *25*, 1901. (b) Grebner, D.; Helbig, M.; Rentsch, S. *J. Phys. Chem.* **1995**, *99*, 16991. (c) Nakanishi, H.; Sumi, N.; Aso, Y.; Otsubo, T. *J. Org. Chem.* **1998**, *63*, 8632. (d) Jones, C. L.; Higgins, S. J. *J. Mater. Chem.* **1999**, *9*, 865.

Scheme 1. Synthesis of Dyes **HY1−4**



increased.[18c] The zero−zero excitation energy estimated from the absorption onset and the oxidation potential was used to calculate the excited state potential (E_{0-0}*). The deduced E_{0-0}* values (see Table 1) are more negative than the conduction band edge of the TiO_2, −0.5 V vs NHE,[19] indicating that the electron injection process is energetically favorable. On the other hand, the first oxidation potentials of the dyes (1.10−1.21 V vs NHE, see Table 1) are more positive than the I^-/I_3^- redox couple (~0.4 V vs NHE).[12] The sufficiently low HOMO energy level of the dye will ensure more effective dye regeneration and suppress the recapture of the injected electrons by the dye cation radical.

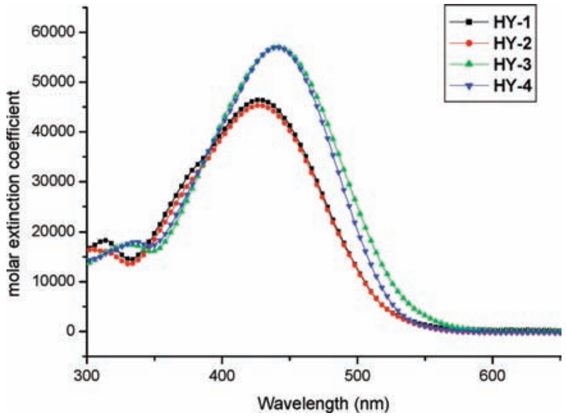


Figure 2. Absorption spectra of dyes.

Table 1. Electrooptical and Electrochemical Parameters of the Dyes

dye	λ_{abs} ($\varepsilon \times 10^{-4}$ $M^{-1}cm^{-1}$)[a] nm	λ_{em} nm	$E_{1/2}(ox)$[b] mV	E_{ox}[c] V	E_{0-0}[d] eV	E_{0-0}*[e] V
HY-1	429 (4.66), 314 (1.84)	552	509 (112)	1.21	2.25	−1.04
HY-2	426 (4.55)	549	503 (115)	1.20	2.35	−1.15
HY-3	440 (5.72), 331 (1.76)	548	411 (127)	1.11	2.30	−1.19
HY-4	440 (5.72), 337 (1.81)	553	398 (118)	1.10	2.31	−1.21

[a] Recorded in THF solutions at 298 K. [b] Recorded in CH_2Cl_2 solutions. Oxidation potential reported is adjusted to the potential of ferrocene ($E_{1/2}(ox)$ = 293 mV vs Ag/$AgNO_3$) which was used as an internal reference. Scan rate: 100 mV/s. [c] E_{ox}: the ground state oxidation potential vs NHE. [d] The bandgap, E_{0-0}, was derived from the observed optical edge. [e] E_{0-0}*: The excited state oxidation potential vs NHE.

DSSCs were fabricated using these dyes as the sensitizers, with an effective area of 0.25 cm^2, nanocrystalline anatase TiO_2 particles, and the electrolyte composed of 0.05 M I_2/0.5 M LiI/0.5 M *tert*-butylpyridine in acetonitrile solution. The performance statistics of the DSSCs fabricated using these dyes as the sensitizers under AM 1.5 illumination are listed in Table 2. Figures 3 and 4 show the photocurrent−voltage (*J*−*V*) curves and the incident photo-to-current conversion efficiencies (IPCE) of the cells, respectively. The device efficiencies are in the order of **HY-3** > **HY-1** > **HY-2** > **HY-4**, and the performances of the devices based on **HY-1**−**HY-3** are ~70% of the standard cell based on ruthenium dye N719.

Table 2. DSSCs Performance Parameters of the Dyes

cell	V_{OC} (V)	J_{SC} (mA/cm^2)	η (%)	FF
HY-1	0.62	12.09	5.02	0.67
HY-2	0.61	12.72	4.99	0.64
HY-3	0.62	13.31	5.15	0.62
HY-4	0.57	9.48	3.54	0.66
N719	0.72	15.63	7.28	0.66

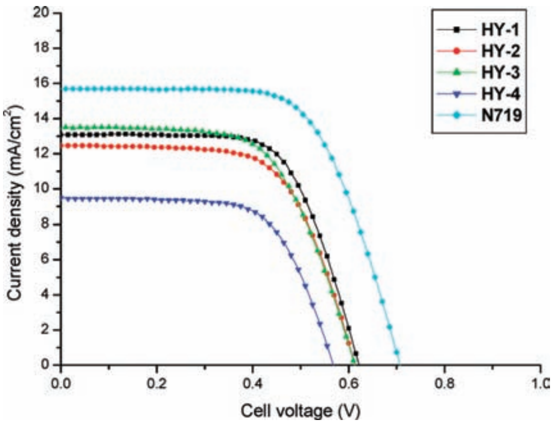


Figure 3. *J*−*V* curves of DSSCs based on the dyes.

The adsorbed dye densities of the sensitizers on TiO_2 were measured to be 3.69×10^{-7}, 3.54×10^{-7}, 3.34×10^{-7}, 2.88×10^{-7}, and 2.10×10^{-7} mol/cm^2 for **HY-1**, **HY-2**, **HY-3**,

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(19) (a) Hara, K.; Sato, T.; Katoh, R.; Furube, A.; Ohga, Y.; Shinpo, A.; Suga, S.; Sayama, K.; Sugihara, H.; Arakawa, H. *J. Phys. Chem. B* **2003**, *107*, 597. (b) Hara, K.; Tchibana, Y.; Ohga, Y.; Shinpo, A.; Suga, S.; Sayama, K.; Sugihara, H.; Arakawa, H. *Sol. Energy Mater. Sol. Cells* **2003**, *77*, 89.

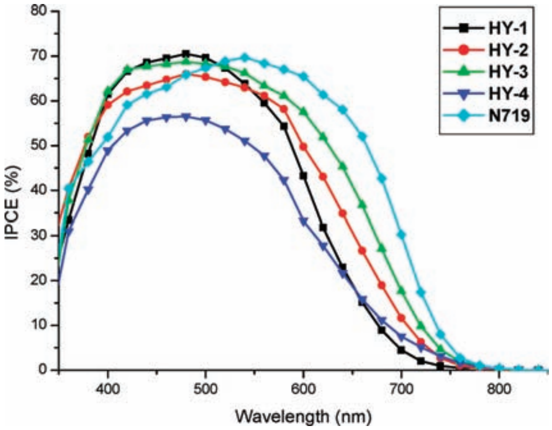

Figure 4. IPCE plots for the DSSCs using **HY1−4** and N719.

HY-4, and N719, respectively. The somewhat higher cell efficiency of **HY-3** than **HY-1** and **HY-2** is attributed to the better light harvesting of **HY-3** despite its slightly lower dye density. **HY-4** has better light harvesting than **HY-1** and **HY-2**, albeit with a lower cell efficiency (including J_{SC} and V_{OC} values). This outcome may be rationalized by the following reasons: (1) **HY-4** has a lower dye density on TiO_2; (2) J-aggregation of **HY-1**−**HY-3** improves their light-harvesting efficiencies significantly; (3) the higher HOMO level of **HY-4** leads to a slower regeneration of the oxidized sensitizer and thus a faster recombination of photoinjected electrons. The recombination time (τ_R) of the photoinjected electrons with the oxidized dyes was determined to be 1.7, 1.7, 1.6, 1.1, and 8.7 ms for **HY-1**, **HY-2**, **HY-3**, **HY-4**, and N719, respectively. Though J-aggregation was reported to be detrimental to device efficiency based on coumarin dyes,[19] there was also a known example of higher efficiency via J-aggregation of dyes.[12a] Strong aggregation of **HY-1** was supported by its nearly invariant spectrum on the TiO_2 film (after normalization) even at a concentration of 50 mM coadsorbate, chenodeoxycholic acid (CDCA). Moreover, there was no change of efficiency for the device based on **HY-1** upon addition of CDCA (10 mM). A cell of thinner TiO_2 film was tested for **HY-2**, and a drop of <0.5% was found as the film thickness decreased from 16 to 6 μm. In comparison, ∼18% drop in efficiency was observed for a cell of N719 with the same thickness variation (Table S1, see Supporting Information). This illustrates the importance of the metal-free dye for solid-state DSSCs in which the thinner film is advantageous.

Density functional calculations show that the HOMOs of these dyes largely populate on the DTT moiety as well as the thienyl conjugation chains, indicating the donor ability of DTT in these dyes (Figures S3 and S4, see Supporting Information). Preliminary TDDFT computations (Table S2, see Supporting Information) also highlight the electron-donating character of DTT toward excitation. The two lowest-lying electronic transitions, S_1 (mainly HOMO → LUMO) and S_2 (mainly HOMO−1 → LUMO and HOMO → LUMO+1), have significant oscillator strength (*f*) and extent of charge separation (i.e., changes in Mulliken charge in the transition) from the DTT to the 2-cyanoacrylic acid. This is consistent with the experimental results.

In summary, we have synthesized a series of amine-free sensitizers based on oligothiophene/dithieno[3,2-*b*:2′,3′-*d*]-thiophene. These dyes exhibit intense electronic absorption, and DSSCs fabricated from them exhibited impressively high efficiencies reaching ∼70% of the standard cell using N719 as the sensitizer. J-aggregation of the sensitizers was found to be beneficial to the conversion efficiencies of DSSCs.

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Supporting Information Available: Synthetic procedures and characterization for new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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