

Photochromism of a diarylethene charge-transfer complex: photochemical control of intermolecular charge-transfer interaction†

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Received (in Cambridge, UK) 27th March 2006, Accepted 25th April 2006

First published as an Advance Article on the web 22nd May 2006

DOI: 10.1039/b604388g

A diarylethene derivative bearing a phenylenediamine group formed radical ions with an electron acceptor molecule in solution, and the concentration of the radical ions was modulated by the photochromic reaction of the diarylethene, reflecting the difference in the electron-donating character between the open- and closed-ring isomers.

Photochromic compounds have attracted great attention owing to their potential application to opto-electronic devices, such as rewritable optical memory media and optical switches.^{1,2} Among the photochromic compounds reported so far, diarylethene derivatives are the most promising candidates for the application because of their thermal stability, fatigue resistance, and high reactivity in the crystalline state.³ The diarylethenes undergo reversible photoisomerization between two isomers, open- and closed-ring forms. The two isomers are different from each other not only in absorption spectra but also in other physical and chemical properties, such as geometrical structures,⁴ refractive indices,⁵ and oxidation/reduction potentials.⁶

Electron donor-acceptor (EDA) complexes have been extensively studied in the widespread fields from biological to materials science.⁷ The association behavior of the complexes and the absorption property of intermolecular charge-transfer (CT) transition are dependent on the ionization potential of the donor, the electron affinity of the acceptor, and environmental conditions. In addition, the EDA complexes have attracted interest as organic conductors because they exhibit unique conducting behavior in the solid state.⁸ The conductivity is controlled by molecular stacking structures and CT interactions between the donor and the acceptor molecules. If a photochromic diarylethene unit could be introduced into the EDA complex, photoinduced reversible changes of oxidation or reduction potential of the diarylethene would lead to the modulation of the properties of the complex, such as the association constant and absorption spectrum of the CT complex. Furthermore, if the reaction would proceed in the crystalline phase, solid-state physical properties of EDA complexes, such as electrical conductivity,⁹ magnetic properties,¹⁰ and non-linear optical properties,¹¹ could be photochemically controlled.

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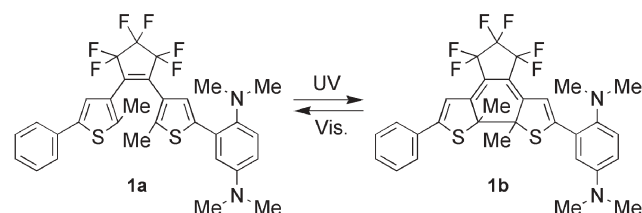
† Electronic supplementary information (ESI) available: Experimental section and supplementary data. See DOI: 10.1039/b604388g

As a first step toward the photochemical control of solid-state physical properties of EDA complexes, we report on an EDA complex that contains a photochromic diarylethene unit. Diarylethene **1** bearing a *N,N,N',N'*-tetramethyl-*p*-phenylenediamine group, which exhibits strong electron-donating character, was synthesized as a photochromic electron donor (Scheme 1; synthetic procedures and analytical data of **1** are described in the supplementary information†). 2,3,5,6-Tetrafluoro-7,7,8,8-tetracyano-*p*-quinodimethane (TCNQF₄) was selected as an electron acceptor. The formation and photochromic behavior of the EDA complex, which consists of **1** and TCNQF₄, in the solution phase were studied.

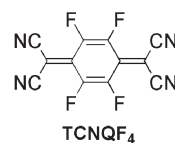
Diarylethene **1** underwent photochromism in acetonitrile. The acetonitrile solution of open-ring isomer **1a** was colourless. Upon irradiation with ultraviolet (UV) light, the colourless solution turned blue. The colour change is due to the formation of closed-ring isomer **1b** by UV-irradiation. **1b** has an absorption maximum at 600 nm in acetonitrile. **1b** was thermally stable in the dark at room temperature. Upon irradiation with visible light ($\lambda > 480$ nm), the blue solution of **1b** was completely bleached, and the absorption spectrum returned to that of **1a**.

The electrochemical property of **1** was studied by cyclic voltammetry.† Both **1a** and **1b** show two oxidation waves (**1a**: -0.01 V and 0.31 V, **1b**: 0.02 V and 0.36 V (vs. ferrocene/ferrocene⁺, in acetonitrile)). *N,N,N',N'*-Tetramethyl-*p*-phenylenediamine (TMPD) also shows two oxidation waves at -0.28 V and 0.30 V. The oxidation waves of **1a** and **1b** correspond to two-step one-electron oxidations of the phenylenediamine moieties in the molecules.¹² The oxidation of the phenylenediamine moiety of **1a**

Photochromic Electron Donor



Electron Acceptor



Scheme 1 Photochromic electron donor **1** (**1a**: open-ring isomer, **1b**: closed-ring isomer) and electron acceptor TCNQF₄.

occurs at more negative potentials than that of **1b**. This indicates that **1a** has stronger electron-donating character than **1b**. TCNQF₄ shows reduction waves at 0.18 V and -0.36 V.†

In order to know the details of the electrochemical response of the diarylethene, molecular orbital calculation was carried out (Hartree-Fock (HF) functional, 6-31G* basis set†), although it shows just a trend not the absolute value in the electrochemistry. According to Koopman's theorem, the negative of the eigenvalue of HOMO calculated at the HF level correlates with the vertical ionization potential, which correlates with the oxidation potential.¹³ The eigenvalues of the HOMOs which localize on the phenylenediamine moieties are -7.5307 eV and -7.6540 eV for **1a** and **1b**, respectively. This indicates that **1a** can be oxidized at lower potential than **1b**. This trend agrees with the electrochemical response.

The EDA complex was prepared by mixing **1a** and TCNQF₄ in a mixed solvent of chloroform and acetonitrile. The solutions of **1a** and TCNQF₄ are colourless and yellow, respectively, as shown in Fig. 1a and 1b. Upon mixing the compounds in the molar ratio of 1 : 1, the solution turned bluish green, as shown in Fig. 1c. The absorption spectrum of the mixed solution has electronic absorption bands in the visible and near-infrared regions, which are not observed in the pure compounds (Fig. 1c). The sharp absorption bands at 863 nm and 760 nm are ascribed to a radical mono-anion of TCNQF₄ (TCNQF₄^{-•}). A potassium salt of TCNQF₄ (K⁺TCNQF₄^{-•}) shows the same absorption spectrum.†¹⁴ The broad band around 600 nm can be assigned to a radical mono-cation of **1a** (**1a**^{+•}), in which the phenylenediamine moiety is one-electron oxidized. The similar absorption around 600 nm is

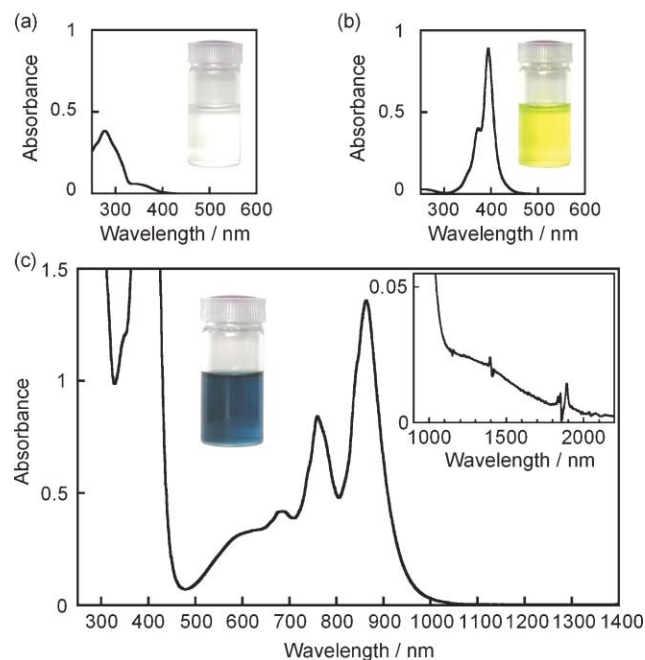


Fig. 1 Absorption spectra and photographs of (a) **1a** (1.0×10^{-5} M), (b) TCNQF₄ (1.0×10^{-5} M), and (c) a 1 : 1 (molar ratio) mixture of **1a** and TCNQF₄ ($[1a] = [TCNQF_4] = 7.5 \times 10^{-5}$ M) in a mixed solvent of chloroform and acetonitrile (v/v 10 : 1). In c, the inset shows an absorption spectrum of high-concentration solution ($[1a] = [TCNQF_4] = 2.5 \times 10^{-4}$ mol dm⁻³) from 900 to 2200 nm.

observed in the absorption spectra of **1a** under the bulk electrolysis at the potential where the first oxidation of **1a** takes place.† It is also reported in previous literature that a radical mono-cation of **TMPD** shows an electronic absorption band around 600 nm.¹⁵ In addition to the absorption bands due to the radical ions, the mixed solution shows a weak absorption at longer wavelength than 1100 nm (Fig. 1c, inset). This absorption band extends to 2000 nm. The weak absorption band can be ascribed to intermolecular CT transition between donor **1a** and acceptor TCNQF₄. A complex composed of **TMPD** and TCNQF₄ has a similar CT band in the near-infrared region.¹⁶ These results indicate that, in the mixed solution of donor **1a** and acceptor TCNQF₄, both the CT complex (**1a**·TCNQF₄) and the radical ions (**1a**^{+•} and TCNQF₄^{-•}) are in equilibrium. Because of strong electron-donating and accepting characters of **1a** and TCNQF₄, the CT complex can dissociate into the radical ions.

Photochromic behavior of the EDA complex of **1** and TCNQF₄ was examined. Fig. 2 shows a photoinduced absorption spectral change in the mixed solvent of chloroform and acetonitrile. A 1 : 1 (molar ratio) mixture of **1a** and TCNQF₄ exhibited bluish green, and has absorption bands due to the radical ions and the CT complex. Upon irradiation with 305 nm light, the absorption intensity around 600 nm increased, indicating that the diarylethene underwent photocyclization reactions to yield the closed-ring isomer. Accompanying this photochromic reaction, the absorption intensity of TCNQF₄^{-•} decreased, and the absorption intensity of the CT complex increased. Upon irradiation with 578 nm light, the absorption intensity around 600 nm decreased along with the increase of the absorption due to TCNQF₄^{-•} and the decrease of the absorption due to the CT complex. The spectral change indicates that dissociation of the CT complex to the radical ions in the mixed solution is controlled by the photochromic reactions of **1**.

In order to interpret the above absorption spectral change, absorption spectra of mixtures of **1a** and TCNQF₄ and **1b** and TCNQF₄ were measured. Fig. 3a shows absorption spectra of the mixtures. Both the mixtures have sharp absorption bands due to TCNQF₄^{-•} and weak ones due to the CT complexes. Closed-ring isomer **1b** also formed a CT complex and radical ions with TCNQF₄. Although the absorption band due to a radical cation of **1b** (**1b**^{+•}) should be observed around 600 nm, it overlaps with the

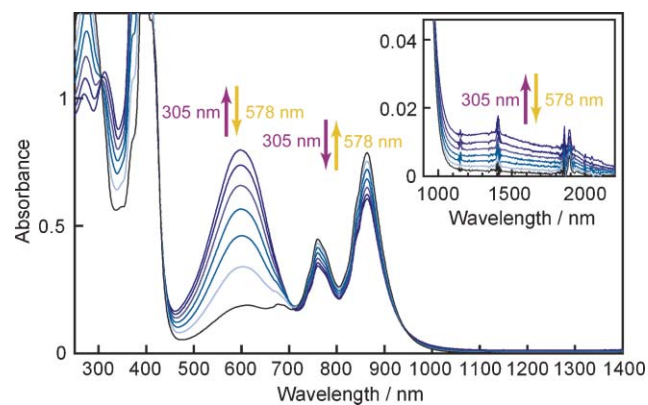


Fig. 2 Photoinduced absorption spectral change of a 1 : 1 (molar ratio) mixture of **1** and TCNQF₄ ($[1] = [TCNQF_4] = 4.0 \times 10^{-5}$ M) in a mixed solvent of chloroform and acetonitrile (v/v 10 : 1).

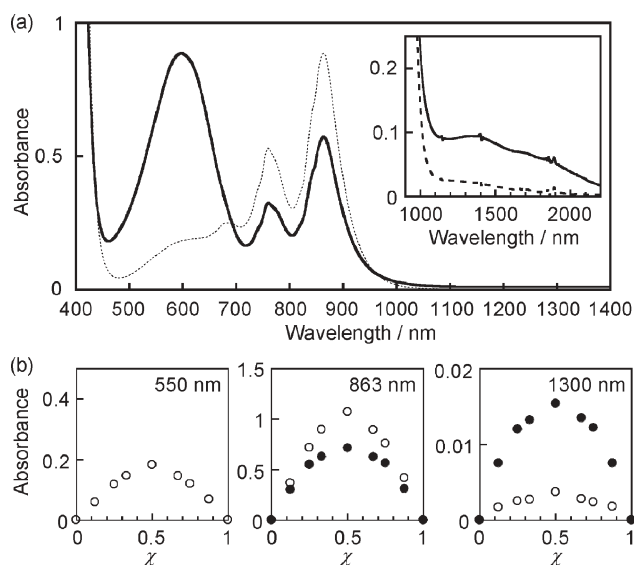
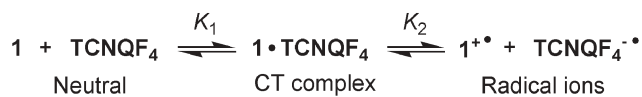


Fig. 3 (a) Absorption spectra of 1 : 1 (molar ratio) mixtures of **1a** and **TCNQF₄** (dotted line) and **1b** and **TCNQF₄** (solid line) (**[1a]** = **[1b]** = **[TCNQF₄]** = 5.0×10^{-5} M) in a mixed solvent of chloroform and acetonitrile (v/v 10 : 1). The inset shows an absorption spectrum of high-concentration solution (**[1a]** = **[1b]** = **[TCNQF₄]** = 2.5×10^{-4} M) from 900 to 2200 nm. (b) Job plots of the absorbance for **1a** and **TCNQF₄** (open circles) and **1b** and **TCNQF₄** (closed circles) at 550, 863, and 1300 nm. χ is molar fractions of donor ($\chi = [\mathbf{1a}]/([\mathbf{1a}] + [\mathbf{TCNQF}_4])$ or $[\mathbf{1b}]/([\mathbf{1b}] + [\mathbf{TCNQF}_4])$).

absorption band due to the diarylethene moiety in the closed-ring form. The stoichiometry of the CT complexes and the radical ions was determined by Job-plot analysis of the corresponding absorption bands.[†] The Job plots shown in Fig. 3b indicate that the donor and acceptor molecules interact in a 1 : 1 ratio. Therefore, the equilibrium in the mixed solutions can be expressed as shown in Scheme 2. It should be noted that the absorption intensities of **TCNQF₄^{•-}** and the CT complexes are dependent on the donors **1a** and **1b**. The absorption intensity of **TCNQF₄^{•-}** is stronger for **1a** than that for **1b**, on the other hand, the intensity of the CT band is weaker for **1a** than that for **1b**. Molar ratios of the radical ions in the mixed solutions are determined to be approximately 48% and 30% for **1a** and **1b**, respectively, by using the molar absorption constant of **K⁺TCNQF₄^{•-}**. The CT complexes and the radical ions are in equilibrium and the concentrations are dependent on the configuration of the donor molecule, **1a** or **1b**. Binding constants of the EDA complexes were determined by absorption-spectral analysis.[†] Because of the weakness of the CT bands, it was impossible to determine each equilibrium value, K_1 and K_2 , in Scheme 2. However, the products of K_1 and K_2 ($K_1K_2 = K$) could be determined, which reflects the process of the radical-ion formation. By the analysis, K values were determined to be 1.01 ± 0.06 and 0.32 ± 0.02 for **1a** and **1b**, respectively. The value for **1a** is larger than that for **1b**. This result indicates that **1a** readily dissociates into radical ions with **TCNQF₄**



Scheme 2 Equilibrium in mixtures of **1** (**1a** or **1b**) and **TCNQF₄**.

in comparison with **1b**. The difference is ascribed to the difference in the electron-donating ability between the open- and closed-ring isomers. The cyclic voltammetry indicates that **1a** shows oxidation waves at more negative potentials than **1b**, that is, **1a** is more electron-donative than **1b**. Such differences in the equilibrium between the open- and closed-ring isomers leads to the photoinduced change in the absorption intensities of the radical ions accompanying the photochromic reactions of the diarylethene, as shown in Fig. 2.

In conclusion, we have demonstrated that the formation of radical ions can be modulated upon photoirradiation using a complex of a diarylethene bearing an electron-donative phenylenediamine unit and **TCNQF₄**. The absorption intensities of the CT complex and the radical ions were controlled by photochromic reactions of the diarylethene. This behavior is ascribed to the difference in the electron-donating character between the open- and closed-ring isomers of the diarylethene. To the best of our knowledge, this is the first example of the photochemical control of intermolecular CT interaction between electron donor and acceptor molecules by the photochromic reaction.

This work was partly supported by Grant-in-Aids for Scientific Research (S) (No. 15105006), Scientific Research on Priority Area (432) (No. 16072214), and the 21st century COE program from the Ministry of Education, Culture, Sports, Science, and Technology of Japan. M. M. wishes to thank Research Fellowships of the Japan Society for the Promotion of Science for Young Scientists.

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