View Article Online / Journal Homepage / Table of Contents for this issue

Organic dyes containing thienylfluorene conjugation for solar cells†

K. R. Justin Thomas,[a] Jiann T. Lin,*[ab] Ying-Chan Hsu[c] and Kuo-Chuan Ho*[c]

Received (in Cambridge, UK) 12th May 2005, Accepted 23rd June 2005
First published as an Advance Article on the web 13th July 2005
DOI: 10.1039/b506732d

New organic dyes that contain variable lengths of conjugation featuring alternating thiophene and fluorene segments have been synthesized and efficient nano-crystalline TiO_2 based dye-sensitized solar cells were fabricated using these molecules as light-harvesting sensitizers.

Electronic devices such as light-emitting diodes,[1] field-effect transistors,[2] and solar cells[3] fabricated using organic materials continue to attract wide attention owing to their ease in manufacturing and structural flexibility towards modification. Although silicon based photovoltaics have received commercial success they are devoid of possibilities for improvement by structural alternation.[4] Recent progress with nanocrystalline TiO_2 based dye-sensitized solar cells (DSSCs) has triggered the demand for the search for organic and organometallic dyes suitable for application in such modules.[5] The organic dyes that were efficient in photocurrent generation all contained a donor and acceptor bridged by π-conjugation. In most designs, amines served as donors while a 2-cyanoacrylic acid or rhodamine unit rendered the acceptor functionality. The presence of a carboxylic acid moiety in the acceptor end assisted the anchoring of the dye molecules on the TiO_2 surface. Donor–acceptor architectured coumarin-,[6] indoline-,[7] cyanine-[8] and hemicyanine-based[9] dyes were found to perform efficiently in DSSCs. A dye possessing broad and intense spectral features that is capable of absorbing the entire solar spectrum is an ideal choice. In this communication we report new dyes that contain a conjugation bridge composed of alternating thiophene and fluorene units, diphenylamine donor and 2-cyanoacrylic acid as acceptor (Fig. 1). In such an architecture we show that by increasing the population of the linking segments, the optical density can be dramatically raised. To the best of our knowledge fluorene-based dyes have not been exploited for the fabrication of DSSCs.

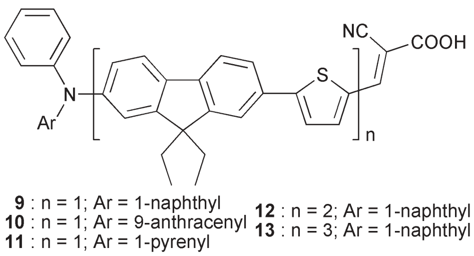


Fig. 1 Structure of the dyes.

The dyes were constructed by the stepwise synthetic protocol illustrated in Scheme 1.‡ From the known compound, 2-(7-bromo-9,9-diethyl-9*H*-fluoren-2-yl)thiophene (**2**), diarylamine substituted fluorenylthiophene derivatives (**3–5**) were obtained by C–N coupling reactions involving Hartwig's catalyst[10] and the corresponding diarylamine. These thiophene derivatives were converted into their corresponding thiophenealdehydes (**6–8**) by lithiation with *n*-butyl lithium and subsequent quenching with dimethylformamide. Later the aldehydes **6–8** were converted to the dyes **9–11** by reaction with cyanoacetic acid in refluxing acetic acid in the presence of ammonium acetate. In another step, the stannylene precursor of **3** prepared by treating the lithium derivative of **3** with tributyltin chloride in thf was used in the Stille reaction with **2** to produce the bis(thienylfluorene) conjugated analog of **3**. This was then converted to the aldehyde which produced the dye **12** on treatment with cyanoacetic acid. One more similar stepwise sequence starting with the bis(thienylfluorene) conjugated analog of **3** was executed to obtain the third generation dye **13**. The dyes are red colored and soluble in thf.

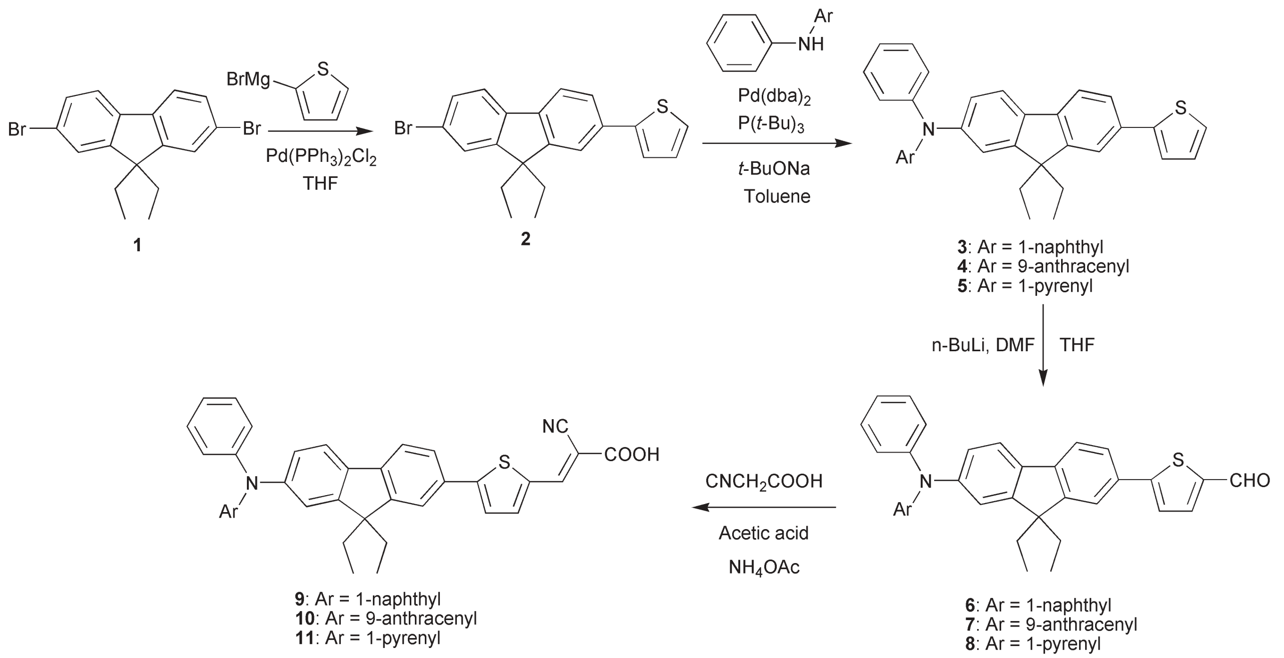
The absorption and emission spectra of the dyes recorded in thf solution are displayed in Fig. 2 and the data are collected in Table 1. All the dyes exhibit a single prominent band probably representing the superposition of π–π* and charge transfer transitions. Though the absorption maximum remains nearly the same for all the compounds, the optical density of this band increases rapidly on extending the conjugation by introducing the additional thienylfluorene segments (Fig. 2). This can be understood from molecular modeling (SPARTAN, PM3) studies on **9** and **12**. The ground state structure of **12** possesses a nearly 90° twist between the thienyl and the fluorenyl segments, while there is only a slight twist in **9**. These compounds are the first examples of DSSC active dyes to date to display larger absorption coefficients. Interestingly the interaction between the donor and acceptor is minimized on increasing the conjugation length of the bridge. This is reflected in the emission band position of the dyes **9**, **12** and **13**. Consequently this slightly decreases the magnitude of charge separation for elongated derivatives **12** and **13**.

The dyes can be reversibly oxidized at moderately high oxidation potentials. The oxidation potentials are more positive than the ferrocene/ferrocenium and I^-/I_3^- redox couples.[11] An oxidation potential higher than that of the iodine couple is necessary to forbid the backward electron transfer to electrolyte solution and ensure forward electron injection into the TiO_2 layer in the DSSC setup. The reversibility of the oxidation couple will be beneficial for the stability of the DSSCs in long run.

---

[a] *Institute of Chemistry, Academia Sinica, 115 Nankang, Taipei, Taiwan. E-mail: jtlin@chem.sinica.edu.tw; Fax: 886-2-27831341; Tel: 886-2-27898522*
[b] *Department of Chemistry, National Central University, 320 Chungli, Taiwan*
[c] *Department of Chemical Engineering, National Taiwan University, Taipei 106, Taiwan. E-mail: kcho@ntu.edu.tw*

† Electronic supplementary information (ESI) available: Characterisation data of the new compounds described in this communication. See http://dx.doi.org/10.1039/b506732d



Scheme 1 Synthesis of the first generation dyes.

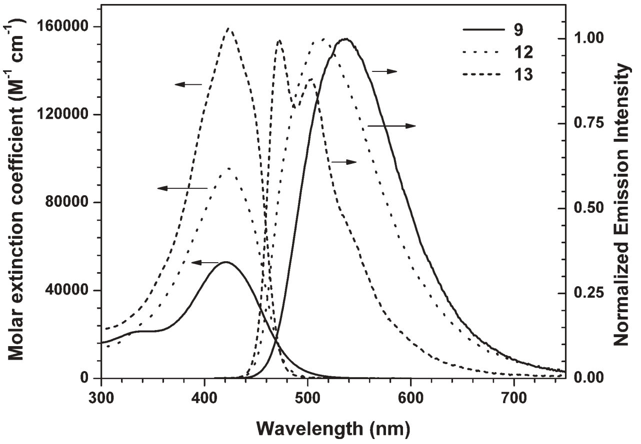


Fig. 2 Absorption and emission spectra of the dyes (**9**, **12** and **13**) recorded in thf.

The DSSCs fabricated, with an effective area of 0.25 cm^2, using these dyes as light harvesting sensitizers, 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 showed impressive photon-to-electron conversion. The device performance statistics under AM 1.5 illumination are listed in Table 1. Particularly the performance of the device manufactured with dye **9** is close to that of the standard ruthenium dye N3. The action and absorption spectra of the dye **9** adsorbed on TiO_2 are presented in Fig. 3. We believe that the more efficient charge separation in **9** compared to **12** and **13** (*vide supra*) accounts for the better performance of DSSCs using **9**, although **12** and **13** have significantly higher absorption coefficients. Another factor that is crucial in affecting the performance of the dyes in DSSCs is the oxidation potential of the dyes. Incidentally the oxidation potential of **9** is slightly higher than that of other dyes. This will increase the driving force for the reduction of the oxidized dye and ensure the retardation of back electron transfer from TiO_2 to dye.

In summary, we have synthesized a new class of dyes featuring thienylfluorene conjugation, diarylamine donors and 2-cyanoacrylic acid acceptors. Despite the lower wavelength absorption, the fact that the DSSC performances achieved for the dyes are nearing that of N3 is intriguing. We are currently extending this strategy to synthesize spirobifluorene based dyes.

Table 1 Optical, redox and DSSC 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 (%)
9	421 (52 900)	538 (0.28)	509 (82)	0.65	12.47	0.65	5.23
10	421 (46 300)	536 (0.19)	451 (109)	0.57	7.59	0.67	2.86
11	425 (54 500)	537 (0.33)	462 (66)	0.60	8.38	0.67	3.35
12	423 (95 500)	512 (0.26)	447 (59), 613 (61)	0.61	9.83	0.65	3.89
13	423 (159 200)	472, 504 (0.37)	437 (65), 569 (70)	0.61	9.81	0.64	3.80
N3				0.62	13.98	0.63	5.50

[a] Absorption and electrochemical data were recorded in tetrahydrofuran solutions. Scan rate: 100 mV s^{-1}, electrolyte: $(n\text{-}C_4H_9)_4NPF_6$; ΔE_p is the separation between the anodic and cathodic peaks. Potentials are quoted with reference to the internal ferrocene standard ($E_{1/2}$ = +265 mV *vs.* Ag/AgNO$_3$). [b] Experiments were conducted using TiO_2 photoelectrodes with approximately 14-μm thickness and 0.25 cm^2 working area on the FTO (7 Ω square^{-1}) substrates.

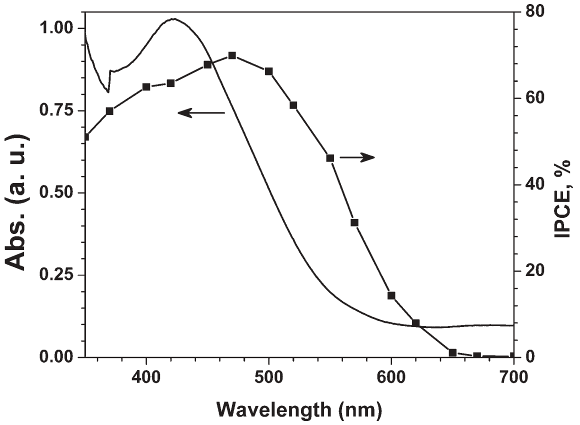


Fig. 3 Absorption spectrum of the dye **9** adsorbed on nanocrystalline TiO_2 and the action spectrum for the DSSC constructed using **9**.

We thank CTCI Foundation, Taipei, Research Centre for Applied Sciences, Academia Sinica (ASCAS) and National Science Council, Taiwan for financial support.

Notes and references

‡ All the dyes described here were thoroughly characterized by ^{1}H NMR and mass spectral methods and elemental analyses. Full synthesis and characterization details are furnished in the supporting information.

1 (*a*) T. W. Kelley, P. F. Baude, C. Gerlach, D. E. Ender, D. Muyres, M. A. Haase, D. E. Vogel and S. D. Theiss, *Chem. Mater.*, 2004, **16**, 4413; (*b*) U. Mitschke and P. Bäuerle, *J. Mater. Chem.*, 2000, **10**, 1471; (*c*) G. Hughes and M. R. Bryce, *J. Mater. Chem.*, 2005, **15**, 94.

2 (*a*) J. A. Merlo, C. R. Newman, C. P. Gerlach, T. W. Kelley, D. V. Muyres, S. E. Fritz, M. F. Toney and C. D. Frisbie, *J. Am. Chem. Soc.*, 2005, **127**, 3997; (*b*) S. Amriou, A. Mehta and M. R. Bryce, *J. Mater. Chem.*, 2005, **15**, 1232; (*c*) C. R. Newman, C. D. Frisbie, D. A. da Silva, J. L. Bredas, P. C. Ewbank and K. R. Mann, *Chem. Mater.*, 2004, **16**, 4436.

3 (*a*) C. Winder and N. S. Sariciftci, *J. Mater. Chem.*, 2004, **14**, 1077; (*b*) H. Hoppe and N. S. Sariciftci, *J. Mater. Res.*, 2004, **19**, 1924; (*c*) H. Spanggaard and F. C. Krebs, *Sol. Energy Mater. Sol. Cells*, 2004, **83**, 125.

4 A. Goetzberger, C. Hebling and H.-W. Schock, *Mater. Sci. Eng., R*, 2003, **40**, 1.

5 (*a*) M. Grätzel, *Chem. Lett.*, 2005, **34**, 8; (*b*) M. S. Dresselhaus and I. L. Thomas, *Nature*, 2001, **414**, 332; (*c*) M. Grätzel, *Pure Appl. Chem.*, 2001, **73**, 459; (*d*) K. Hara, T. Sato, R. Katoh, A. Furube, T. Yoshihara, M. Murai, M. Kurashige, S. Ito, A. Shinpo, S. Suga and H. Arakawa, *Adv. Funct. Mater.*, 2005, **15**, 246; (*e*) T. Horiuchi, H. Miura, K. Sumioka and S. Uchida, *J. Am. Chem. Soc.*, 2004, **126**, 3014; (*f*) R. Argazzi, N. Y. M. Iha, H. Zabri, F. Odobel and C. A. Bignozzi, *Coord. Chem. Rev.*, 2004, **248**, 1299; (*g*) M. Grätzel, *Nature*, 2001, **414**, 338; (*h*) U. Bach, D. Lupo, P. Comte, J. E. Moser, F. Weissortel, J. Salbeck, H. Spreitzer and M. Grätzel, *Nature*, 1998, **395**, 583; (*i*) B. O'Regan and M. Grätzel, *Nature*, 1991, **353**, 737; (*j*) A. Hagfeldt and M. Grätzel, *Acc. Chem. Res.*, 2000, **33**, 269.

6 (*a*) K. Hara, K. Sayama, Y. Ohga, A. Shinpo, S. Suga and H. Arakawa, *Chem. Commun.*, 2001, 569; (*b*) K. Hara, M. Kurashige, Y. Dan-oh, C. Kasada, A. Shinpo, S. Suga, K. Sayama and H. Arakawa, *New J. Chem.*, 2003, **27**, 783.

7 (*a*) T. Horiuchi, H. Miura and S. Uchida, *Chem. Commun.*, 2003, 3036; (*b*) T. Horiuchi, H. Miura and S. Uchida, *J. Photochem. Photobiol., A*, 2004, **164**, 29.

8 A. Ehret, L. Stuhl and M. T. Spitler, *J. Phys. Chem. B*, 2001, **105**, 9960.

9 (*a*) Q.-H. Yao, F.-S. Meng, F.-Y. Li, H. Tian and C.-H. Huang, *J. Mater. Chem.*, 2003, **13**, 1048; (*b*) Z.-S. Wang, F.-Y. Li and C.-H. Huang, *Chem. Commun.*, 2000, 2063.

10 J. F. Hartwig, M. Kawatsura, S. I. Hauck, K. H. Shaughnessy and L. M. Alcazar-Roman, *J. Org. Chem.*, 1999, **64**, 5575; J. F. Hartwig, *Acc. Chem. Res.*, 1998, **31**, 852.

11 The I^-/I_3^- couple is located at 0.2 V *vs.* SCE (or −0.18 V *vs.* Fc). A. Hagfeldt and M. Grätzel, *Chem. Rev.*, 1995, **95**, 49.