

Organic Dyes Containing Furan Moiety for High-Performance Dye-Sensitized Solar Cells

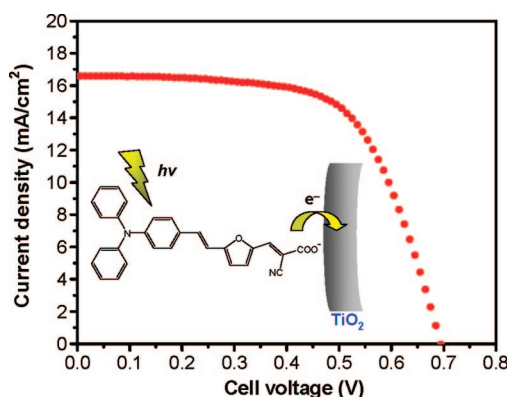
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Received October 31, 2008

ABSTRACT



New metal-free dyes with a furan moiety in the conjugated spacer between the arylamine donor and the 2-cyanoacrylic acid acceptor have been synthesized, and high efficiency dye-sensitized solar cells were fabricated using these molecules as light-harvesting sensitizers.

The increasing demand for power supply as well as environmental concern for the consumption of fossil fuel have triggered global research on the development of clean and renewable energy sources.¹ Among possible alternates for fossil fuel energy, solar energy appears to be very attractive: covering 0.16% of the Earth with 10% efficient solar conversion systems would provide power nearly twice the world's consumption rate of fossil energy.² Although silicon- and other semiconductor-based solar cells (known as photovoltaic cells)³ have dominated the solar cell market for decades, dye-sensitized solar cells (DSSCs) have also

attracted considerable interest ever since the breakthrough was made by Grätzel and co-workers.⁴ An efficiency record of ~11% has been achieved with ruthenium-based sensitizers developed by Grätzel and other groups.⁵ Although being developed later than ruthenium dyes, metal-free sensitizers also attract much attention, and a high efficiency of ~9% has also been achieved for DSSCs using metal-free sensitizers.⁶

Various metal-free dyes have been used for the construction of DSSCs.⁷ Previously we reported metal-free sensitizers

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(1) Armaroli, N.; Balzani, V. *Angew. Chem., Int. Ed.* **2007**, *46*, 52.

(2) Service, R. F. *Science* **2005**, *309*, 548.

(3) Goetzberger, A.; Hebling, C.; Schock, H.-W. *Mater. Sci. Eng. R-Rep.* **2003**, *40*, 1.

(4) (a) O'Regan, B.; Grätzel, M. *Nature* **1991**, *353*, 737. (b) Hagfeldt, A.; Grätzel, M. *Chem. Rev.* **1995**, *95*, 49. (c) Grätzel, M. *Nature* **2001**, *414*, 338. (d) Grätzel, M. *J. Photochem. Photobiol. A* **2004**, *164*, 3. (e) Grätzel, M. *Chem. Lett.* **2005**, *34*, 8.

(5) (a) Nazeeruddin, M. K.; DeAngelis, F.; Fantacci, S.; Selloni, A.; Viscardi, G.; Liska, P.; Ito, S.; Takeru, B.; Grätzel, M. *J. Am. Chem. Soc.* **2005**, *127*, 16835. (b) Chiba, Y.; Islam, A.; Watanabe, Y.; Komiya, R.; Koide, N.; Han, L. *Jpn. J. Appl. Phys., Part 2* **2006**, *45*, L638. (c) Gao, F.; Wang, Y.; Zhang, J.; Shi, D.; Wang, M.; Humphrey-Baker, R.; Wang, P.; Zakeeruddin, S. M.; Grätzel, M. *Chem. Commun.* **2008**, 2629.

which consisted of an arylamine as the electron donor, a 2-cyanoacrylic acid as the electron acceptor, and a conjugated bridge containing thiophene moieties.⁸ Compared with benzenoid moieties, the thiophene can provide more effective conjugation and lower the energy of the charge transfer transition⁹ because of its smaller resonance energy (thiophene, 29; benzene, 36 kcal/mol).¹⁰ It is therefore interesting to incorporate the furan ring with a smaller resonance energy (16 kcal/mol) in the spacer. In this letter, we report new metal-free compounds **1–4** (Figure 1) consisting of a

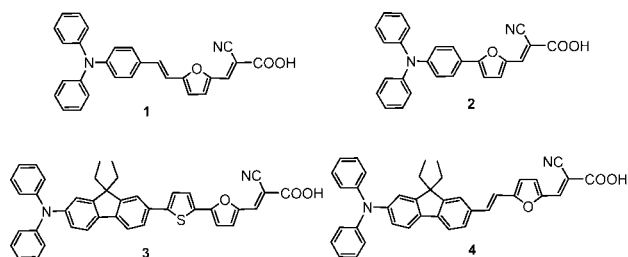


Figure 1. Structure of the dyes.

diphenylamine donor, a 2-cyanoacrylic acid acceptor, and a bridge with a furan moiety.

The dyes were obtained in moderate yields by the synthetic protocol illustrated in Scheme 1. Compounds **1** and **4** were

synthesized from Wittig reagents containing a triphenylamine or a diphenylamino-2-fluorene moiety. Reactions of these Wittig reagents with 2-furaldehyde provided intermediates **1b** and **4b**, which underwent formylation to form **1c** and **4c**. The desired products were obtained from the subsequent Knoevenagel condensation of **1c** (or **4c**) with cyanoacetic acid. For the preparation of **2** and **3**, 5-bromo-2-furaldehyde was allowed to react with appropriate phenylboronic acid via Suzuki coupling¹¹ and with a stannyl compound via Stille coupling,¹² respectively, to form intermediates **2b** and **3b**. Subsequent reactions of the intermediates with cyanoacetic acid afforded the desired compounds.

The absorption of **1–4** recorded in THF solution and the absorption spectrum of **1** in MeCN (vide infra) are displayed in Figure 2, and the data are collected in Table 1. The emission spectra are shown in Figure S1, Supporting Information (see ESI). A prominent band at ~400–600 nm can be attributed to the superposition of $\pi-\pi^*$ and charge transfer transitions. The charge transfer characteristic in these dyes is also supported by the large Stokes shifts between the absorption and the emission bands (3225–4895 cm^{-1}). A negative solvatochromism, i.e., blue shift of the charge transfer band in more polar solvents, was noticed in these dyes. For example, the absorption maxima (λ_{max}) of **1** are 485 and 439 nm in toluene and acetonitrile, respectively. This phenomenon can be attributed to the deprotonation of the carboxylic acid, which decreases the strength of the electron acceptor.^{7j,8d,e,13}

A quasi-reversible wave (E_{ox} in Table 1) observed for each compound in the cyclic voltammetry measurements may be attributed to the oxidation of the arylamine. Because of the shorter spacers in **1** and **2**, the electron-withdrawing acceptor has greater influence on the arylamine and results in higher oxidation potentials of the arylamines. The excited-state potential (E_{0-0}^*) of the compounds (–0.74 to –0.80 V vs NHE), deduced from E_{ox} and the zero–zero excitation energy (E_{0-0}) from the absorption band edge, is more negative than the conduction-band-edge energy level of the TiO_2 electrode (–0.5 V vs NHE)¹⁴ and assures that the electron injection process is energetically favorable.

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 device performance statistics under AM 1.5 illumination are listed in Table 1. Figure 3 shows the photocurrent–voltage (*J*–*V*) curves of the cells. The incident photon-to-current conversion efficiencies (IPCE) of the dyes on TiO_2 are plotted in Figure 4. The cells exhibit very high conversion efficiencies (6.12 to 7.36%), and the best performance of the device reaches ~96% of a N719-based DSSC (7.69%) fabricated

(6) (a) Ito, S.; Zakeeruddin, M.; Hummehrey-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) (a) Hara, K.; Kurashige, M.; Dan-oh, Y.; Kasada, C.; Shinpo, A.; Suga, S.; Sayama, K.; Arakawa, H. *New J. Chem.* **2003**, *27*, 783. (b) Horiuchi, T.; Miura, H.; Sumioka, K.; Uchida, S. *J. Am. Chem. Soc.* **2004**, *126*, 12218. (c) Ehret, A.; Stuhl, L.; Spitler, M. T. *J. Phys. Chem. B* **2001**, *105*, 9960. (d) Yao, Q.-H.; Meng, F.-S.; Li, F.-Y.; Tian, H.; Huang, C.-H. *J. Mater. Chem.* **2003**, *13*, 1048. (e) Sayama, K.; Tsukagoshi, S.; Mori, T.; Hara, K.; Ohga, Y.; Shinpo, A.; Abe, Y.; Suga, S.; Arakawa, H. *Sol. Energy Mater. Sol. Cells* **2003**, *80*, 47. (f) Ferrere, S.; Zaben, A.; Gregg, B. A. *J. Phys. Chem. B* **1997**, *101*, 449. (g) Ferrere, S.; Gregg, B. A. *New J. Chem. B* **2002**, *26*, 1155. (h) Hara, K.; Horiguchi, T.; Kinoshita, T.; Sayama, K.; Sugihara, H.; Arakawa, H. *Chem. Lett.* **2000**, *29*, 316. (i) 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. (j) Hagberg, D. P.; Edvinsson, T.; Marinado, T.; Boschloo, G.; Hagfeldt, A.; Sun, L. *Chem. Commun.* **2006**, 2245. (k) Hagberg, D. P.; Marinado, T.; Karlsson, K. M.; Nonomura, K.; Qin, P.; Boschloo, G.; Brinck, T.; Hagfeldt, A.; Sun, L. *J. Org. Chem.* **2007**, *72*, 9550. (l) Koumura, N.; Wang, Z.-S.; Mori, S.; Miyashita, M.; Suzuki, E.; Hara, K. *J. Am. Chem. Soc.* **2006**, *128*, 14256. (m) 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. (n) Choi, H.; Lee, J. K.; Song, K. H.; Song, K.; Kang, S. O.; Ko, J. *Tetrahedron* **2007**, *63*, 1553. (o) Kim, D.; Lee, J. K.; Kang, S. O.; Ko, J. *Tetrahedron* **2007**, *63*, 1913. (p) Choi, H.; Lee, J. K.; Song, K.; Kang, S. O.; Ko, J. *Tetrahedron* **2007**, *63*, 3115.

(8) (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.

(9) (a) Morley, J. O.; Push, D. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 3021. (b) Wu, I.-Y.; Lin, J. T.; Luo, J.; Li, C.-S.; Tsai, C.; Wen, Y. S.; Hsu, C.-C.; Yeh, F.-F.; Liou, S. *Organometallics* **1998**, *17*, 2188.

(10) March, J. *Advanced Organic Chemistry*, 4th ed.; Wiley: New York, 1992; p 45.

(11) Suzuki, A. *J. Organomet. Chem.* **1999**, *576*, 147.

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

(13) Nazeeruddin, M. K.; Péchy, P.; Renouard, T.; Zakeeruddin, S. M.; Humphrey-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.

(14) 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.

Scheme 1. Synthesis of Dyes 1–4

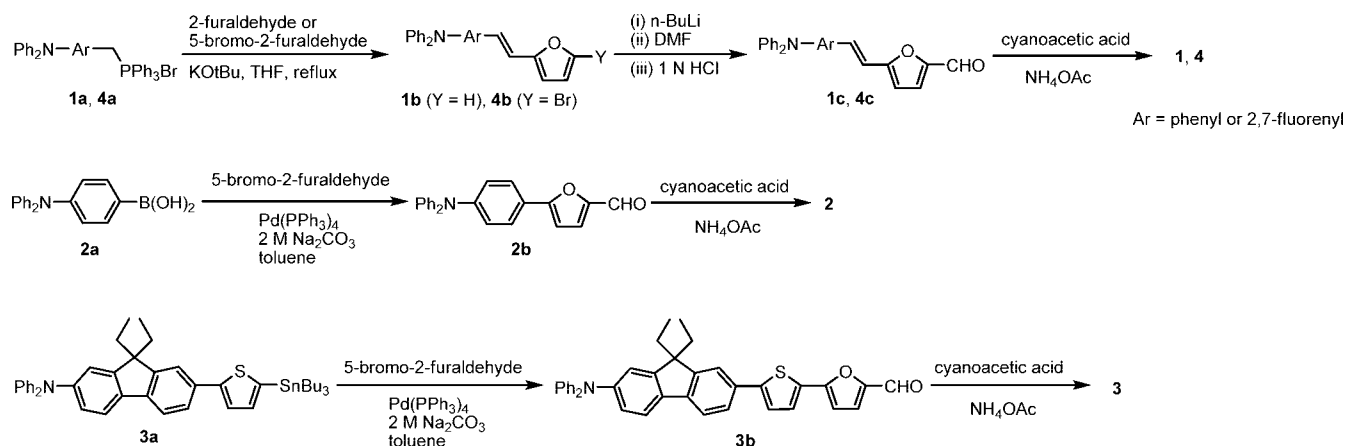


Table 1. Optical, Redox, and DSSCs Performance Parameters of the Dyes^{a,b}

dye	λ_{abs} , nm (ϵ , M ⁻¹ cm ⁻¹)	λ_{em} , nm (Φ_F)	E_{ox} (ΔE_p), mV	V_{OC} , V	J_{SC} , mA/cm ²	ff	η , %	τ_R , ms
1	469 (33000)	533	500 (220)	0.69	16.59	0.64	7.36	4.9
2	456 (33500)	496	570 (140)	0.68	14.16	0.66	6.30	5.8
3	457 (44900)	526	460 (130)	0.68	14.08	0.65	6.20	4.3
4	459 (35500)	534	440 (110)	0.68	13.44	0.67	6.12	3.1
D5	476 (45900)			0.64	14.61	0.65	6.09	4.3
N719				0.73	16.77	0.63	7.69	10.4

^a Absorption, emission, and electrochemical data were recorded in THF solutions. The absorption spectrum of D5 was recorded in MeCN. Scan rate: 100 mV/s; Electrolyte: (n-C₄H₉)₄NPF₆; ΔE_p : separation between the anodic and cathodic peaks. Potentials are quoted with reference to the internal ferrocene standard ($E_{1/2}$ = +265 mV vs Ag/AgNO₃). τ_R : recombination lifetime from the photovoltage measurements. ^b Experiments were conducted using TiO₂ photoelectrodes with approximately 15 μm thickness and 0.25 cm² working area on the FTO (7 $\Omega/\text{sq.}$) substrates.

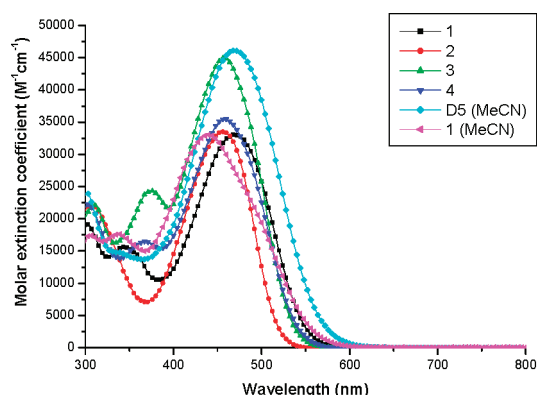


Figure 2. Absorption spectra of dyes.

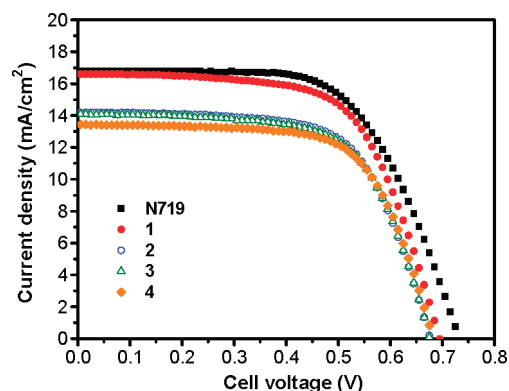


Figure 3. J – V curves of DSSCs based on the dyes.

and measured under similar conditions. The device efficiencies are in the order of **1** > **2** > **3** > **4**, and the difference between structurally similar **1** and **2** may be rationalized by the following factors: (a) the compound with better absorption in the longer wavelength region is expected to have better light-harvesting, i.e., **1** > **2**; and (b) the higher dye density adsorbed on TiO₂ (**1**, 4.5; **2**, 4.1×10^{-7} mol/cm²) is beneficial to light-harvesting, i.e., **1** > **2**. The recombination lifetimes (Table 1) of the photoinjected electron with the

oxidized dye (τ_R : **1**, 4.9; **2**, 5.8; **3**, 4.3; **4**, 3.1; N719, 10.4 ms) were also measured by transient photovoltage at open circuit¹⁵ and found to be in parallel with the trend of the cell efficiencies.

A comparison is made on **1** and the thiophene congener, 3-(5-4-(diphenylamino)styryl)thiophen-2-yl-2-cyanoacrylic

(15) Kopidakis, N.; Benkstein, K. D.; van de Lagemaat, J.; Frank, A. J. *J. Phys. Chem. B* **2003**, *107*, 11307.

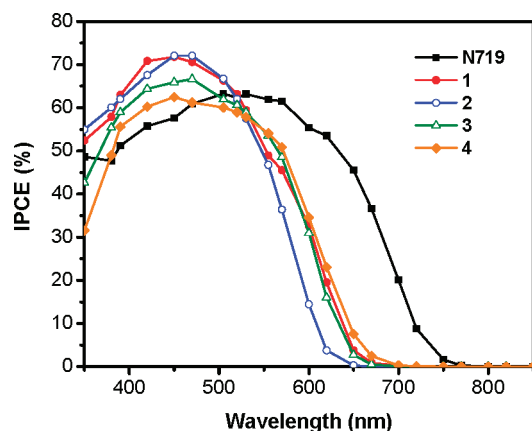


Figure 4. IPCE plots for the DSSCs using dyes 1–4

acid (D5).^{7j,k} Though D5 has slightly better light-harvesting ($\lambda_{\text{abs}} = 476 \text{ nm}$ ($45\,900 \text{ M}^{-1}\text{cm}^{-1}$) in MeCN (Figure 2); dye density on $\text{TiO}_2 = 4.8 \times 10^{-7} \text{ mol/cm}^2$) than **1** ($\lambda_{\text{abs}} = 439 \text{ nm}$ ($33\,000 \text{ M}^{-1}\text{cm}^{-1}$) in MeCN; dye density on $\text{TiO}_2 = 4.5 \times 10^{-7} \text{ mol/cm}^2$), the performance of DSSC based on **1** is superior to that based on D5 ($V_{\text{OC}} = 0.64 \text{ V}$; $J_{\text{SC}} = 14.61 \text{ mA/cm}^2$; $ff = 0.65$; $\eta = 6.09\%$) fabricated and measured

under similar conditions. Faster recombination lifetimes of D5 ($\tau_{\text{R}} = 4.3 \text{ ms}$) may deteriorate the efficiency of the cell. Possible nonbonded S–S interaction¹⁶ in D5 may be also detrimental to electron injection of the excited dye into TiO_2 . Another possibility for the lower efficiency of D5 may be due to the slightly higher tendency of thiophene to trap charge from the arylamine, based on our preliminary computation results using time-dependent density functional theory (TDDFT) at the B3LYP/6-31G* level of theory.

In summary, we have synthesized a new series of metal-free sensitizers containing the furan entity for high-performance DSSCs. The highest efficiency nearing to that of N719 is intriguing. More detailed elucidation of the cell performance and extension of this synthetic strategy to better sensitizers are currently ongoing.

Acknowledgment. We thank Academia Sinica, National Science Council (Taiwan), and Plasmag Technology, Inc. for financial support.

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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(16) Yamada, K.; Okamoto, T.; Kudoh, K.; Wakamiya, A.; Yamaguchi, S.; Takeya, J. *Appl. Phys. Lett.* **2007**, *90*, 072102.