## Novel 4-Trifluoromethylthiazole-5-carboxylic Acid as Acceptor in Photosensitized Dyes

Satoru Iwata,\*1 Misa Aoyama,1 Satoshi Uchida,2 and Kiyoshi Tanaka\*1

<sup>1</sup>Laboratory of Molecular Control, Faculty of Science and Technology, Seikei University, Musashino, Tokyo 180-8633

<sup>2</sup>Research Center for Advanced Science and Technology, The University of Tokyo, Meguro-ku, Tokyo 153-8904

(Received July 6, 2012; CL-120721; E-mail: iwata@st.seikei.ac.jp, tanaka@st.seikei.ac.jp)

Novel photosensitized dyes containing 4-trifluoromethylthiazole-5-carboxylic acid as an acceptor are synthesized. Stilbene-type dyes with this acceptor show high performance as dye-sensitized solar cells. The trifluoromethyl group is assumed to act as a suppressor of electron back-donation from the TiO<sub>2</sub> conduction band to the electrolyte and as an accelerator of charge separation in the photoexcited state.

Dye-sensitized solar cells (DSCs) have reached the stage of practical applications. High performances of DSCs have been reported using ruthenium complexes, which exhibit  $\eta$  (solar energy to electricity conversion efficiency) values above 11%.<sup>1</sup> Recently, metal-free sensitizers have been reported to have effective performances ( $\eta = 7-10\%$ ).<sup>2</sup>

The architecture of a metal-free sensitizer needs an electron donor, a spacer ( $\pi$ -conjugated bridge), and an electron acceptor linked with an anchor. Conjugated amines such as triphenylamine have been widely used as donor parts,<sup>3</sup> and stilbenes, phenylenes, and conjugated thiophenes have been used as spacers.<sup>4</sup> However, the diversity of acceptors is not enough; most effective sensitized dyes consist of cyanoacrylic acid or rhodanine acetic acid.<sup>5</sup> In this communication, we report novel sensitized dyes with trifluoromethyl (CF<sub>3</sub>-) thiazolecarboxylic acid as an acceptor. Previously we reported that azo dyes containing trifluoromethyl-thiazolecarboxylate show long wavelength absorption,<sup>6</sup> and so it is expected that the introduction of trifluoromethyl-thiazolecarboxylic acid to the sensitized dyes as an acceptor will lead to absorption over a wide range of wavelengths of sun light.

The synthetic procedures for the dyes are shown in Scheme 1 (details are shown in the  $\mathrm{ESI}^{14}$ ). Dyes with a CF<sub>3</sub> group, i.e., **MCL05** and **MCL06**, and dyes with no CF<sub>3</sub> group, i.e., **MCL08** and **MCL09**, were synthesized via Horner–Wadsworth–Emmons reactions using the corresponding thiazolemethylphosphonates **3a** and **3b** obtained by Michaelis–Arbuzov reactions of (bromomethyl)thiazole **2a** or **2b**.



**Scheme 1.** Synthesis of dyes. Reagents (a) NBS, AIBN/CCl<sub>4</sub>; (b) P(OEt)<sub>3</sub>; (c) R<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CHO, MeONa/THF; (d) KOH/EtOH, HCl.

The absorption spectra of the obtained dyes are shown in Figure 1, and the absorption and the redox potential data are summarized in Table 1. The absorptions of the dyes with no CF<sub>3</sub> group, **MCL08** and **MCL09**, are slightly blue-shifted compared to those of the CF<sub>3</sub>-containing dyes, **MCL05** and **MCL06**. The oxidation potentials,  $E_{ox}$ , were measured from the peak potential  $E_p$  (revised using the ferrocene oxidation potential). The redox energy gaps ( $E_{0-0}$ ) were calculated from the cross points between the abscissa and the tangent to the curve where the slope was the strongest, and the  $E_{red}$  values were calculated from  $E_{ox} - E_{0-0}$ .

The HOMO and LUMO energy levels of the dyes were calculated using DFT with B3LYP6-31G<sup>\*</sup> under vacuum conditions (Figure 2). The experimental HOMO and LUMO levels were estimated from the values of  $E_{ox}$  and  $E_{red}$ , respectively, according to the following equation.<sup>7</sup>



Figure 1. Absorption spectra of dyes in acetonitrile solution,  $[dye] = 1.0 \times 10^{-5} \text{ M.}$ 

Table 1. Absorption and redox properties of dyes

Dye	$\frac{\lambda_{abs}{}^a/nm}{(\epsilon/\times10^4\mathrm{M}^{-1}\mathrm{cm}^{-1})}$	$E_{\rm ox}^{b}/V$ (vs. NHE)	$E_{0-0}^{\rm c}/{\rm eV}$	$E_{\rm red}^{\rm d}/{\rm V}$
MCL05	420 (2.4)	1.06	2.54	-1.48
MCL06	433 (3.3)	0.86	2.45	-1.59
MCL08	399 (2.7)	1.02	2.63	-1.61
MCL09	423 (2.3)	0.83	2.48	-1.65

<sup>a</sup>Absorption was recorded in an acetonitrile solution ( $1.0 \times 10^{-5}$  M). <sup>b</sup> $E_{ox}$  shows oxidation peak potential vs. NHE. Cyclic voltammetry was measured in an acetonitrile solution containing 0.1 M tetrabutylammonium perchlorate as a supporting electrolyte. Working electrode: platinum, counter electrode: platinum wire, reference electrode: Ag/Ag<sup>+</sup> calibrated with ferrocene/ferrocenium, scanning rate: 100 mV s<sup>-1</sup>. <sup>c</sup>The  $E_{0-0}$  value was estimated from the cross point between the abscissa and the tangent to the curve where the slope was the strongest. <sup>d</sup> $E_{red}$  was calculated from  $E_{ox} - E_{0-0}$ .



Figure 2. Diagram of HOMO and LUMO energy levels.



Figure 3. Photocurrent–voltage (xenon lamp) and dark current–voltage charts of DSCs.

$$E (eV) = -[E (V vs. NHE) + 4.2]$$
 (1)

The calculated values are comparable to the measured values. With regard to the energy levels of DSCs, the following requirements should be satisfied; the HOMO energy level is below the  $I^-/I_3^-$  redox potential (-4.6 eV or 0.4 V vs. NHE), and the LUMO energy level is above the conduction band (CB) edge of TiO<sub>2</sub> (-3.7 eV or -0.5 V vs. NHE).<sup>8</sup> Moreover, it has been reported that the energy gaps between the CB and the LUMO should be more than 0.2–0.3 eV,<sup>9</sup> and the HOMO energy level separated from the  $I^-/I_3^-$  redox potential by as little as 0.15 eV for efficient electron injection.<sup>10</sup> All the dyes seem to satisfy these requirements.

The DSCs were fabricated using screen-printed  $TiO_2$  (0.25 cm<sup>2</sup>) on FTO glass. The photovoltaic performances of the DSCs were measured using a xenon lamp (light > 650 nm filtered out) and an AM1.5G solar simulator, where the light intensity was adjusted to 100 mW cm<sup>-2</sup> (the light source spectra are shown in Figure S1<sup>14</sup>). The photocurrent–voltage and the dark current–voltage charts are shown in Figure 3, and the photovoltaic properties are summarized in Table 2, where **D149** dye<sup>2</sup> data are added as a reference for our fabricating conditions. These results show that the thiazolecarboxylic acid works as a new type of acceptor and anchor unit of the DSC.

 Table 2. Photovoltaic performances of DSSCs<sup>a,b</sup>

Dye	$V_{\rm oc}/{ m V}$	$J_{\rm sc}/{ m mAcm^{-2}}$	$\eta/\%$	ff
MCL05	0.68	8.8	3.6	0.60
	0.66	6.8	2.8	0.63
MCL06	0.63	10.7	4.0	0.59
	0.63	8.7	3.3	0.60
MCL08	0.67	9.4	3.6	0.57
	0.67	6.3	2.7	0.64
MCL09	0.61	9.7	3.7	0.62
	0.61	8.2	3.1	0.62
D149 <sup>c</sup>	0.70	12.9	5.1	0.57
	0.67	12.9	4.8	0.56

<sup>a</sup>Irradiated with 300 W Xe lamp (100 mW cm<sup>-2</sup>), and light > 650 nm was filtered out. The cell size:  $0.25 \text{ cm}^2$ , counter electrode: platinum-coated FTO glass. The electrolyte ingredients; I<sub>2</sub> (0.05 M), LiI (0.10 M), 1,2-dimethyl-3-propylimidazolium iodide (0.60 M), *t*-butylpyridine (0.05 M) in 3-meth-oxypropionitrile. <sup>b</sup>Values listed in boldface are derived from the measurements under AM1.5G. <sup>c</sup>The reference data using chenodeoxycholic acid as a coadsorbent.



**Figure 4.** IPCE spectra and absorption spectra on  $TiO_2$  of the DSCs. The absorption spectra on  $TiO_2$  were normalized<sup>12</sup> and absorptions <350 nm were deleted due to  $TiO_2$  self-absorbance.

It has been reported that the dark current is caused by the reverse current from the CB of TiO2 to the electrolyte (the backdonation current) and that the back-donation current at low voltage reflects a small open-circuit voltage  $(V_{oc})$ .<sup>1,11</sup> Indeed, the order of  $V_{\rm oc}$  values of the DSCs is MCL09 < MCL06 < MCL08 < MCL05 (under irradiation with a xenon lamp), and this order is comparable to the order of the starting voltages of their dark currents (Figure 3). Therefore, the diphenylamino and CF<sub>3</sub> groups seem to defend the back-donation current by their steric hindrance effects. The  $\eta$  values are dependent on the shortcircuit photocurrent densities  $(J_{sc})$ ; MCL06, having the largest  $J_{\rm sc}$  value, shows the best performance. The CF<sub>3</sub> group in MCL06 is assumed to play an effective role in charge separation in the photoexcited state, leading to the large  $J_{\rm sc}$  value. The influence of the light source (AM1.5G or xenon lamp) on the cell performance is explained by the light source spectra, i.e., the light intensity was adjusted to  $100 \,\mathrm{mW \, cm^{-2}}$  in all spectrum areas, so the narrow spectrum light (xenon lamp) has a relatively strong intensity. This is the reason why xenon-lamp irradiation shows good performances compared to the AM1.5G lamp.

The incident photo-to-current conversion efficiency (IPCE) spectra and the absorbance spectra on the TiO<sub>2</sub> cell are shown in Figure 4. The absorption spectra on the TiO<sub>2</sub> cell are broad compared to those in solution. The IPCE spectra show a similar pattern to absorption on the TiO<sub>2</sub> cell. The stilbene-type dyes show satisfactory IPCE spectra; in particular, **MCL05** recorded 86% at 430 nm. When photoabsorption loss by the cell<sup>13</sup> is considered, this record shows almost perfect photo-to-current conversion.

In conclusion, novel photosensitized dyes containing 4trifluoromethylthiazole-5-carboxylic acid as an acceptor show high performances, with  $\eta$  values of 3–4% in DSCs. The CF<sub>3</sub> group is assumed to act as a suppressor of electron backdonation from TiO<sub>2</sub> to the electrolyte and as an accelerator of charge separation in the photoexcited state. The optimizations of the cell fabrication conditions are not enough, so superior performances are expected.

## **References and Notes**

- 1 M. Grätzel, Inorg. Chem. 2005, 44, 6841.
- 2 a) T. Horiuchi, H. Miura, K. Sumioka, S. Uchida, J. Am. Chem. Soc. 2004, 126, 12218. b) S. Ito, H. Miura, S. Uchida, M. Takata, K. Sumioka, P. Liska, P. Comte, P. Péchy, M. Grätzel, Chem. Commun. 2008, 5194. c) W.-H. Liu, I.-C. Wu, C.-H. Lai, C.-H. Lai, P.-T. Chou, Y.-T. Li, C.-L. Chen, Y.-Y. Hsu, Y. Chi, Chem. Commun. 2008, 5152. d) S. Hwang, J. H. Lee, C. Park, H. Lee, C. Kim, C. Park, M.-H. Lee, W. Lee, J. Park, K. Kim, N.-G. Park, C. Kim, Chem. Commun. 2007, 4887. e) Z.-S. Wang, Y. Cui, Y. Dan-oh, C. Kasada, A. Shinpo, K. Hara, J. Phys. Chem. C 2008, 112, 17011. f) A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo, H. Pettersson, Chem. Rev. 2010, 110, 6595.
- 3 a) C.-H. Yang, H.-L. Chen, Y.-Y. Chuang, C.-G. Wu, C.-P. Chen, S.-H. Liao, T.-L. Wang, *J. Power Sources* 2009, 188, 627. b) D. P. Hagberg, J.-H. Yum, H. Lee, F. De Angelis, T. Marinado, K. M. Karlsson, R. Humphry-Baker, L. Sun, A. Hagfeldt, M. Grätzel, Md. K. Nazeeruddin, *J. Am. Chem. Soc.* 2008, 130, 6259. c) W. Xu, B. Peng, J. Chen, M. Liang, F. Cai, *J. Phys. Chem. C* 2008, 112, 874.
- 4 a) Z.-S. Wang, Y. Cui, Y. Dan-oh, C. Kasada, A. Shinpo, K. Hara, *J. Phys. Chem. C* 2007, *111*, 7224. b) D. P. Hagberg, T. Marinado, K. M. Karlsson, K. Nonomura, P. Qin, G.

Baschloo, T. Brinck, A. Hagfeldt, L. Sun, *J. Org. Chem.* **2007**, *72*, 9550. c) G. Li, K.-J. Jiang, Y.-F. Li, S.-L. Li, L.-M. Yang, *J. Phys. Chem. C* **2008**, *112*, 11591.

- 5 a) T. Horiuchi, H. Miura, S. Uchida, *Chem. Commun.* 2003, 3036. b) H. Tian, X. Yang, R. Chen, R. Zhang, A. Hagfeldt, L. Sun, *J. Phys. Chem. C* 2008, *112*, 11023. c) Y.-T. Li, C.-L. Chen, Y.-Y. Hsu, H.-C. Hsu, Y. Chi, B.-S. Chen, W.-H. Liu, C.-H. Lai, T.-Y. Lin, P.-T. Chou, *Tetrahedron* 2010, *66*, 4223. d) D. Kuang, P. Comte, S. M. Zakeeruddin, D. P. Hagberg, K. M. Karlsson, L. Sun, Md. K. Nazeeruddin, M. Grätzel, *Sol. Energy* 2011, *85*, 1189. e) W. Xu, J. Pei, J. Shi, S. Peng, J. Chen, *J. Power Sources* 2008, *183*, 792. f) W. H. Howie, F. Claeyssens, H. Miura, L. M. Peter, *J. Am. Chem. Soc.* 2008, *130*, 1367.
- 6 a) K. Tanaka, K. Nomura, H. Oda, S. Yoshida, K. Mitsuhashi, J. Heterocycl. Chem. 1991, 28, 907. b) K. A. Bello, J. Griffiths, J. Chem. Soc., Chem. Commun. 1986, 1639.
- 7 a) G. Zhou, N. Pschirer, J. C. Schöneboom, F. Eickemeyer, M. Baumgarten, K. Müllen, *Chem. Mater.* 2008, 20, 1808.
  b) A. J. Bard, L. R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, Wiley, New York, 1980.
- 8 M. Liang, W. Xu, F. Cai, P. Chen, B. Peng, J. Chen, Z. Li, J. Phys. Chem. C 2007, 111, 4465.
- 9 a) K. Hara, T. Sato, R. Katoh, A. Furube, Y. Ohga, A. Shinpo, S. Suga, K. Sayama, H. Sugihara, H. Arakawa, *J. Phys. Chem. B* **2003**, *107*, 597. b) J. Hahn, S. E. Webber, *Langmuir* **2004**, *20*, 4211. c) S. A. Haque, T. Park, A. B. Holmes, J. R. Durrant, *ChemPhysChem* **2003**, *4*, 89.
- S. Wenger, P.-A. Bouit, Q. Chen, J. Teuscher, D. Di Censo, R. Humphry-Baker, J.-E. Moser, J. L. Delgado, N. Martín, S. M. Zakeeruddin, M. Grätzel, *J. Am. Chem. Soc.* 2010, *132*, 5164.
- 11 K. Hara, Y. Dan-oh, C. Kasada, Y. Ohga, A. Shinpo, S. Suga, K. Sayama, H. Arakawa, *Langmuir* **2004**, *20*, 4205.
- 12 The absorbance of dye on  $TiO_2$  was normalized by the  $\varepsilon$  of dye in an acetonitrile solution.
- 13 There are little absorptions >350 nm of TiO<sub>2</sub> cell without dye.
- 14 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.