Synthesis and Visible-Light Photochromism of a Donor-Acceptor Type of Dimethyl 2,3-bis(arylethynyl)fumarate

Ryota Sakamoto

***Abstract*—Herein, the author synthesized a donor-acceptor type of photochromic dimethyl 2,3-bis(arylethynyl)fumarate, (*E*)-2, where ferrocene and 4-nitrobenzene were employed as donor and acceptor arenes, respectively. Compared to parent dimethyl 2,3-bis(ferrocenylethynyl)fumarate, (*E*)-2 enjoyed more profound donor-acceptor interaction, leading to a red-shifted intramolecular charge transfer band. (*E*)-2 underwent visible-light photochromism upon excitation with the intramolecular charge transfer band.**

***Index Terms*—Photochromism, ferrocene, donor-acceptor interaction.**

I. INTRODUCTION

Ethynylethene was indeed synthesized several decades ago [1], though, it is Dierderich who has put spotlight on this series of compounds in photochemical and synthetic aspects [2]-[7]. This class of compounds has an extended π-system and shows *E* to *Z* photoisomerization around the C=C bond upon excitation of the π–π* transition. Unlike azobenzene and a portion of stilbene, the *Z* form is thermally stable, which is one of the virtues of ethynylethene. In addition, good accessibility to a variety of substituents through the ethynyl bond is also one of the features in ethynylethene, by utilizing cross coupling reactions such as Sonogashira-Hagiwara [8], [9] and Stille reactions [10]. Dierderich and coworkers have synthesized a wide range of ethynylethene derivatives, to realize a three-dimensional photoswitching system [3], and emitters with high quantum yields [4].

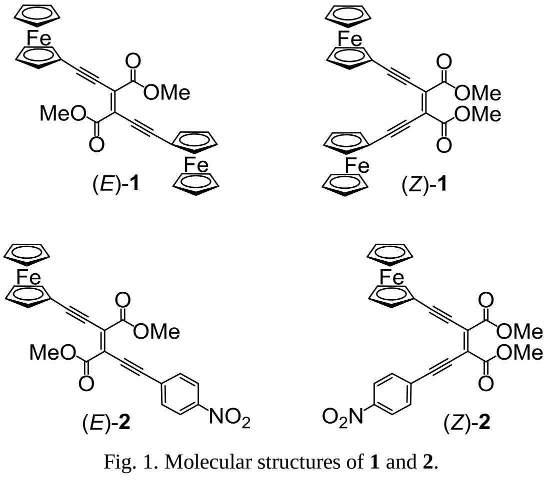

Fig. 1. Molecular structures of **1** and **2**.

We have found a new class of diethynylethene frameworks, dimethyl 2,3-bis(arylethynyl)fumarate/maleate, to be an excellent photochromic and acceptor fragment [11], [12]. In combination with electron-donating ferrocene, unique system (*E*)-**1**, or dimethyl 2,3-bis(ferrocenylethynyl)fumarate/maleate (Fig. 1), was established to produce an optical switch in the electronic communication with photoisomerization triggered by the excitation of a intramolecular charge transfer (ICT) band in the visible region [11], [12].

Herein, the author synthesizes anew a donor-acceptor type of dimethyl 2,3-bis(arylethynyl)fumarate, (*E*)-**2**, where ferrocene and 4-nitrobenzene are employed as donor and acceptor arenes, respectively (see Fig. 1). Its donor-accepter interaction and visible-light photochromism are investigated.

II. EXPERIMENTAL

A. Materials

Ethynylferrocene, [11] dimethyl 2,3-dibromofumarate,[12] dimethyl 2,3-bis(ferrocenylethynyl)fumarate, (*E*)-1,[Angew] were prepared according to the literature procedures. Trimethylamine (Et_3N) was distilled with KOH tablets and stored with KOH tablets. THF was stored under N_2 atmosphere without any stabilizer and distilled with metal Na and benzophenone just before reactions. 1,4-Dioxane (Dehydrated grade) was further dried with activated molecular sieves (3A). The other materials were used as purchased. CuI was provided by Wako Pure Chemical Industries, Ltd. $PdCl_2(PPh_3)_2$ and 4-iodonitrobenzene were supplied by Tokyo Chemical Industry Co., Ltd. The other chemicals were supplied by Kanto Chemical Co., Inc.

B. Syntheses of 1-(4-Nitrophenyl)-2-triisopropylsilyllacethylene

4-Iodonitrobenzene (3.0g, 12 mmol), $PdCl_2(PPh_3)_2$ (96 mg), and CuI (94 mg) were suspended in THF (140 mL) under a nitrogen atmosphere. To the suspension triisopropylsilylacethylene (5 mL, 22 mmol) and Et_3N (60 mL) were added. The dark-orange solution was then refluxed for 14 h. The reaction mixture was filtrated through *celite*, and after evaporation the residue was purified with column chromatography (Al_2O_3, activity II-III) with a mixture of hexane and dichloromethane (3:1 v/v) as eluent The yellow fraction was collected, evaporated, and then recrystallized from dichloromethane and hexane to give pale brown solid of 1-(4-nitrophenyl)-2-triisopropylsilyllacethylene: yield; 3.0 g

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Ryota Sakamoto is with the University of Tokyo, Japan (e-mail: sakamoto@chem.s.u-tokyo.ac.jp).

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(82%). ^{1}H-NMR (Chloroform-d_1) : δ 8.15 (d, (8.9), 2H), 7.58 (d, (8.9), 2H), 1.15-1.05 (m, 21H).

C. Synthesis of 4-Nitrophenylacethylene

1-(4-Nitrophenyl)-2-triisopropylsilyllacethylene (3.0g, 9.9 mmol) was dissolved in THF (200 mL) under a nitrogen atmosphere. To the solution ^{n}Bu$_4$NF in THF (with 5w% H_2O) (12 ml, 12 mmol) was added dropwise in five minutes, which afforded color change from brown to dark blue. After stirring 5 min, to the solution ether and water was added, and the organic phase was separated and washed with water and brine. Dried over Na_2SO_4, the solution was evaporated and residue was purified with alumina column chromatography (activity II-III) with ether as eluent. The yellow fraction was collected and evaporated, and the residue was recrystallized from dichloromethane and hexane to give pale brown soft solid of 4-nitrophenylacethylene: yield; 1.1 g (76%).

D. Synthesis of (E)-Dimethyl 2-(ferrocenylethynyl)-3-(4-nitrophenylethynyl)fumarate, (E)-**2**

To dimethyl 2,3-dibromofumarate (443 mg, 1.5 mmol), CuI (14 mg), $PdCl_2(PPh_3)_2$ (12 mg), 4-nitroethynylbenzene (210 mg, 1.4 mmol), and ethynylferrocene (300 mg, 1.4 mmol), dehydrated Et_3N (50 mL) were added under a nitrogen atmosphere. The brown suspension was heated at 100˚C, which brought it into red suspension. After refluxing 2 h, to the red suspension dichloromethane was added, and the red solution was filtered through *celite*. After removing the solvents black-red residue was purified by alumina (activity II-II) column chromatography with hexane-dichloromethane (1 : 1 v/v) as eluent. The deep-red fraction was evaporated to obtain (*E*)-**2** as deep-red solid: yield; 29 mg (4.1%). Recrystallization from dichloromethane and hexane in dark afforded deep-red crystals of (*E*)-**2**. ^{1}H-NMR (Toluene-d_8) : δ 7.62 (d, (8.8), 2H), 4.38 (dd, (1.9, 1.9), 2H), 3.98-3.97 (m, 7H), 3.50 (s, 3H), 3.41 (s, 3H) (Residual protons were hidden by signals derived from Toluene-d_8).

E. UV-Vis Spectroscopy

As a UV-Vis spectrometer, a set of V-570 (by JASCO Inc.) and PC as a recorder was implemented. To observe absorptions in the UV region quartz cells (optical path: 1 cm) were utilized. Each solution was fabricated to have a maximum optical density around 0.5. Dichloromethane (High Performance Liquid Chromatography grade, Kanto Chemical Co., Inc.), DMF (Spectroscopy grade, Kanto Chemical Co., Inc.), and heptane (Special grade, Kanto Chemical Co., Inc.) were used as purchased.

F. DFT Calculation

In the DFT calculation, the three-parameterized Becke-Lee-Yang-Parr (B3LYP) hybrid exchange-correlation functional was employed. The geometry of (*E*)-**1** was optimized by the DFT(B3LYP) method without solvent effect, using the crystal structure as the initial value. As to (*E*)-**2**, the initial values were employed from the optimized structure of (*E*)-**1**. As a basis set Lanl2DZ (Hay-Wadt ECP) was employed for all atoms. For the comparison with the electronic spectra observed in dichloromethane, the solvent effect was considered with the polarized continuum model (PCM) in the TD-DFT method. A series of calculation mentioned here is implemented with Gaussian 03 or Gaussian 03W (revision-B.05) [15].

G. Tracking of the Photoisomerization Behavior

As an NMR spectrometer a set of Bruker 500 MHz and PC as a recorder was implemented. To irradiate the UV light directly, NMR tubes made of quartz were utilized. As a deuterized solvent, toluene-d_8 (Ample-sealed, Sigma-Aldrich Co.) was used as purchased. To avoid the evaporation of the solvent the sample tubes were tightly sealed with rubber septums, Para film, and Teflon tape. As a photon source an Hg high pressure lamp (Ushio Inc.) was implemented, assorting certain bright lines with a monochromator (CT-10T, JASCO Inc.), or visible cut-off, IR-cut, and UV transmission filters (Asahi Techno Glass Inc.).

III. UV-VIS SPECTROSCOPY

The exploration of the nature of a charge transfer band and solvatochromism on that greatly correlates with the ability as second-order non-linear optics (NLOs), though there are other parameters to be considered, such as the molecular and crystallographic symmetry, for actual application.

In the two-level model [13] the relationship between the ability and nature of an electronic band is given as

$$\beta(0) \propto (\mu_{ee} - \mu_{gg}) \frac{\mu_{ge}^2}{E_{ge}^2} \qquad (1)$$

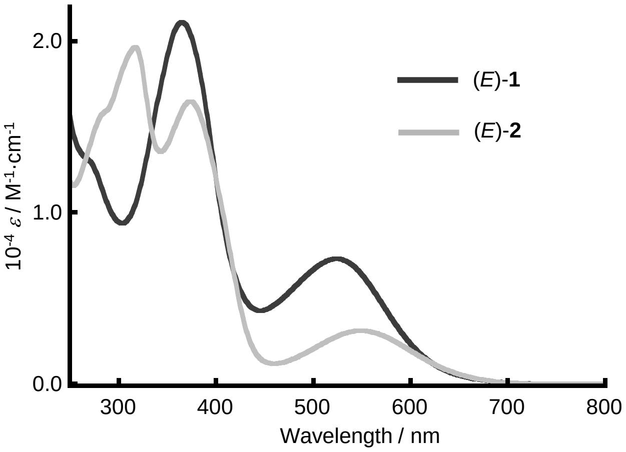

Fig. 2. UV-Vis spectra of (*E*)-**1** and (*E*)-**2** in dichloromethane.

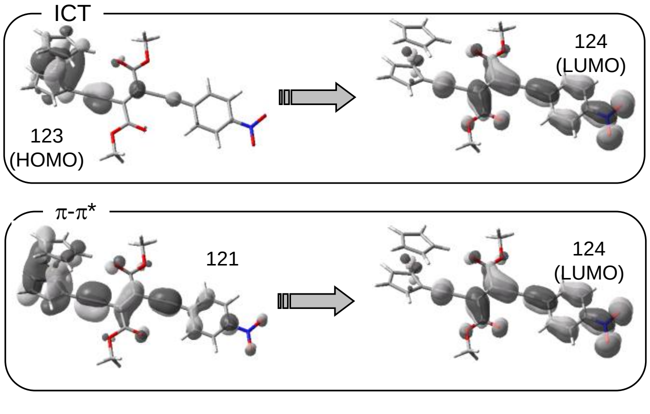

Fig. 3. Main transitions in the ICT and π-π* band of (*E*)-**2**.

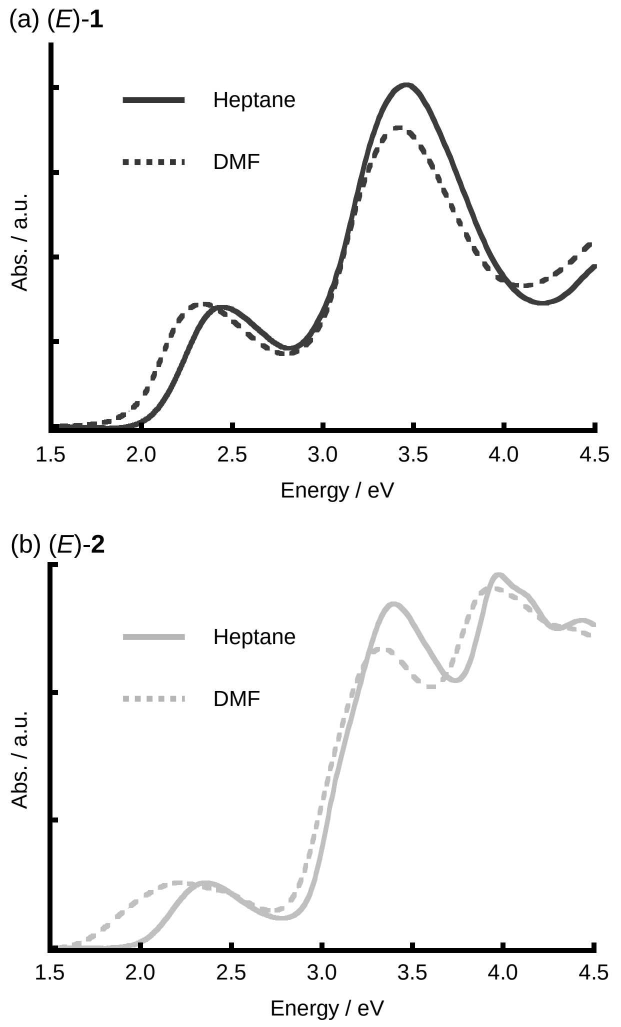

Fig. 4. UV-Vis spectra of (*E*)-**1** and (*E*)-**2** in hexane and DMF .

TABLE I: OPTICAL PROPERTIES OF (*E*)-**1** AND (*E*)-**2**

Compound	Solvent	π-π* / eV (nm)	ICT / eV (nm)
(*E*)-**1**	DMF	3.42 (363)	2.33 (532)
	Dichloromethane	3.40 (365)	2.37 (524)
	Heptane	3.45 (359)	2.44 (508)
(*E*)-**2**	DMF	3.33 (372)	2.21 (559)
	Dichloromethane	3.32 (374)	2.26 (548)
	Heptane	3.40 (365)	2.36 (526)

where $\beta(0)$ denotes the static molecular hyperpolarizability, which correlates with the second-order optical ability, μ_{ee} and μ_{gg} indicate the molecular dipole moment in the excited and ground states, and μ_{ge} and E_{ge} are the transition dipole moment and transition energy of the electronic band, respectively. This equation implies that compounds bearing the larger absorption (μ_{ge}) with the longer wavelength maximum (Ege), and the greater difference in the molecular dipole moment between the excited and ground state (μ_{ee} - μ_{gg}), are more favorable as second-order NLOs. Compounds with charge transfer bands suit this condition pretty well. Such compounds tend to show intense solvatochromism due to the large change in (μ_{ee} − μ_{gg}) that accompanies the optical electron transfer, hence the extent of the solvatochromism can be one of the most accessible indicators.

Fig. 2 shows the electronic spectra of (*E*)-**1** and (*E*)-**2** in dichloromethane, and Table 1 enumerates their parameters. As the author reported previously, the two distinctive absorption bands in (*E*)-**1** at 365 and 524 nm, are, respectively, assignable to the π-π* localized on the dimethyl 2,3-diethynylfumarate framework, and ICT transitions from ferrocene(d) to the π* of the dimethyl 2,3-diethynylfumarate framework [11],[12]. These bands are redshifted in (*E*)-**2**, which implies that the LUMO is replaced with the unoccupied orbital mainly contributed by the 4-nitrobenzene moiety, and it is a better acceptor than the ethynylethene framework. This idea is favored with the DFT calculation (Fig. 3). It discloses that the band at 548 nm is assignable to ICT from ferrocene(d) to the π* orbital of the 4-nitrobenzene moiety, whereas that at 374 nm is fundamentally π-π* transition of the dimethyl 2,3-diethynylfumarate framework, with bear a slight charge transfer nature.

Fig. 4 shows the normalized electronic spectra of (*E*)-**1** and (*E*)-**2** in heptane and DMF, and Table 1 displays the solvatochromic shift of the absorption maxima on both π-π* and ICT bands. (*E*)-**2** showed larger redshifts as to both bands than those of (*E*)-**1**. In addition, in both compounds the ICT band exhibited a larger bathochromic shift than the π-π* band. This series of facts ensures that the lowest-lying electronic bands in (*E*)-**1** and (*E*)-**2** are charge transfer bands, and (*E*)-**2** may be a potential second-order NLO material.

IV. PHOTOISOMERIZATION

Upon irradiation with 546 and 578 nm visible light, (*E*)-**2** in toluene-d_8 underwent ^{1}H NMR spectral change as shown in Fig. 5. This series of spectral changes are typical of *E* to *Z* photoisomerization in dimethyl 2,3-bis(arylethynyl)fumarate [11],[12] (Fig. 1). The conversion ratio was calculated to be 29%, judging from the integral ratio of the signals of the two isomeric forms. The quantum yield for the isomerization was apparently too low to conduct a quantitative analysis.

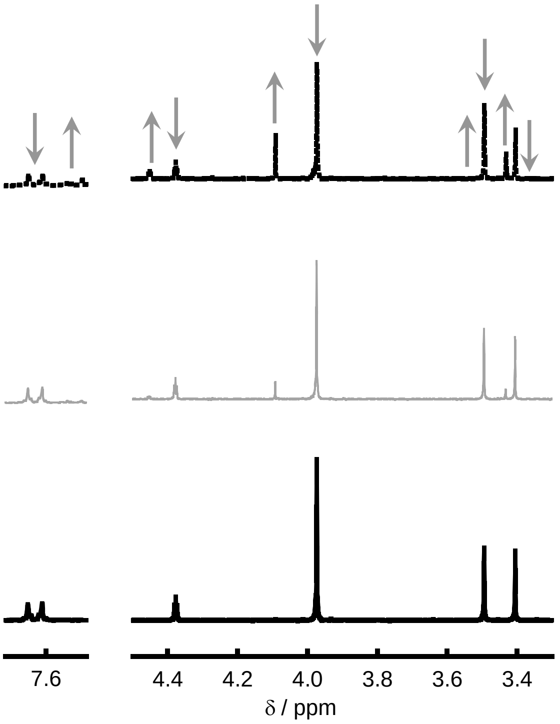

Fig. 5. Time-course ^{1}H-NMR spectral changes of (*E*)-**2** upon irradiation with light at 546 and 578 nm in toluene-d_8.

V. CONCLUSION

The author synthesized a donor-acceptor type of photochromic dimethyl 2,3-bis(arylethynyl)fumarate, (*E*)-**2**, where ferrocene and 4-nitrobenzene were employed as donor and acceptor arenes, respectively. Compared to parent (*E*)-**1**, (*E*)-**2** enjoyed more profound donor-acceptor interaction, leading to a red-shifted ICT band, and is potentially a second-order NLO material. (*E*)-2 underwent visible-light photochromism to (*Z*)-**2** upon excitation with the ICT band.

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Ryota Sakamoto was born in Yamagata Vil., Nagano, Japan, in 1980. He graduated from the University of Tokyo, Japan in 2002, and received his PhD degree from the same university in 2007 under the supervision of Prof. Hiroshi Nishihara.

Then he was appointed as an assistant professor at the Tokyo University of Science (Japan), working with Prof. Takeshi Yamamura. In 2010 he moved to the University of Tokyo, joining Prof. Nishihara's group again. His current research interest lies in the construction of molecule-based nanostructures, and photonic and electronic devices using them.