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COMMUNICATION

A photon-working on/off switch for intramolecular donor-acceptor interactions and invisible modulation of the fluorescence†

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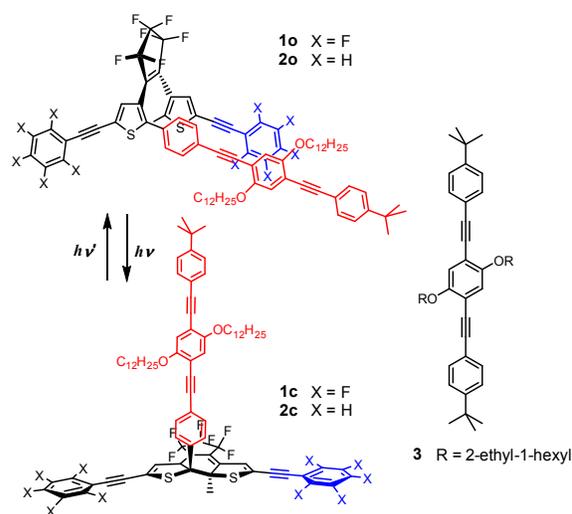
Sakiko Takeuchi, Tetsuya Nakagawa* and Yasushi Yokoyama*

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An on/off switching for charge-transfer interactions between side chains of a diarylethene based on photochromic reactions has been proved by the disappearance and appearance of an additional fluorescence band of the charge-transfer complex.

Light-induced fluorescence modulation of photochromic molecules has attracted much attention due to their potential applications to ultra-high density optical memory media¹ and bioimaging² including ultra-high resolution fluorescent microscopy.³ Among such photochromic molecules, diarylethene⁴ derivatives are one of the most promising candidates for applications due to their high fatigue resistance and thermal stability. In particular, advances in the molecular design of fluorescent diarylethene derivatives for light-induced fluorescence modulation have contributed significantly to their potential use.⁵

Until now, two main mechanisms of light-induced fluorescence modulation induced by photochromism have been introduced. One is the turn-off fluorescence modulation⁶ in which the fluorescence intensity is mainly switched off by intramolecular energy or electron transfer from a fluorescent unit to a closed form upon a photochromic reaction. The other is the turn-on fluorescence modulation⁷ in which the fluorescence intensity is switched on by a structural change from the open form to closed form by the photochromic reaction. Although turn-off and turn-on fluorescent diarylethenes have been widely studied, a fluorescent diarylethene that shows fluorescence in both the open and closed forms with fluorescence modulation capability remains quite rare.^{5,8}



Scheme 1 Diarylethenes 1 and 2 and the reference compound 3.

In the present study, we report on the synthesis of the diarylethene **1o** showing the on/off switch of the charge-transfer interactions between its side chains upon photochromic reaction which was proved by the modulation of the fluorescence band shape. Interestingly, this change, however, is not detectable by the human eyes.

Our design of the photochromic diarylethene **1** was (1) to attach an electron-donating phenyleneethynylene unit on C2 of a 3-thienyl ring and an electron-accepting pentafluorophenyl unit on C5 of the other 3-thienyl ring, and (2) to attach another pentafluorophenyl unit to C5 of the former 3-thienyl ring to render a repulsive interaction between two pentafluorophenyl rings if **1o** takes the parallel conformation. Therefore the antiparallel conformation of **1o** is much more stable than the parallel conformation because of the electronically favourable interactions between the side chains (Scheme 1). Details of the synthetic procedures of **1o** are given in the ESI.†

Department of Advanced Materials Chemistry, Graduate School of Engineering, Yokohama National University, 79-5, Tokiwadai, Hodogaya-ku, Yokohama, 240-8501 Japan.

E-mail: tnakagawa@ynu.ac.jp, yyokoyam@ynu.ac.jp.

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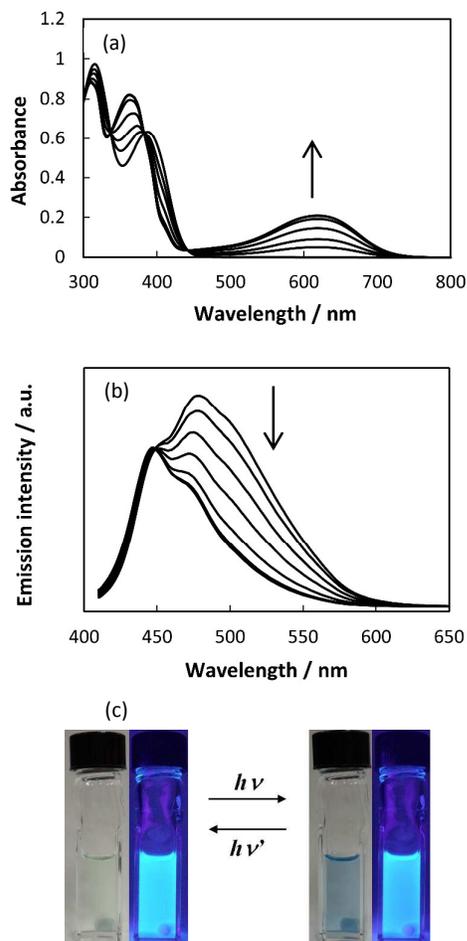


Fig. 1 (a) Absorption spectral change of **1** in hexane upon 405-nm light irradiation. Concentration: 1.34×10^{-5} mol dm^{-3} . Light intensity: 0.089 mW cm^{-2} . Irradiation time/min: 0, 0.5, 1, 2, 4, 8, 16. (b) Emission spectral change of **1** in hexane upon 405-nm light irradiation. Concentration: 1.34×10^{-5} mol dm^{-3} . Light intensity: 0.090 mW cm^{-2} . Irradiation time/min: 0, 0.25, 0.5, 1, 2, 4, 8. $\lambda_{\text{exc}} = 400$ nm. (c) Photographs of the hexane solutions of **1** before (left) and after (right) irradiation with 405-nm light. Excitation: 365 nm light.

Fig. 1(a) shows changes in the absorption spectra of **1o** upon irradiation with 405 nm light in hexane. The pale yellow solution of **1o** turned blue upon irradiation of 405 nm light and a new absorption band appeared at around 600 nm. The coloured solution was completely bleached after irradiation with 622 nm light. These colouration and bleaching cycles were repeated at least 10 times with an isosbestic point appearing at 382 nm, indicating its ability to undergo stable

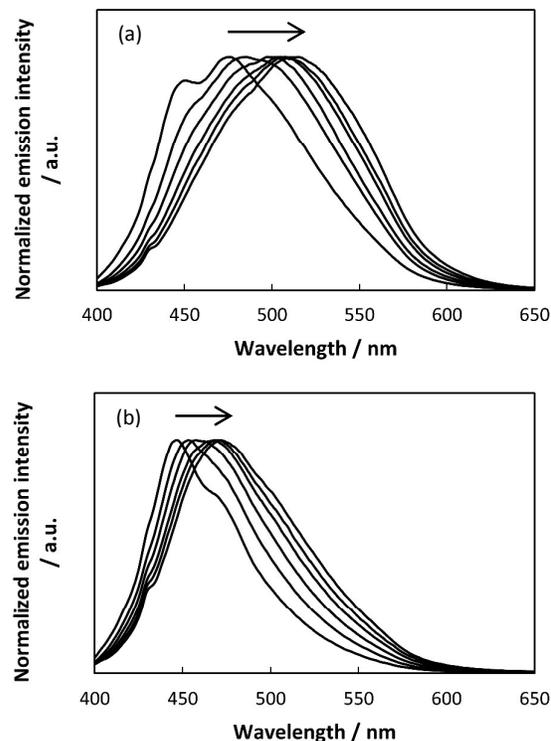


Fig. 2 Emission spectra of (a) **1o** and (b) **1** at pss of 405-nm light irradiation. Solvent: hexane:ethyl acetate = 1.0:0, 0.9:0.1, 0.8:0.2, 0.7:0.3, 0.6:0.4, 0.5:0.5 (left to right). $\lambda_{\text{exc}} = 382$ nm.

photochromic reactions. The conversion ratio to **1c** at the photostationary state (pss) of 405 nm light irradiation in hexane was determined to be 95% by HPLC.

The fluorescence spectra of **1o** upon excitation at 382 nm are shown in Fig. 1(b). Blue fluorescence with a fluorescence quantum yield of 0.08 was observed for **1o**. Although almost no fluorescence colour change was observed for human eyesight during photochromic reactions as shown in Fig. 1(c), the fluorescence band at around 480-nm region decreased gradually upon irradiation with 405 nm light and a more structured fluorescence band appeared at around 450 nm. After 622 nm light irradiation, the initial fluorescence shape was recovered. It should be noted that these changes in the fluorescence spectra are very much different from typical turn-off fluorescence modulation behaviours. In the case of turn-off fluorescence modulation, only the emission intensity changes upon photochromic reactions since the non-radiative decay process of the fluorescence unit is mainly modulated by the photochromic reactions.⁶⁾

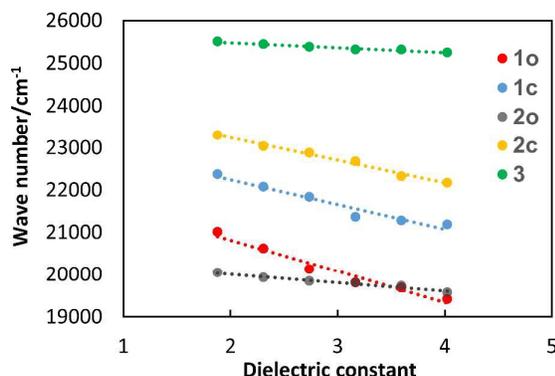


Fig. 3 The relationship between the emission wave number of **1o**, **1c**, **2o**, **2c** and **3** and the dielectric constant values of the solvents.

In order to clarify the reasons for the changes in the fluorescence spectra of **1** by photochromic reactions, we measured its solvent polarity dependence in pure hexane and hexane/ethyl acetate mixed solutions before and after 405 nm light irradiation. As shown in Fig. 2(a), the fluorescence spectra of **1o** became structureless with an increase in solvent polarity. Solvent polarity dependence of the fluorescence maximum wavelength was also observed. These results clearly indicate that the excited state of **1o** has an intramolecular charge-transfer character from the electron-donating phenyleneethynylene unit to the electron-accepting pentafluorophenyl unit. Similar spectral broadening was also observed in its pss solution with an increase in solvent polarity, as shown in Fig. 2(b). However, solvent polarity dependence of the fluorescence wave number was much smaller than that of **1o**, indicating the weaker charge transfer character of **1c**. Our observations on the solvent polarity dependence of the fluorescence in **1** are well supported by a previously reported fluorescent diarylethene derivative that shows photochromism as well as solvatochromism.⁹⁾

These results can be explained on the basis of the difference in the charge transfer interaction¹⁰⁾ between the phenyleneethynylene unit and the pentafluorophenyl unit of **1o** and **1c**. In the case of **1o**, the phenyleneethynylene unit is aligned parallel to a pentafluorophenyl unit. On the other hand, these phenyleneethynylene and pentafluorophenyl units are almost orthogonally aligned in **1c** since the ring closing sp^2 carbon atoms in **1o** are converted to sp^3 carbon atoms after the photocyclization reaction. These structural changes are well supported by DFT calculations at the B3LYP/6-31G(d) level (see Fig. S5). Furthermore, we found that **1o** shows a relatively high photocyclization quantum yield¹¹⁾ of 0.61 in hexane. It is known that diarylethene derivatives take parallel and antiparallel conformations in solution. Since the photocyclization reaction takes place only from the antiparallel conformation, the photocyclization quantum yield of typical diarylethene derivatives is less than 0.5 in many cases.⁴⁾ Therefore, the antiparallel conformation in the molecular conformation of **1o** at the ground state is dominant because of

its high photocyclization quantum yield. These facts also support the assumption that the phenyleneethynylene unit of **1o** is aligned parallel to the pentafluorophenyl unit in the ground state.

To confirm this hypothesis, we synthesized the reference compound **2**¹²⁾ (details of its synthetic procedures are given in the ESI†) containing phenyl rings instead of the pentafluorophenyl rings in **1**, and examined its solvent polarity effects on the fluorescence spectra. As shown in Fig. S6, reference compound **2** also showed similar spectral broadening and fluorescence wavelength shifts with an increase in the solvent polarity. Linear relationships between the fluorescence maximum wave number and the dielectric constants of the solvents for diarylethene derivatives **1** and **2** were clearly observed, as shown in Fig. 3. However, it should be noted that the slope of **1o** is larger than that of **2o**. This phenomenon is in good agreement with the fact that **1o** has an electron-accepting pentafluorophenyl group which experiences a larger charge transfer interaction from the electron-donating phenyleneethynylene unit compared with the phenyl group in **2o**. On the other hand, the slope of **1c** in Fig. 3 is similar to that of **2c**, indicating that the charge transfer interactions in **1c** and **2c** are similar due to little orbital overlapping of the electron-donating and accepting moieties since their orthogonal alignment to each other was formed after the photocyclization reaction.

In addition to **1** and **2**, we examined the solvent polarity dependence of the emission properties of 2,5-bis(2-ethylhexyloxy)-1,4-bis[4-*t*-butylphenylethynyl]benzene **3** as a reference compound. As shown in Fig. 3, **3** showed little solvent polarity dependence compared to **1** (for emission spectra of **3**, see Fig. S7). This result is in good accordance with the fact that **3** is composed only of the donor moiety. We have, therefore, concluded that photoswitching of the charge transfer interactions plays an important role in modulating the fluorescence characteristics of diarylethene derivative **1**. Although some diarylethene derivatives are known to show fluorescence both in their open and closed forms with fluorescence colour change capabilities,¹³⁾ the invisible fluorescence modulation described in this communication has not yet been reported to date.

Conclusions

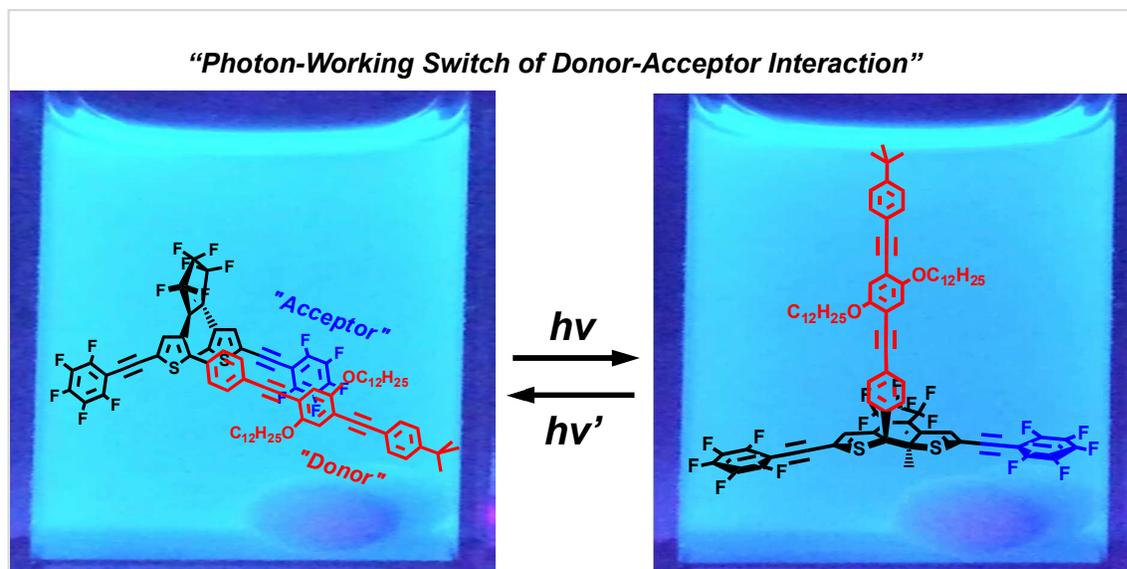
An invisible fluorescence modulation based on the photoswitching of a charge transfer interaction between the side chains of a diarylethene **1o** was reported. We believe that these findings will open up new fields of research such as fluorescent security materials based on fluorescent photochromic compounds.

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