Reversible photochromism of a ferrocenylazobenzene monolayer controllable by a single green light source†

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Received (in Cambridge, UK) 28th August 2007, Accepted 9th October 2007
First published as an Advance Article on the web 16th October 2007
DOI: 10.1039/b713107k

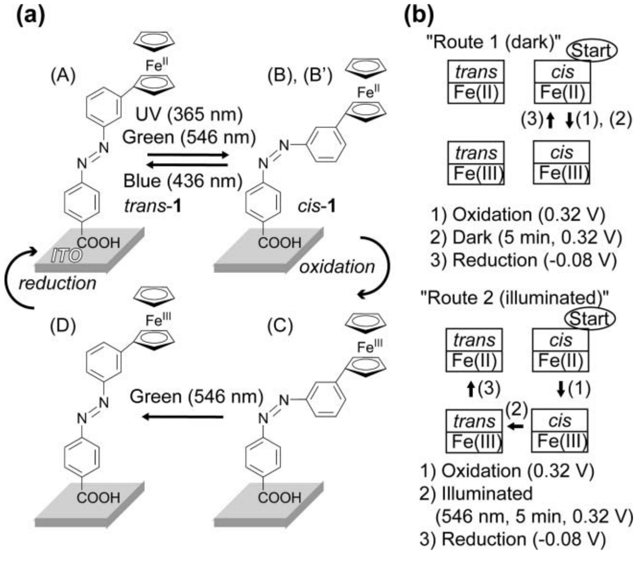
A 3-ferrocenylazobenzene monolayer on an ITO electrode exhibits reversible azobenzene isomerization using a single green light source, assisted by electrochemical control of the ferrocene redox state.

Optical data storage is a key issue for today's information technology, and photochromic molecules have been intensely studied for their application to molecular-sized devices.[1] Assemblies of photochromic azobenzene derivatives have attracted much attention because they can achieve immobilization and high density of the switching units.[2–5] Azobenzene-based photoswitches are usually manipulated with two different light sources, UV light for a *trans*-to-*cis* isomerization and blue light for the reverse isomerization. For the application to high-density data storage manipulated with fine-focused light irradiation, focusing dual light sources on the same small region can be a problem from the perspective of both technical difficulty and cost performance. Therefore, reversible isomerization of azobenzene in monolayers with a single light source would be greatly advantageous.

We have previously reported the redox-conjugated reversible photoisomerization of 3-ferrocenylazobenzene (**3-FcAB**).[6,7] As shown in Scheme 1a, **3-FcAB** in the reduced Fe(II) state undergoes *trans*-to-*cis* isomerization by the excitation of an MLCT band with 546-nm green light in addition to the normal UV and blue light response (*trans*-to-*cis* isomerization by excitation of the azo π–π* band with 365-nm UV light, and the reverse *cis*-to-*trans* isomerization by excitation of the *cis*-azo n–π* band with 436-nm blue light). Once this compound is chemically or electrochemically oxidized to **3-FcAB**$^+$ in the Fe(III) state, the MLCT band disappears and *cis*-to-*trans* reverse isomerization occurs with the same 546-nm light. This compound therefore shows reversible isomerization with a single green light coupled with the reversible redox reaction between Fe(II) and Fe(III). It is thus interesting to assemble **3-FcAB** derivatives on an electrode surface with the aim of creating molecular-sized optical data storage. We selected an indium-tin oxide (ITO) substrate as a transparent electrode compatible with the characteristics of **3-FcAB**, and designed a carboxylate-modified **3-FcAB**, 3-ferrocenyl-4′-carboxylazobenzene (**1**), as a single-light-controllable chromophore to be immobilized on an ITO electrode.

1 was newly synthesized *via* the acid-catalyzed coupling of 3-ferrocenylaniline with 4-nitrosobenzyl alcohol and subsequent oxidation (Scheme S1). The photoreactivity of **1** in ethanol solution was tested, and reversible photoisomerization behaviour was observed (the *cis* molar ratio in its photostationary state (PSS) was 59% with 365-nm UV light, 26% with 546-nm green light, and 13% with 436-nm blue light, see Fig. S1). Photoisomerization behaviours on ITO nanoparticles were also examined by diffuse reflectance UV–vis spectroscopy (Figs. S2 and S3) because the aggregation of chromophores often prevents photoisomerization.[8] Effective photoisomerization of **1** was observed on particles of ITO as received, but was not observed on ITO particles hydrophilized by H_2O_2–NH_3 aq.–H_2O = 1 : 1 : 5 solution to improve immobilization.[9] This result suggests that **1** was too crowded on the hydrophilic surface and caused aggregation between azobenzene chromophores or ferrocene parts, and that photoisomerization of **1** was prevented by the intermolecular stacking effects. ITO–glass electrodes used in the following studies were therefore treated without a hydrophilization process.

The monolayer of **1** on an ITO–glass electrode (**1**/ITO) was prepared by the following method. An ITO–glass substrate was washed with acetone, detergent solution, water, and ethanol



Scheme 1 Schematic images of the redox-coupled single-light isomerization of **1**/ITO. (a) Relation of *trans*–*cis* isomerization and a redox cycle. (b) The procedures to confirm the photoisomerization with the green light in its Fe(III) state.

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† Electronic supplementary information (ESI) available: Synthetic scheme of **1** (Scheme S1); UV–vis spectra of **1** (Fig. S1) and **1** on ITO particles (Figs. S2 and S3); immersion time dependence of cyclic voltammograms of **1**/ITO (Fig. S4); a sketch of the spectroscopic cell (Fig. S5); UV–vis spectral changes of **1**/ITO in redox coupled isomerization measurement (Fig. S6); experimental section. See DOI: 10.1039/b713107k

(30 min each with sonication) and sonicated in a 1 mM ethanol solution of **1** at 20 °C, washed with ethanol and finally dried by nitrogen blow.

Cyclic voltammograms of **1**/ITO were measured to confirm the immobilization of **1** and to evaluate the degree of the molecular aggregate in the monolayer. In the cyclic voltammograms of the monolayer in Bu_4NClO_4–ethanol shown in Fig. 1a, a reversible peak appeared at 0.05 V *vs.* ferrocenium/ferrocene (Fc^+/Fc), almost equal to the value in ethanol solution (0.06 V *vs.* Fc^+/Fc). The peak current was proportional to the scan rate (Fig. 1a), indicating that the peak can be ascribed to the Fe(III)/Fe(II) couple of the ferrocene moieties of surface-confined **1**.[10]

Surface coverage of redox active molecules (Γ) in the monolayer was estimated from the anodic charge integration in the voltammogram at a sweep rate of 0.1 V s^{-1}. The dependence of Γ on the period of sonication indicates that the value was saturated to *ca.* 1.7×10^{-10} mol cm^{-2} within 20 min (Fig. S4). The relatively small Γ value against the saturated value of the monolayer of usual ferrocene derivatives, *ca.* 6×10^{-10} mol cm^{-2}, and a small peak shift on the formation of the monolayer suggest that molecules of **1** in the prepared monolayer were loosely packed and may not have had too much intermolecular interaction for the photoisomerization reaction,[11] even if local molecular aggregation was observed in the UV–vis spectrum as shown below. The contact angle of water on the substrate was also measured, and the angle was increased from 31(1)° to 63(2)° after sonication for 1 h with the solution of **1**. This increase suggests that the substrate was surely covered with hydrophobic molecules. The **1**/ITO samples used in the following experiments were prepared by immersion for 24 h and sonication for 1 h. All UV–vis spectra of **1**/ITOs shown below were measured in a cell shown in Fig. S5 for the convenience of the redox- and photoirradiation-coupled measurement. These spectra are the sum of two layers on the two substrates to increase the absorption signal, and the absorption of bare ITO substrates in the blank measurement was subtracted.

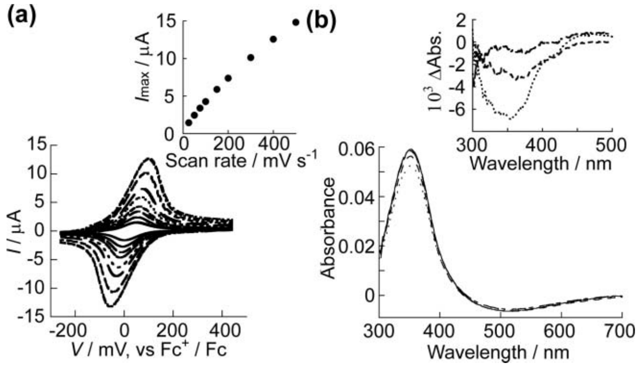

Fig. 1 Electrochemical and photochemical properties of **1**/ITO. (a) Cyclic voltammograms of **1**/ITO in 0.1 M Bu_4NClO_4–ethanol *vs.* Fc^+/Fc at a scan rate of 25, 50, 75, 150, 200, 300, 400, and 500 mV s^{-1} (from inside to outside). Inset: The peak current plot *vs.* scan rate. The monolayer was prepared by the immersion method with 1 h sonication. (b) UV–vis absorption spectrum of **1**/ITO (solid line) and its 546-nm (dashed line), 365-nm (dotted line), and 436-nm (dash-dotted line) photoirradiated spectra. These spectra are the sum of two substrates. Inset: Differences in the UV–vis absorption spectra of **1**/ITO between before irradiation and after 546-nm (dashed line, A), 365-nm (dotted line, B), and 436-nm (dash-dotted line, C) irradiation. Immersion time: 25 h (including 1 h sonication). Irradiation time: 1 h.

Fig. 1b shows the UV–vis absorption spectral changes upon photoirradiation. In the initial spectrum of *trans*-**1**/ITO, the π–π* transition of the azobenzene moiety was observed at 352 nm. A 27-nm red shift of the band compared with that in its ethanol solution and an increase of the band intensity (from $\varepsilon_{max} = 2.1 \times 10^4$ dm^3 mol^{-1} cm^{-1} in ethanol to *ca.* 2.7×10^4 dm^3 mol^{-1} cm^{-1}, which was evaluated from the Γ value obtained from the cyclic voltammogram) were derived from the *J*-aggregation of the azobenzene moiety.[12] The azo π–π* band decreased in intensity with green (546 nm) light and further decreased with UV (365 nm) light, and the band intensity was recovered with blue (436 nm) light. Reproducibility was tested for 3 cycles. These behaviours are characteristic of the *trans*-to-*cis* and *cis*-to-*trans* isomerization, respectively, and are similar to the behaviours in solution. The *cis* molar ratios of the azo moieties in the PSS were estimated to be 20% with the UV light, 10% with the green light, and almost 0% with the blue light. These values are approximately one-third of those in solution, probably because the isomerization of azo moieties was restrained by the effect of *J*-aggregation.[8]

The single-light photoisomerization cycle of **1**/ITO was achieved by the combination of green light and electrochemical or chemical redox reactions. Four states of **1**/ITO during a single-light photoisomerization cycle and the operations to change these states are summarized in Scheme 1a. In the case of electrochemical redox-coupled measurements, large UV–vis spectral changes of the bare ITO substrate and the electrolyte solution were observed when the potential was applied. In order to eliminate this perturbation, the absorption spectra obtained from two different sets of experiments at the same potential, route 1 (‘dark’) and route 2 (‘illuminated’) in Scheme 1b, were compared to prove the single-light photoisomerization event.

A *trans*-**1**/ITO in the reduced Fe(II) state in Bu_4NClO_4–MeCN (A state in Scheme 1a) was irradiated with the green light to reach the PSS (B state), and the resulting mixture of *trans*- and *cis*-forms was electrochemically oxidized to the Fe(III) state by holding the potential at 0.32 V *vs.* Fc^+/Fc for 5 min in the dark (C state), followed by a reduction to the Fe(II) state by holding the potential at −0.08 V *vs.* Fc^+/Fc for 30 s (B′ state), and the spectrum was measured. The next run was carried out under the same conditions and with the same procedures, but the monolayer was irradiated with the green light during 5 min oxidation, which should cause isomerization to the D state. After the reduction to the Fe(II) state (A′ state), the spectrum was measured. The differences in the UV–vis spectral changes between the ‘dark’ and ‘illuminated’ conditions are shown in Fig. 2a-A (see Fig. S6 for difference absorption spectra in both conditions). Based on the amount of increase in the absorption intensity in the π–π* region, approximately 10% of **1** was converted to the *trans*-form by the green light. This ratio is almost equal to the ratio in the *trans*-to-*cis* photoisomerization with green light in the Fe(II) state (see Fig. 1b). This spectrum therefore indicates that the *cis*-form generated by the green light irradiation to **1**/ITO in the reduced Fe(II) state did not return to the *trans*-form with oxidation to the Fe(III) state and the following re-reduction, and returned to the *trans*-form by the photoreaction of 1^+/ITO with the irradiation of green light in the oxidized Fe(III) state. It is noteworthy that the *trans*-**1**/ITO in the re-reduced Fe(II) state could again be converted to the *cis*-form by irradiation with

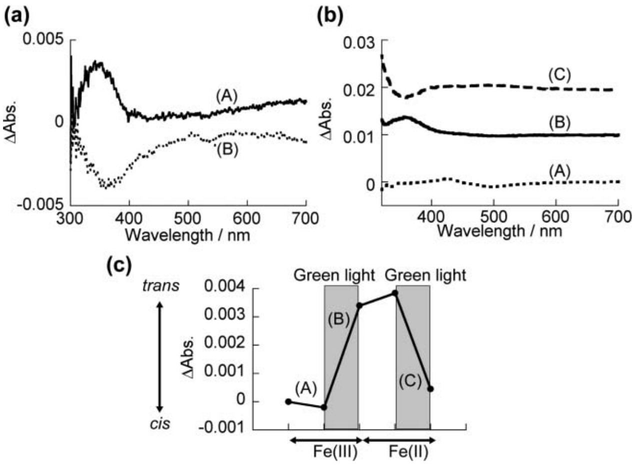

Fig. 2 Reversible photoisomerization of **1**/ITO using a single 546-nm light source and redox reaction of ferrocene moieties. (a) Differences in the UV–vis absorption spectra of **1**/ITO upon 546-nm photoirradiation in its oxidized state (A) and in its reduced state (B). (b) Differences in the UV–vis absorption spectra of $\mathbf{1}^+$/ITO in ethanol between before and after in the dark with iodine (A) and upon 546-nm photoirradiation with iodine (B), and upon 546-nm photoirradiation in its re-reduced state by washing with ethanol (C). Horizontal lines are shifted for clarity. (c) Absorbance change of **1**/ITO at 352 nm upon addition and removal of iodine coupled with 546-nm light irradiation. These spectra are the sum of two substrates.

the green light (see Fig. 2a-B). We can thus conclude that the isomerization behaviour of **1**/ITO can easily be controlled by an electrochemical redox reaction of the ferrocene moiety, which does not pollute the photoswitching system and is totally repeatable.

Direct observation of *cis*-to-*trans* photoisomerization of $\mathbf{1}^+$/ITO in the Fe(III) state by UV–vis spectral changes was also achieved with chemical oxidation by iodine. The *cis*-$\mathbf{1}^+$/ITO in ethanol, which was prepared by 546-nm photoirradiation and subsequent addition of an excess amount of iodine (500 equiv.), was stable in the dark (Fig. 2b-A) and showed *cis*-to-*trans* photoisomerization with 546-nm light (Fig. 2b-B). These behaviours indicate that *cis*-to-*trans* isomerization in the Fe(III) state truly occurred with 546-nm light-irradiation, and not with a redox reaction.

In summary, we have succeeded in constructing a single-light controllable azobenzene monolayer system by electrochemical oxidation, which affords easy and clean manipulation of the isomerization behaviour. This single green light photoisomerization system is suitable to be combined with fine-focused light irradiation and to be applied to a new high-density optical data storage device.

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