CL-130931 Received: October 4, 2013 | Accepted: November 9, 2013 | Web Released: November 14, 2013

Dye-sensitized Solar Cells Based on 1,3-Dithiol-2-ylidene Derivatives: Substituent and π-Spacer Effects on the Efficiency

Atsushi Wada,[1] Jun-ichi Nishida,[1] Masato M. Maitani,[2] Yuji Wada,[2] and Yoshiro Yamashita*[1]
[1]*Department of Electronic Chemistry, Tokyo Institute of Technology,*
G1-8, 4259 Nagatsuta-cho, Midori-ku, Yokohama, Kanagawa 226-8502
[2]*Department of Chemistry, Tokyo Institute of Technology,*
E4-3, 2-12-1 Ookayama, Meguro-ku, Tokyo 152-8552

(E-mail: yoshiro@echem.titech.ac.jp)

Four novel 1,3-dithiol-2-ylidene dyes BDY-**1**, BDY-**2**, BDY-**3**, and BDY-**4** were developed for dye-sensitized solar cells. Among these dyes, BDY-**4** containing a 9,9-dibutyl-9*H*-fluorene spacer and a phenyl group at the vinyl position showed the highest efficiency (3.26%), indicating the importance of the phenyl substituent and the fluorene unit in improving the efficiency.

Dye-sensitized solar cells (DSSCs) using a nanocrystalline TiO_2 electrode have attracted much attention due to their possibilities for providing electricity with low cost and simple fabrication.[1,2] Dyes strongly affect the power-conversion efficiency (PCE) through their important roles in light harvesting and electron injection. So far, various kinds of dyes, including metal complexes such as ruthenium complexes and zinc porphyrins, have been developed and applied to the DSSCs.[3,4] The highest conversion efficiency of 12.3% has been achieved using a porphyrin dye.[5] However, metal complexes are difficult to synthesize and they are also expensive. On the other hand, organic dyes without metals have received increasing attention due to the large molecular extinction coefficients and easy modification, in addition to their lower costs. Donor–(π-spacer)–acceptor (D–π–A)-type organic dyes have been designed to extend the absorption region, in which various arylamines, including triarylamines, carbazoles, phenothiazines, and indolines, have been used as electron-donating moieties.[6] However, the number of dyes that do not use arylamine as the donor is limited. Therefore, it is still important to explore new materials for making progress in this field. 1,3-Dithiol-2-ylidene has a strong electron-donating property and has been used as a donor unit in donor–acceptor systems.[7] Although D–π–A dyes containing a 1,3-dithiol-2-ylidene unit for DSSCs have been also reported, they have not been fully developed.[8] We have now prepared novel dyes containing these units and investigated the relationship between the structures of dyes and the DSSC performances.

We have developed four novel 1,3-dithiol-2-ylidene dyes: BDY-**1**, BDY-**2**, BDY-**3**, and BDY-**4**. Their structures are depicted in Figure 1. BDY-**1** is a donor–acceptor compound composed of benzo-1,3-dithiol-2-ylidene, a biphenyl π-spacer, and an electron-accepting cyanoacrylic acid unit. A phenyl group is substituted at the vinyl position in BDY-**2**. Introducing the phenyl group was expected to prevent the dimerization of the cation radical and sterically protect the aggregation of the 1,3-dithiole moiety. BDY-**3** has a 9,9-dibutyl-9*H*-fluorene unit as a π-spacer. The unit was expected to enhance the conjugation between the donor and acceptor groups compared to the twisted biphenyl unit. The alkyl groups of the fluorene can suppress the aggregation of dyes.[9] BDY-**4** has both the phenyl group and the fluorene π-spacer unit.

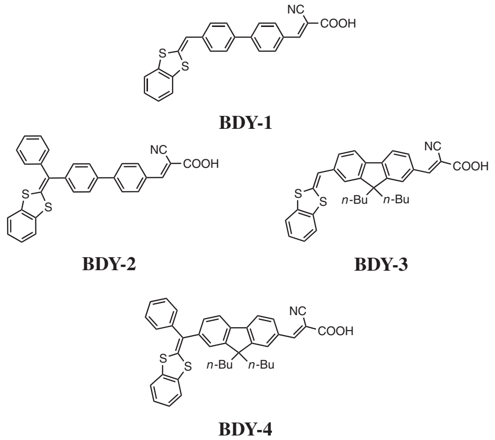

Figure 1. Benzo-1,3-dithiol-2-ylidene dyes, BDY-**1**, BDY-**2**, BDY-**3**, and BDY-**4**.

The syntheses of the 1,3-dithiol-2-ylidene dyes were achieved by four steps using Wittig, Friedel–Crafts, Suzuki–Miyaura, and Knoevenagel reactions. The synthetic procedures are outlined in Supporting Information.[10] The products were purified by silica gel chromatography and were characterized with NMR and MS spectra.

DFT calculations based on the B3LYP method with 6-31G(d) level were performed to gain an insight into the structure and electronic states of dyes. Figure S1 shows the HOMO and LUMO orbitals of BDY dyes.[10] The calculations show that the HOMOs are mainly located at the benzo-1,3-dithiol-2-ylidene part, while the LUMOs are located at the cyanoacrylic acid unit. The HOMO part is far from the TiO_2 surface and the LUMO part is close to the TiO_2, which is favorable for electron injection from the dyes and protecting the back electron transfer from TiO_2 to the dyes. The HOMO is delocalized to the additional phenyl group at the vinyl position.

The UV–vis absorption spectra of 1,3-dithiol-2-ylidene dyes in solution are shown in Figure 2 (dot-line; in THF). The spectroscopic date are summarized in Table S1.[10] All these dyes have two absorption peaks in THF. The absorption in a shorter-wavelength region (300–350 nm) corresponds to the π–π* electronic transition. BDY-**3** with a fluorene unit shows the absorption (326 nm, $3.10 \times 10^4\,M^{-1}\,cm^{-1}$) at a longer wavelength than BDY-**1** with a biphenyl unit (315 nm, $2.43 \times 10^4\,M^{-1}\,cm^{-1}$). Similarly, the absorption of BDY-**4** with a

© 2014 The Chemical Society of Japan

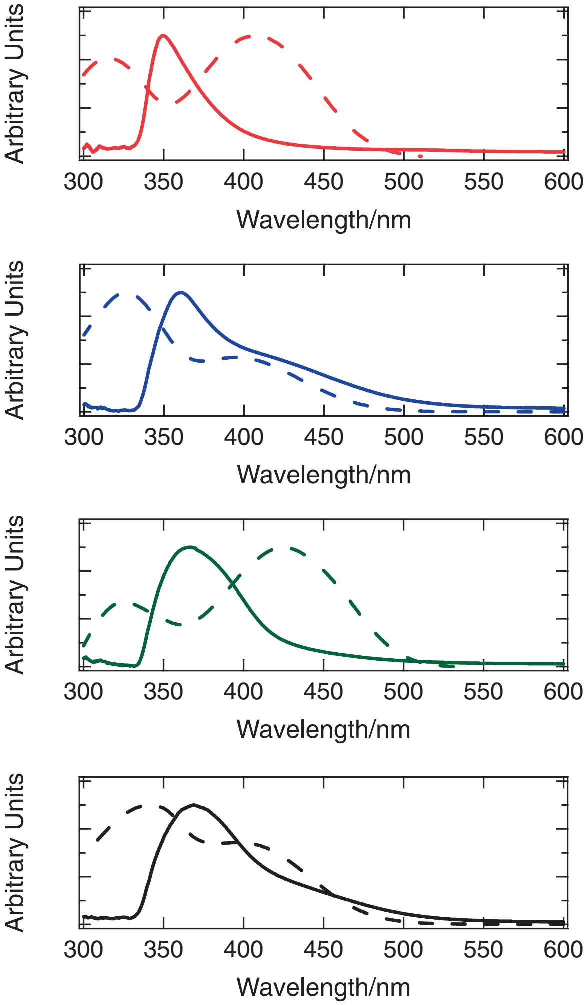

Figure 2. UV–vis absorption spectra of BDY dyes in THF and on TiO_2. Absorption spectra of BDY-**1**, BDY-**2**, BDY-**3**, and BDY-**4** are shown in red, blue, green, and black lines. The dotted lines are spectra in THF and the solid lines are specta on TiO_2.

fluorene unit (341 nm, $2.92 \times 10^4\,M^{-1}\,cm^{-1}$) is red-shifted compared with BDY-**2** with a biphenyl unit (326 nm, $3.46 \times 10^4\,M^{-1}\,cm^{-1}$). This fact indicates that the conjugation between the donor and acceptor parts is more favorable in the fluorene unit than in the biphenyl one due to the more planar geometry of the fluorene. Due to the extension of π-conjugation, the absorption of BDY-**2** with the phenyl group is red-shifted compared with that of BDY-**1**. The absorption in a longer-wavelength region (400–500 nm) is attributed to the intramolecular charge transfer. The absorption in BDY-**3** with a fluorene unit (425 nm, $5.78 \times 10^4\,M^{-1}\,cm^{-1}$) is observed at a longer wavelength than BDY-**1** (406 nm, $2.99 \times 10^4\,M^{-1}\,cm^{-1}$) with a biphenyl unit. On the other hand, the spectra of BDY-**2** (395 nm, $1.58 \times 10^4\,M^{-1}\,cm^{-1}$) and BDY-**4** (396 nm, $2.00 \times 10^4\,M^{-1}\,cm^{-1}$) show that the introduction of the phenyl substituent brings about the blue shifts of the absorption band and weaker intensities compared with those of BDY-**1** and BDY-**3**. This result may be explained by considering that the phenyl group disturbs the conjugation between the 1,3-dithiole unit and the spacer parts.

The absorption edges of BDY-**3** and BDY-**4** with a fluorene unit are red-shifted compared with those of BDY-**1** and BDY-**2** with a biphenyl unit. The red shift of the absorption edges suggests a more effective intramolecular charge-transfer interaction in the planar fluorene system. The UV–vis absorption spectra of BDY dyes on TiO_2 are shown in Figure 2 (solid line; on TiO_2) and Figure S2, where the TiO_2 film was immersed in the THF solution of dyes (0.5 mM) for 12 h.[10] The absorption spectra of BDY-**1** and BDY-**3** are blue-shifted compared to those in solution. Considering the planar structures of BDY-**1** and BDY-**3**, the formation of H-aggregates on the TiO_2 surface may be responsible for the formation of blue shifts.[10] In contrast, BDY-**2** and BDY-**4** do not exhibit such blue shifts. This result suggests that introducing the phenyl group at the vinyl position is useful for suppressing the aggregation of dyes on TiO_2.

The orbital energy levels of the dyes were deduced from the cyclic voltammograms (CVs) in DMF containing $TBAPF_6$ as a supporting electrolyte and a Pt working electrode (Table S1).[10] All of the dyes exhibited irreversible oxidation waves. The HOMO levels were obtained from the first oxidation potentials (E_{ox}) calculated as $E_{pa} - 0.03$ in the CVs. The E_{ox} of BDY-**3** and BDY-**4** having a fluorene unit are slightly lower than those of BDY-**1** and BDY-**2**. Their values are more positive than the iodine/iodide redox potential (0.4 V vs. NHE), indicating that these dyes can be regenerated with the iodine/iodide redox system. The excitation transition energies ($E_{0\text{–}0}$) were determined by the edge of absorption. The LUMO levels of BDY dyes calculated as $E_{ox} - E_{0\text{–}0}$ are sufficiently negative relative to the conduction-band edge of TiO_2 (−0.5 V vs. NHE). This fact indicates that carrier separation takes place smoothly from the excited dyes to TiO_2.

The photovoltaic characteristics of BDY dyes for DSSCs were evaluated with sandwich cells. The film thickness of TiO_2 is 6.5 µm. The redox electrolyte consists of 0.6 M DMPImI, 0.1 M LiI, 0.05 M I_2, and 0.5 M *tert*-butylpyridine in acetonitrile. Figure 3 shows the current density–voltage curve of DSSCs under AM 1.5G solar irradiation. The photovoltaic data, including short-circuit current (J_{sc}), open-circuit voltage (V_{oc}), fill factor (*FF*), and photon-to-current efficiency (PCE), are listed in Table 1. The J_{SC} and V_{OC} values of BDY-**2** with the additional phenyl group were higher than those of BDY-**1**. A similar effect of the phenyl group can be seen in a comparison of BDY-**3** with BDY-**4**. The high J_{SC} value can be explained by considering that the phenyl group disturbs the aggregation of the dyes, as suggested in the absorption spectra (Figure S2).[10] The phenyl group also protects the approach of I_3^- to the TiO_2 electrode, which is useful for disturbing the back electron transfer from the TiO_2 to I_3^-, resulting in an increase in V_{OC}.[11] BDY-**3** and BDY-**4** with a fluorene unit showed higher J_{SC} values than the corresponding dyes with a biphenyl unit. This is attributed to the better conjugation between the donor and acceptor parts in the fluorene-containing dyes. DSSCs based on BDY-**4** containing both the phenyl group and fluorene unit showed the highest efficiency (3.26%) among these BDY dyes. The incident photon-to-current efficiency (IPCE) spectra for DSSCs of BDY-**1**, BDY-**2**, and BDY-**4** are shown in Figure S5. The IPCE values of **2** and **4** (ca. 80%) are significantly higher than that of **1** (ca. 50%), confirming the effect of the phenyl group on the conversion efficiency.[10]

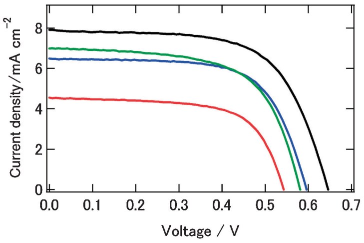

Figure 3. Photocurrent–voltage curves of the DSSCs based on BDY dyes. BDY-**1**, BDY-**2**, BDY-**3**, and BDY-**4** are shown in red, blue, green, and black lines.

Table 1. Photovoltaic performance of DSSCs based on BDY dyes

	J_{SC}/mA cm^{-2}	V_{OC}/V	*FF*	PCE/%
BDY-**1**	4.55	0.54	0.65	1.61
BDY-**2**	6.49	0.6	0.66	2.56
BDY-**3**	6.98	0.58	0.63	2.54
BDY-**4**	7.91	0.65	0.64	3.26
N719	14.69	0.68	0.56	5.53

In summary, we have developed a series of benzo-1,3-dithiol-2-ylidene dyes by a facile synthetic method. A 9,9-dibutyl-9*H*-fluorene π-spacer is effective in improving the J_{SC} value by protecting the aggregation of dyes and increasing the efficiency of intramolecular charge transfer. The additional phenyl group at the vinyl position is effective in increasing the V_{OC} value. Further development of novel dyes based on such donor–acceptor systems containing a 1,3-dithiol-2-ylidene unit is in progress.

References and Notes

1 a) B. O'Regan, M. Grätzel, *Nature* **1991**, *353*, 737. b) M. Grätzel, *Nature* **2001**, *414*, 338. c) A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo, H. Pettersson, *Chem. Rev.* **2010**, *110*, 6595.

2 A. Hagfeldt, M. Grätzel, *Chem. Rev.* **1995**, *95*, 49.

3 Y. Tachibana, S. A. Haque, I. P. Mercer, J. R. Durrant, D. R. Klug, *J. Phys. Chem. B* **2000**, *104*, 1198.

4 M.-G. Ju, W. Liang, *J. Phys. Chem. C* **2013**, *117*, 14899.

5 A. Yella, H.-W. Lee, H. N. Tsao, C. Yi, A. K. Chandiran, M. K. Nazeeruddin, E. W.-G. Diau, C.-Y. Yeh, S. M. Zakeeruddin, M. Grätzel, *Science* **2011**, *334*, 629.

6 a) N. Koumura, Z.-S. Wang, S. Mori, M. Miyashita, E. Suzuki, K. Hara, *J. Am. Chem. Soc.* **2006**, *128*, 14256. b) 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. c) G. Zhang, H. Bala, Y. Cheng, D. Shi, X. Lv, Q. Yu, P. Wang, *Chem. Commun.* **2009**, 2198. d) D. Cao, J. Peng, Y. Hong, X. Fang, L. Wang, H. Meier, *Org. Lett.* **2011**, *13*, 1610. e) S. H. Kim, H. W. Kim, C. Sakong, J. Namgoong, S. W. Park, M. J. Ko, C. H. Lee, W. I. Lee, J. P. Kim, *Org. Lett.* **2011**, *13*, 5784.

7 a) S. Inoue, Y. Aso, T. Otsubo, *Chem. Commun.* **1997**, 1105. b) A. J. Moore, A. Chesney, M. R. Bryce, A. S. Batsanov, J. F. Kelly, J. A. K. Howard, I. F. Perepichka, D. F. Perepichka, G. Meshulam, G. Berkovic, Z. Kotler, R. Mazor, V. Khodorkovsky, *Eur. J. Org. Chem.* **2001**, 2671.

8 a) M. Komatsu, K. Tamaki, J. Nakazaki, S. Uchida, T. Kubo, H. Segawa, *ECS Trans.* **2009**, *16*, 65. b) S. Wenger, P.-A. Bouit, Q. Chen, J. Teuscher, D. D. Censo, R. Humphry-Baker, J.-E. Moser, J. L. Delgado, N. Martín, S. M. Zakeeruddin, M. Grätzel, *J. Am. Chem. Soc.* **2010**, *132*, 5164. c) K. Guo, K. Yan, X. Lu, Y. Qiu, Z. Liu, J. Sun, F. Yan, W. Guo, S. Yang, *Org. Lett.* **2012**, *14*, 2214.

9 A. Baheti, P. Tyagi, K. R. J. Thomas, Y.-C. Hsu, J. T. Lin, *J. Phys. Chem. C* **2009**, *113*, 8541.

10 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chemlett/index.html.

11 J.-i. Nishida, T. Masuko, Y. Cui, K. Hara, H. Shibuya, M. Ihara, T. Hosoyama, R. Goto, S. Mori, Y. Yamashita, *J. Phys. Chem. C* **2010**, *114*, 17920.

© 2014 The Chemical Society of Japan