

Synthesis and Characterization of 5'-Hexyl-2,2'-bithiophene Based on Organic Dyes for Dye-Sensitized Solar Cell Applications

CHINNUSAMY SARAVANAN,¹ WOOSUM CHO,¹ YULHEE KIM,¹ SUNG-HO JIN,^{1,*} YEONG-SOON GAL,² AND JAE WOOK LEE³

¹Department of Chemistry Education, Graduate Department of Chemical Materials, and Institute for Plastic Information and Energy Materials, Pusan National University, Busan, Republic of Korea ²Department of Chemistry, Dong-A University, Busan, Republic of Korea ³Polymer Chemistry Lab, College of General Education, Kyungil University,

Hayang, Republic of Korea

A series of new organic dyes, 2-(2,6-bis((E)-2-(5'-hexyl-2,2'-bithiophen-5-yl)vinyl)pyran-4-ylidene)-2-cyanoacetic acid (OD-1) and 2,2'-(2-((E)-2-(5'-hexyl-2,2'bithiophen-5-yl)vinyl)-1H-indene-1,3(2H)-diylidene)bis(2-cyanoacetic acid) (OD-2), were synthesized as a sensitizers for the application of dye-sensitized solar cells (DSSCs). The introduction of the 5'-hexyl-2,2'-bithiophene units as an electron donor group and 2,6-dimethyl-pyran-4-one or 1,3-indandione as a π -spacers units increased the conjugation length of the sensitizers and thus improved their molar absorption coefficient and light harvesting efficiency.

Keywords organic dyes; dye-sensitized solar cells; optical properties

Introduction

Increasing energy demands and concerns about global warming have led to a greater focus on renewable energy sources during the last years. The effective conversion of solar energy into electricity has become a very important issue in the last few years due to rising energy cost and demand [1]. In recent years, dye-sensitized solar cells (DSSCs) based on nanocrystalline TiO_2 (nc- TiO_2) films have received significant attention because of their high efficiency and low cost compared to those of silicon-based inorganic solar cells [2]. In DSSCs, the sensitizing dye molecules must be chemically adsorbed on the porous nc- TiO_2 surfaces and be capable of harvesting solar light ranging from the visible to the near-IR regions. Up to now, the efficient sensitizers are ruthenium (Ru) complexes, which show effective charge separation at the metal to ligand (Ru-bpy) and ligand to metal

^{*}Address correspondence to Sung-Ho Jin, Department of Chemistry Education, Graduate Department of Chemical Materials, and Institute for Plastic Information and Energy Materials, Pusan National University, Busan 609-735, Korea. E-mail: shjin@pusan.ac.kr

(SCN-Ru) absorption bands in the visible light region. With regard to the Ru sensitizers such as cis-dithiocyanato bis(4,4'-dicarboxy-2,2'-bipyridine)ruthenium(II) (N3) [3], its bis(tetrabutylammonium) salt (N719) [4], and trithiocyanato (4,4',4''-tricarboxy-2,2':6',2''terpyridine)ruthenium(II) (black dye) [5], the zinc porphyrin dye (YD2-o-C8) gave the best power conversion efficiency (PCE) over 12 % measured at the AM1.5G condition [6]. Recently, metal-free organic dyes have recently been stimulating intensive research efforts because of their advantages as sensitizers for DSSCs due to the high molar absorption coefficients than that of Ru sensitizers, which increase the light-harvesting capabilities over the wide spectral region of sunlight. Organic dyes need to overcome disadvantages such as narrow absorption band, π -stacked aggregation, and stability. Thiophene and its derivatives have high thermal stability, being ordinarily easy for structural design and modifications. In addition, they are very easy to prepare and solubilized by wide range of organic solvents. Here, we introduced n-hexyl chains on the terminal thiophene unit to enhance the solubility, to suppress charge recombination, improve the open-circuit voltage, suppress the aggregation of the sensitizers resulting in increase the power conversion efficiency. Finally, the hydrophobic n-hexyl chains could also enhance the long-term stability of the solar cell by preventing water induced dye desorption from the TiO_2 surface. The carboxylic acid group is the most employed group for attachment of the sensitizers to the semiconductor surface. And the cyanoacrylic acid is the most commonly used unit in the dyes for DSSCs due to its strong electronic withdrawing properties. These anchoring groups are increasing the conjugation length of dye that increases the light harvesting efficiency.

Herein, we report two types organic dyes using a 5'-hexyl-2,2'-bithiophene unit as an electron donor, the 2,6-dimethyl-pyran-4-one and 1,3-indandione as the π -spacer and cyanoacrylic acid as an anchoring group. The thermal, photophysical, and electrochemical properties have been investigated.

Experimental

¹H-NMR spectra were recorded in CDCl₃ on a Varian Mercury 300, and chemical shifts were recorded in ppm. The absorption spectra were measured using a Jasco V-570 UV-visible spectrometer. Thermal analyses were carried out on a Mettler Toledo TGA/SDTA 851e analyzer under a nitrogen atmosphere at a heating rate of 8 °C/min. Cyclic voltammetry (CV) was carried out with a Bioanalytical Systems CV-50W voltametric analyzer at a potential scan rate of 100 mV/s in a 0.1 M solution of tetrabutylammonium perchlorate in anhydrous CHCl₃. A platinum wire was used as the counter electrode and an Ag/AgNO₃ electrode was used as the reference electrode. All of the electrochemical experiments were performed in a glove box under an N₂ atmosphere at room temperature. 5-Formyl-5'-hexyl-2,2'-bithiophene (3) was synthesized according to the previously literature [7]. 2-(2,6-Dimethyl-pyran-4-ylidene)-2-cyanoacrylic acid (4) and 2,2'-(1H-indene-1,3(2H)-diylidene)bis(2-cyanoacetic acid) (6) were synthesized according to the reported literature with slightly modification [8].

Synthesis of 2-(2,6-bis((E)-2-(5'-hexyl-2,2'-bithiophen-5-yl)vinyl)-pyran-4-ylidene)-2-cyanoacetic acid (OD-1) (1)

5-Formyl-5'-hexyl-2,2'-bithiophene (3) (1.5 g, 5.23 mmol) and 2-(2,6-dimethyl-pyran-4-ylidene)-2-cyanoacrylic acid (4) (0.5 g, 2.62 mmol) were allowed to react in acetonitrile in the presence of piperidine (0.13 ml, 1.3 mmol). The solution was refluxed at 80°C for 18 h.

After removal of acetonitrile in *vacuo*, the crude product was extracted with methylene chloride and water. The crude product was purified by column chromatography using chloroform as an eluent to give a 2-(2,6-bis((E)-2-(5'-hexyl-2,2'-bithiophen-5-yl)vinyl)-pyran-4-ylidene)-2-cyanoacetic acid (OD-1) (0.38 g, 20%). ¹H-NMR (CDCl₃, δ ppm) 8.13(s, 1H), 7.54(m, 2H), 7.20 (d, 2H), 7.14(d, 2H), 6.83 (s, 1H), 6.68 (d, 2H), 6.58 (d, 2H), 6.51(d, 2H), 2.79(t, 4H),1.70 (m, 4H), 1.29 (m, 12H), 0.86 (s, 6H). ¹³C-NMR (CDCl₃, δ ppm) 174.5, 163.9, 142.5, 140.6, 137.5, 134.2, 128.7, 127.9, 125.4, 120.1, 97.5, 91.0, 42.9, 32.8, 31.8, 22.4, 14.6

Synthesis of 2,2'-(2-((E)-2-(5'-hexyl-2,2'-bithiophen-5-yl)vinyl)-1H-indene-1,3(2H)-diy lidene)bis(2-cyanoacetic acid) (OD-2) (2)

5-Formyl-5'-hexyl-2,2'-bithiophene (3) (0.55 g, 1.96 mmol) and (2Z, 2'Z)-2,2'-(1H-indene-1,3(2H)-diylidene)bis(2-cyanoacetic acid) (6) (0.5 g, 1.78 mmol) were allowed to react in acetonitrile in the presence of piperidine (0.09 ml, 0.89 mmol). The solution was refluxed at 80 °C for 18 h. After removal of acetonitrile in *vacuo*, the crude product was extracted with methylene chloride and water. The crude product was purified by column chromarography using chloroform as an eluent to give 2,2'-(2-((E)-2-(5'-hexyl-2,2'-bithiophen-5-yl)vinyl)-1H-indene-1,3(2H)-diylidene)bis(2-cyanoacetic acid) (OD-2) (0.26 g, 27%). ¹H-NMR (CDCl₃, δ ppm) 7.95 (m, 2H), 7.85 (d, 1H), 7.76(m, 2H), 7.32(d, 1H), 7.21(d, 1H), 6.77 (d, 1H) 6.65 (d, 1H), 6.57 (d, 1H), 3.52 (s, 1H) 2.82 (t, 2H) 1.78(m, 2H) 1.37 (m, 6H), 0.92 (m, 3H). ¹³C-NMR (CDCl₃, δ ppm) 141.9, 141.5, 137.5, 134.4, 128.7, 128,4, 127.6, 126.4, 125.8, 95.6, 43.2, 32.9, 31.9, 31.8, 22.7, 14.2

Result and Discussion

The synthetic routes for the OD-1 and OD-2 are described in Scheme 1. 2-Bromo-5formylthiophene (1) was synthesized by bromination of 2-thiophene aldehyde with NBS in DMF solvent. After synthesized the 2-(tri-n-butylstannyl)-5-hexylthiophene (2), 5-formyl-5'-hexyl-2,2'-bithiophene (3) was synthesized by Stille coupling reaction between compounds (1) and (2). 2,6-Dimethyl-pyran-4-one coupled with cyanoacetic acid in acetic anhydride to give a 2-(2,6-dimethyl-pyran-4-ylidene)-2-cyanoacrylic acid (4). 2,2'-(1H-indene-1,3(2H)-diylidene)bis(2-cyanoacetic acid) (6) was also synthesized with a similar reaction condition for the synthesis of (4). 2-(2,6-Dimethyl-pyran-4-ylidene)-2-cyanoacrylic acid (4) and 2,2'-(1H-indene-1,3(2H)-diylidene)bis(2-cyanoacetic acid) (6) were coupled with 5-formyl-5'-hexyl-2,2'-bithiophene (3) by the Knoevenagel condensation reaction to give a OD-1 and OD-2, respectively. The structure and thermal properties of the OD-1 and OD-2 were identified by ¹H-NMR, ¹³C-NMR, TGA, and CV.

The ¹H-NMR spectra of the OD-1 and OD-2 indicated doublet peaks by vinylic bond, which confirmed the double bond between thiophene moiety and 2,6-dimethyl-pyran-4-one and 1,3-indandione as the π -spacer by Knoevenagel reaction.

The bithiophene unit was introduced n-hexyl groups to suppress the charge recombination and/or aggregation of the sensitizers and hence to increase the photovoltaic performance [9]. The hydrophobic n-hexyl aliphatic chains will be enhanced the long-term stability of the DSSCs through preventing water induced dye desorption from the TiO₂ surface [10–11]. Finally, we used 2,6-dimethyl-pyran-4-one and 1,3-indandione as a π -spacers and introduced the cyanoacrylic acid as an anchoring group. The cyanoacrylic acid group is by far the most employed group for attachment of the sensitizers to the semiconductor surface. 160/[502]



Scheme 1. Synthetic Route for OD-1 and OD-2.

TGA thermograms of the OD-1 and OD-2 revealed a 5% weight loss at 162° C under a N₂ atmosphere. Thermal stability of the OD-1 and OD-2 based on 5-hexylbithiophene prevents degradation of the active layer during the operation of DSSCs. The thermal, electrochemical, and optical properties of OD-1 and OD-2 are summarized in Table 1.

Fig. 1 shows the normalized UV-visible absorption spectra of OD-1 and OD-2 in chloroform solution. The OD-1 and OD-2 show the absorption maximum at 528 and 491 nm, respectively, indicate that the dyes are absorbed at the medium visible range. By comparing these absorption spectra with other reported dyes, the absorption coverage must be improved.

To investigate the charge carrier injection properties of the OD-1 and OD-2 and evaluate their highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels, we carried out redox measurements using CV. The HOMO values were calculated from E_{ox} as -5.08 eV for OD-1 and -5.34 eV for OD-2. The LUMO energy level of OD-1 and OD-2 was approximated by subtracting the optical band gap from

	able in Thomas, optical and creationneal properties of OD 1 and OD 2				
dye	$\lambda_{abs} (nm)$	DSC (T _g) ^a	TGA ^b	$E_{HOMO}^{c}(V)$	E _{LUMO} ^d (V)
OD-1	528	74	162	2.52	-1.20

162

2.27

-0.74

 Table 1. Thermal, optical and electrochemical properties of OD-1 and OD-2

^aDetermined by DSC at a heating rate of 10°C/min under N₂ atmosphere.

75

^bTGA was measured at temperature of 5% weight loss for the polymer.

^cHOMO: Determined by onset oxidation of CV curves.

 $^{d}LUMO = HOMO + E_{g}$.

491

OD-2



Figure 1. UV-visible absorption spectra of OD-1 and OD-2.

the HOMO value and these values are listed in Table 1. The energy band diagrams of OD-1 and OD-2 are displayed in Fig. 2. The results confirmed the thermodynamic favorability of electron injection from the excited OD-1 and OD-2 into the conduction band of TiO_2 and also oxidized OD-1 and OD-2 are easily reduced by accepting the electrons from I^- ions, generating the ground state of the OD-1 and OD-2 [12].



Figure 2. Energy band diagram of OD-1 and OD-2 dyes.

162/[504]

C. Saravanan et al.

Conclusion

In this study, we have successfully designed and synthesized a new series of 5'-hexyl-2,2'bithiophene based on OD-1 and OD-2 as a sensitizer for DSSCs. The synthesized OD-1 and OD-2 were characterized by ¹H-NMR, ¹³C-NMR, TGA, UV-visible, and CV. Their optical, thermal and electrochemical properties were measured. Optical and electrochemical measurements exhibited that OD-1 and OD-2 confirmed the thermodynamic favorability of electron injection from the excited OD-1 and OD-2 sensitizers into the conduction band of TiO₂.

Acknowledgment

This work was financially supported by the 2013 Post-Doc. Development Program of Pusan National University.

References

- [1] Bilgen, S., Kaygusuz, K., & Sari. A. (2004). Energy Sources, 26, 1119.
- [2] O'Regan, B., & Grätzel, M. (1991). Nature, 353, 737.
- [3] Gao, F., Wang, Y., Shi, D., Zhang, J., Wang, M. K., Jing, X. Y., Humphry-Baker, R., Wang, P., Zakeeruddin, S. M., & Grätzel, M. (2008). J. Am. Chem. Soc., 130, 10720.
- [4] Nazeeruddin, M. K., Angelis, F. D., Fantacci, S., Selloni, A., Viscardi, G., Liska, P., Ito, S., Takeru, B., & Grätzel, M. (2005). J. Am. Chem. Soc., 127, 16835.
- [5] Nazeeruddin, M. K., Pechy, 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. (2001). J. Am. Chem. Soc., 123, 1613.
- [6] Yella, A., Lee, H. W., Tsao, H. N., Yi, C. Y., Chandiran, A. K., Nazeeruddin, M. K., Diau, E. W. G., Yeh, C. Y., Zakeeruddin, S. M., & Grätzel, M. (2011). *Science.*, *334*, 629.
- [7] Song, M., Ryu, T. I., Lee, M. J., Jin, S. H., Kang, S., Lee, J. Y., Lee, J. W., Lee, C. W., & Gal, Y. S. (2009). Bull. Korean. Chem. Soc., 30, 2329.
- [8] Wang, Z. S., Koumura, N., Cui, Y., Takahashi, M., Sekiguchi, H., Mori, A., Kubo, T., Furube, A., & Hara, K. (2008). *Chem. Mater.*, 20, 3993.
- [9] Koumura, N., Wang, Z. S., Mori, S., Miyashita, M., Suzuki, E., & Hara, K. (2006). J. Am. Chem. Soc., 128, 14256.
- [10] Choi, H., Baik, C., Kang, S. O., Ko, J., Kang, M. S., Nazeeruddin, M. K., & Grätzel, M. (2008). Angew. Chem. Int. Ed., 47, 327.
- [11] Wang, P., Zakeeruddin, S. M., Comte, P., Charvet, R., Humphry-Baker, R., & Grätzel, M. (2003). J. Phys. Chem. B., 107, 14336.
- [12] Hagfeldt, A., & Grätzel, M. (1995). Chem. Rev., 95, 49.

Copyright of Molecular Crystals & Liquid Crystals is the property of Taylor & Francis Ltd and its content may not be copied or emailed to multiple sites or posted to a listserv without the copyright holder's express written permission. However, users may print, download, or email articles for individual use.