Short Articles

Bull. Chem. Soc. Jpn. Vol. 83, No. 6, 709–711 (2010) 709

X-ray Crystallography of D149 Ethyl Ester

Masaki Matsui,*[1] Tomoki Fujita,[1]
Yasuhiro Kubota,[1] Kazumasa Funabiki,[1]
Hidetoshi Miura,[2] and Motoo Shiro[3]

[1]Department of Materials Science and Technology, Faculty of Engineering, Gifu University, Yanagido, Gifu 501-1193

[2]Chemicrea Co., Ltd., 2-1-6 Sengen, Tsukuba 305-0047

[3]X-ray Research Laboratory, Rigaku Corporation,
3-9-12 Matsubara-cho, Akishima, Tokyo 196-8666

Received January 26, 2010
E-mail: matsuim@gifu-u.ac.jp

D149 ethyl ester molecules are arranged in a "herringbone" fashion. Cyclopentane, phenylene, and one of the phenyl moieties surround a planar π-conjugated chromophore to weaken π–π stacking between the molecules arranged in parallel.

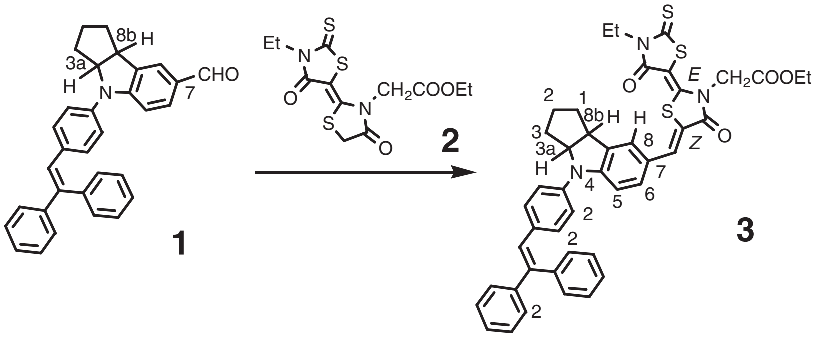
Indoline dyes are important compounds as sensitizers in a dye-sensitized solar cell. Three series of indoline dyes, cyanoacrylic, single, and double rhodanine derivatives have been reported to show high IPCE.[1–4] Among the series, a double rhodanine derivative named D149 is known to show excellent solar-to-electricity conversion efficiency (η) 9.0% on titanium oxide.[5] Recently, the octyl derivative, D205, has been reported to exhibit improved efficiency of 9.4%.[6] The theoretical approach,[7,8] modification of the structure,[9,10] investigation of the energy level,[11] and decomposition mechanism[12] of indoline dyes have been reported. The indoline dyes have unique structures such as cyclopentane, 4-(2,2-diphenylethenyl)phenyl, double rhodanine moieties, and two asymmetric carbons. However, no detailed studies on the chemical structure have been reported so far. Therefore, it is of significance to clarify the structure. We report herein the X-ray crystallography of D149 ethyl ester.

Results and Discussion

A 7-formylindoline derivative **1** was allowed to react with the ethyl ester of double rhodanine acetic acid **2** in the presence of ammonium acetate in acetic acid to afford D149 ethyl ester **3** as shown in Scheme 1. The product was purified by column chromatography and recrystallized from toluene. As in the course of synthesis of indoline precursor, hydrogenation of 1,2,3,4-tetrahydrocyclopenta[*b*]indole to 1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indole is performed on Pd/C surface by using hydrogen gas or by sodium borohydride, *syn*-addition reaction at the 3a- and 8b-positions occurs. Therefore, compound **3** has two asymmetric centers in the molecule.

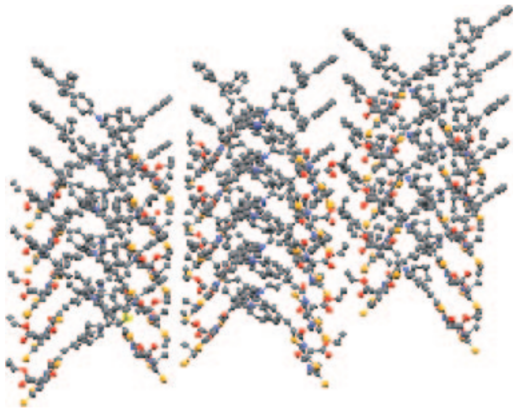
Figure 1 depicts the packing motif of **3**. Molecules are arranged in a "herringbone" fashion. This packing motif is different from that of J-aggregates, in which molecules are arranged in parallel with slipping angle smaller than 54.7°.[13] Two pairs of enantiomers, (3a-*S*,8b-*S*) and (3a-*R*,8b-*R*) isomers, are packed in a unit cell. CH/O and CH/π interactions are observed between the enantiomers. Weak CH/S interaction is observed between adjacent molecules. Molecules packed in parallel for A are shown in Figures 1c and 1d. The figures indicate that weak π–π interactions are observed between indoline moieties, there being the interplanar distance 3.70 Å. This is slightly long compared to usual π–π stacking. The slip angle of molecules A, B, and C is 51.9°, suggesting that D149-type indoline dyes can form J-aggregates. The figures also depict that the cyclopentane moiety and phenyl group E can act as steric hindrance to prevent strong π–π interactions among A, B, and C.

Figure 2 shows the ORTEP of (3a-*S*,8b-*S*)-**3**. The double rhodanine moiety is in *E*-form. The cyclopentane moiety is an envelope form. The methylene-carbon at the 2-position in the cyclopentane ring is bent toward the inside of the molecule. As the carbon atoms at the 3a- and 8b-positions are sp^3 hybridized, the dihedral angle between the cyclopentane ring and planar π-conjugated chromophoric moiety is 120°. The methine moiety on the 7-position is *Z*-form. The hydrogen atom at the 8-position on the indoline moiety and carbonyl-oxygen at the inner rhodanine ring is *anti*-form, due to steric hindrance between them. The dihedral angle between the phenylene group D at the 4-position and the planar chromophore is 35°. One of the phenyl groups E is also twisted with respect to the chromophore, there being the dihedral angle 68°, due to steric repulsion between the phenyl groups E and F. The phenyl

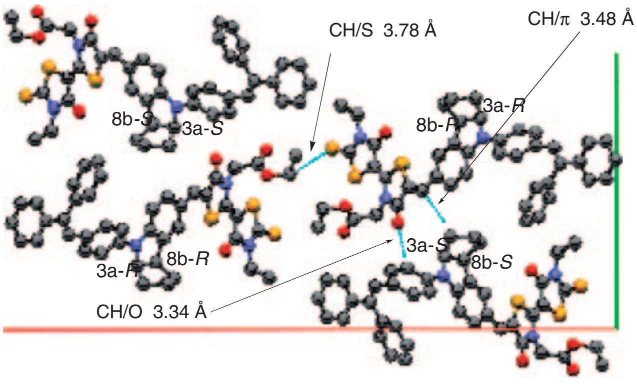


Scheme 1. Reagents and conditions: **2** (1.0 equiv), AcONH$_4$ (cat), 110 °C, AcOH, 3 h.

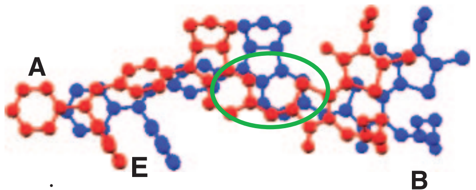
Published on the web May 28, 2010; doi:10.1246/bcsj.20100021



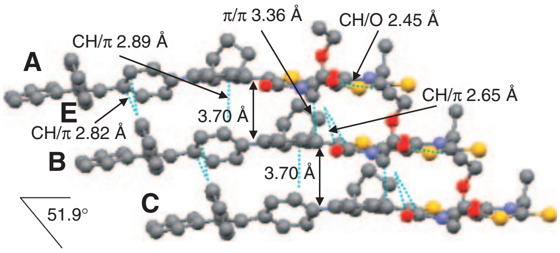
a) overal packing



b) unit cell



c) top view

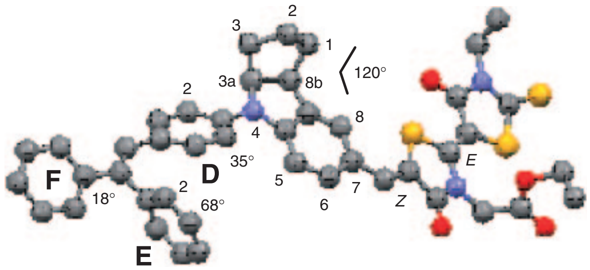


d) side view

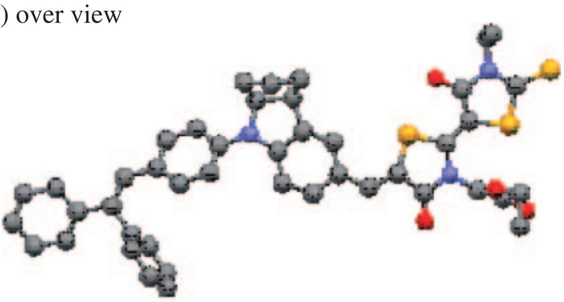
Figure 1. X-ray crystallography of D149 ethyl ester **3**. Hydrogen atoms are omitted for clarifity.

group F is almost planar to the chromophore, the dihedral angle being 18°. In most cases, dye aggregates could suppress the performance, even if a coadsorbate such as cholic acid is present. However, in the case of indoline dyes, the cyclopentane, phenylene, and phenyl moieties surround the almost planar π-chromophoric moiety to prevent π–π stacking.

In conclusion, single-crystal X-ray crystallography of D149 ethyl ester was performed. Molecules are arranged in a "herringbone" fashion. Two pairs of enantiomers are packed in a unit cell. CH/O and CH/π Interactions are observed between the enantiomers. The double rhodanine moiety is *E*-form. The methine moiety is *Z*-form, there being the hydrogen at the 4-position on the indoline moiety and carbonyl-oxygen at the inner rhodanine ring is *anti*-form. No strong interactions are observed among neighboring pair of enantiomers. The cyclopentane, phenylene, and phenyl moieties could act as steric hindrance to weaken π–π stacking among the molecules arranged in parallel.



a) over view



b) top view

c) side view

Figure 2. ORTEP of (3a-*S*,8b-*S*)-**3**. Hydrogen atoms are omitted for clarifity.

Experimental

Instruments. Melting point was measured with a Yanagimoto MP-52 micro-melting-point apparatus. NMR spectrum was taken with a JEOL JNM-ECX 400P spectrometer. MS spectrum was recorded on a JEOL MStation 700 spectrometer.

Materials. Compounds **1** and **2** were prepared as described in the literature.[9]

Synthesis of D149 Ethyl Ester 3. To acetic acid (20 mL) were added 7-formyl derivative **1** (442 mg, 1.0 mmol) and double rhodanine acetic acid ethyl ester **2** (346 mg, 1.0 mmol). The mixture was heated to 110 °C. Then, to the mixture was added ammonium acetate (20 mg). The mixture was heated at 110 °C for 3 h. After the reaction was completed, the solvent was removed in vacuo. The residue was poured into chloroform–water (1:1) mixed solvent. The chloroform layer was separated and dried over anhydrous sodium sulfate. The product was purified by column chromatography (SiO_2, $CHCl_3$: two times, CH_2Cl_2: one time). Yield 515 mg (67%); mp 147–

149 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.30 (t, $J = 7.1$ Hz, 3H), 1.34 (t, $J = 7.1$ Hz, 3H), 1.40–1.53 (m, 1H), 1.63–1.70 (m, 1H), 1.73–1.82 (m, 1H), 1.84–1.94 (m, 2H), 2.02–2.14 (m, 1H), 3.80–3.89 (m, 1H), 4.18 (q, $J = 7.1$ Hz, 2H), 4.30 (q, $J = 7.1$ Hz, 2H), 4.81–4.90 (m, 1H), 4.84 (s, 2H), 6.91–7.10 (m, 4H), 7.23–7.48 (m, 14H), 7.71 (s, 1H); HRFABMS (NBA) m/z 770.2237 (MH^+), calcd for $C_{44}H_{40}N_3O_4S_3$: 770.2181.

X-ray Crystallography of 3. The diffraction data were collected by a Rigaku RAXIS RAPID diffractometer using graphite monochromated Cu Kα radiation ($\lambda = 1.54187$ Å). The structure was solved by direct methods SHELX97,[14] and refined by fill-matrix least-squares calculations. Crystal data: $C_{44}H_{39}N_3O_4S_3$, $M_r = 769.99$, orthorhombic, $Pna2_1$ (#33), $Z = 4$, $a = 38.8710(7)$, $b = 17.6021(3)$, $c = 5.53697(10)$ Å, $D_{calcd} = 1.350$ g cm^{-3}, $T = 93$ K, 45628 reflections were collected, 6093 unique ($R_{int} = 0.080$), 2245 parameters, $R_1 = 0.0506$, $wR_2 = 0.1286$, GOF = 1.103, refinement on F^2. Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition number CCDC 762266 for compound **3**. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, U.K.; Fax +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

This work was financially supported in part by Grants-in-Aid for Science Research (No. 21550180) from Japan Society for the Promotion of Science (JSPS) and Research for Promoting Technological Seeds.

Supporting Information

Molecular structure (Figure S1), bond lengths (Table S1), and angles (Table S2) of **3**. These materials are available free of charge on web at http://www.csj.jp/journals/bcsj/.

References

1 D. Kuang, S. Uchida, R. Humphry-Baker, S. M. Zakeeruddin, M. Grätzel, *Angew. Chem., Int. Ed.* **2008**, *47*, 1923.

2 T. Horiuchi, H. Miura, S. Uchida, *J. Photochem. Photobiol., A* **2004**, *164*, 29.

3 T. Horiuchi, H. Miura, K. Sumioka, S. Uchida, *J. Am. Chem. Soc.* **2004**, *126*, 12218.

4 T. Horiuchi, H. Miura, S. Uchida, *Chem. Commun.* **2003**, 3036.

5 S. Ito, S. M. Zakeeruddin, R. Humphry-Baker, P. Liska, R. Charvet, P. Comte, M. K. Nazeeruddin, P. Péchy, M. Takata, H. Miura, S. Uchida, M. Grätzel, *Adv. Mater.* **2006**, *18*, 1202.

6 S. Ito, H. Miura, S. Uchida, M. Takata, K. Sumioka, P. Liska, P. Comte, P. Péchy, M. Grätzel, *Chem. Commun.* **2008**, 5194.

7 R. Jose, A. Kumar, V. Thavasi, K. Fujihara, S. Uchida, S. Ramakrishna, *Appl. Phys. Lett.* **2008**, *93*, 023125.

8 W. H. Howie, F. Claeyssens, H. Miura, L. M. Peter, *J. Am. Chem. Soc.* **2008**, *130*, 1367.

9 T. Dentani, Y. Kubota, K. Funabiki, J. Jin, T. Yoshida, H. Minoura, H. Miura, M. Matsui, *New J. Chem.* **2009**, *33*, 93.

10 M. Matsui, A. Ito, M. Kotani, Y. Kubota, K. Funabiki, J. Jin, T. Yoshida, H. Minoura, H. Miura, *Dyes Pigm.* **2009**, *80*, 233.

11 M. Matsui, T. Fujita, Y. Kubota, K. Funabiki, J. Jin, T. Yoshida, H. Miura, *Dyes Pigm.* **2010**, *86*, 143.

12 H. Tanaka, A. Takeichi, K. Higuchi, T. Motohiro, M. Takata, N. Hirota, J. Nakajima, T. Toyoda, *Sol. Energy Mater. Sol. Cells* **2009**, *93*, 1143.

13 M. Kasha, H. R. Rawls, M. A. El-Bayoumi, *Pure Appl. Chem.* **1965**, *11*, 371.

14 G. M. Sheldrick, *SHELXL-97, Program for the Refinement of Crystal Structures*, University of Göttingen, Germany, **1997**.