

Supplementary Information

Reversible Photochromism of a Ferrocenylazobenzene Monolayer Controllable by a Single Green Light Source

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Experimental Section

1) Materials

3-Ferrocenylaniline was prepared according to the literature procedure.⁷ 4-Nitrobenzyl alcohol and indium tin oxide nanopowder (< 50 nm particle size) were purchased from SIGMA-ALDRICH corp., and ethanol and acetonitrile (HPLC grade), dehydrated tetrahydrofuran, and all the other reagents were purchased from KANTO CHEMICAL CO., INC., and used as received.

2) Syntheses

4-nitrosobenzyl alcohol

4-Nitrobenzyl alcohol (1.86 g, 12.1 mmol) and ammonium chloride (0.818 g, 15.3 mmol) were dissolved in 40 mL of a 2-methoxyethanol-water 10:1 mixture under a nitrogen atmosphere. To the solution, zinc powder (1.95 g, 29.8 mmol) was added at room temperature. The suspension was stirred for 30 minutes, and the insoluble matter was filtered. This pale yellow filtrate was poured into 200 mL aqueous solution of iron chloride hexahydrate (3.31 g, 12.2 mmol) at 0°C, and the solution turned green. The solution was extracted 3 times by 50 mL of dichloromethane. Evaporation of the extract gave 1.142 g of brown powder, which was a mixture of 4-nitrosobenzyl alcohol and 4-nitrobenzyl alcohol. This powder was used without further purification. ¹H NMR for 4-nitrosobenzyl alcohol (400 MHz, CDCl₃) δ (ppm) 7.90 (d, *J* = 8.8 Hz, 2H, C₆H₄), 7.60 (d, *J* = 8.8 Hz, 2H, C₆H₄).

3-ferrocenyl-4'-hydroxymethylazobenzene

The mixture of 4-nitrosobenzyl alcohol and 4-nitrobenzyl alcohol was dissolved in nitrogen-saturated acetic acid, and 3-ferrocenylaniline was added to the brown solution under a nitrogen atmosphere. This solution was stirred for 72 h at room temperature, and the acetic acid was evaporated. Brown residue was treated with silica-gel (10 wt% water) column chromatography with chloroform as an eluent and purified by HPLC (GPC-chloroform). yield; 0.830 g (2.09 mmol, 47.2%) ¹H NMR for

3-ferrocenyl-4'-hydroxymethylazobenzene (400 MHz, CDCl₃) δ (ppm) 7.94 (m, 3H, C₆H₄), 7.70 (d, J = 7.8 Hz, 2H, C₆H₄), 7.54 (m 3H, C₆H₄), 7.41 (dd, J = 7.7 Hz, 7.7 Hz, 1H, C₆H₄), 4.88 (dd, J = 1.8 Hz, 1.8 Hz, 2H, C₅H₄), 4.81 (s, 2H, CH₂), 4.49 (dd, J = 2.0 Hz, 2.0 Hz, 2H, C₅H₄), 4.18 (s, 5H, C₅H₅). Anal. calcd. for C₂₃H₂₀N₂OFe 69.71, H 5.09, N 7.07; found C 69.55, H 5.24, N 7.09.

3-ferrocenyl-4'-calboxyazobenzene

3-ferrocenyl-4'-hydroxymethylazobenzene (98.1 mg, 0.248 mmol) was dissolved in 15 mL of dehydrated tetrahydrofuran. To this orange solution, sodium *t*-butoxide (60.5 mg, 0.539 mmol) was added and the colour of the solution was immediately changed to dark brown. Next, 17.6 mg (0.088 mmol) of lauric acid was added and the solution was stirred at room temperature for 18 h. The solution was open to the air and stirred for 10 min with 10 mL of 1 M hydrochloric acid and extracted with dichloromethane, after which the organic layer was collected. After removing the solvents, brown residue was purified by silica-gel (5 wt% water) column chromatography with chloroform as eluent, and the second orange fraction was evaporated to obtain 3-ferrocenyl-4'-calboxyazobenzene as a red powder. yield; 63.3 mg (0.154 mmol, 62.3%) ¹H NMR for 3-ferrocenyl-4'-calboxyazobenzene (400 MHz, CDCl₃) δ (ppm) 8.29 (d, J = 8.2 Hz, 2H, C₆H₄), 8.07 (s, 1H, C₆H₄), 8.02 (d, J = 8.2 Hz, 2H, C₆H₄), 7.78 (d, J = 7.3 Hz, 1H, C₆H₄), 7.64 (d, J = 7.3 Hz, 1H, C₆H₄), 7.46 (dd, J = 7.3 Hz, 7.3 Hz, 1H, C₆H₄), 4.76 (s, 2H, C₅H₄), 4.38 (s, 2H, C₅H₄), 4.09 (s, 5H, C₅H₅). Anal. Calcd. for C₂₃H₁₈N₂FeO₂: C, 67.34; H, 4.42; N, 6.83; Found: C, 67.09; H, 4.53; N, 6.80.

3) Apparatus

Electrochemical data were recorded with ALS 750A electrochemical analyser, and UV-vis spectra were recorded with Jasco V-570.

4) Supply of monochromic light

Monochromic light was supplied by a high-pressure mercury lamp (Ushio-500D). The bright lines were splitted by a monochromator (Jasco CT-10T).

5) Diffuse reflectance UV-vis spectroscopy

The UV-vis spectral changes of **1** immobilized on ITO nanoparticles were measured as follows. The ITO nanoparticles as received or hydrophilic ITO nanoparticles were immersed in a 1 mM ethanol solution of **1** for 10 minutes, washed by ethanol, dried, and finally dispersed into powdery potassium chloride. Resulting mixtures were put into a quartz cell and diffuse reflectance UV-vis spectra were measured before and after photoirradiation.

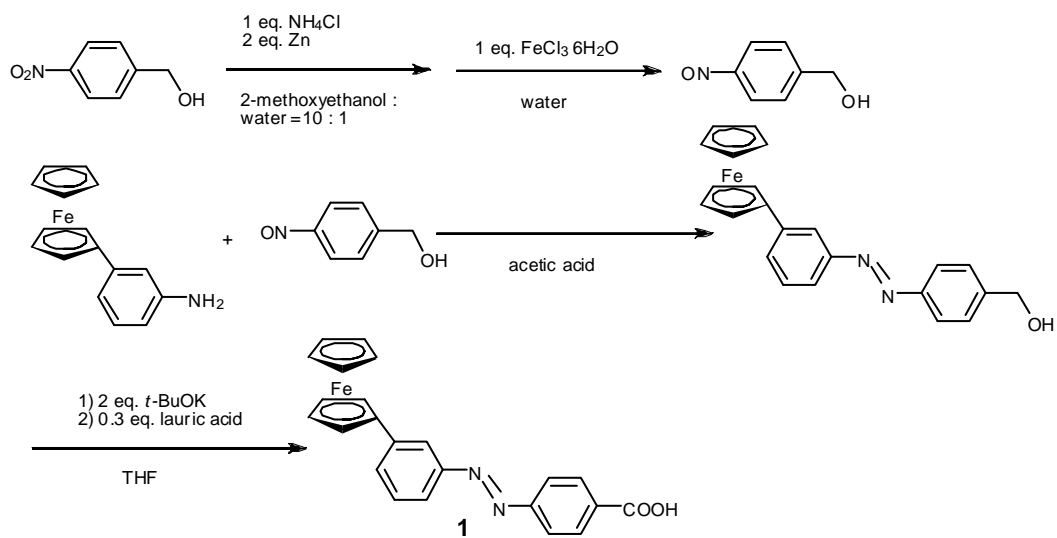
6) Preparation of **1**/ITO for UV-vis spectral measurement

Two ITO substrate sized 2 cm × 1 cm were attached to the cell shown in Fig. S5, and **1** was fixed via the method described in the main text. The space between two substrates was filled with acetonitrile solution of Bu₄NClO₄ (0.1 M, 5 mL) in the case of electrochemical redox-coupled measurement, and with ethanol (5 mL) or ethanol solution of iodine (0.3 mM, 5 mL) in the case of chemical redox-coupled measurement. The open circuit potential was changed from -0.08 V to 0.19 V vs. Fc⁺ / Fc with an addition of iodine.

7) Measurement of UV-vis spectral changes and determination of *cis* molar ratio

UV, blue and green lights were irradiated parallel to the substrate. Standard irradiation times were 30 minutes with UV and blue light and 1 h with green light for **1** in solution, and 1 h with UV and blue light and 3 h with green light for **1**/ITO. The PSS spectra were compared to the further photoirradiated spectra to confirm that the spectra were surely obtained at the photostationary state. The *cis* molar ratios in solution were determined by ¹H NMR, and approximate ratios of **1**/ITO were calculated by the degree of UV-vis spectral changes using the value ϵ_{trans} and ϵ_{cis} at the π - π^* band obtained by UV-vis spectra in solution ($\epsilon_{cis} / \epsilon_{trans} = 0.17$).

Scheme S1 Synthesis of 3-ferrocenyl-4'-carboxylazobenzene(**1**)



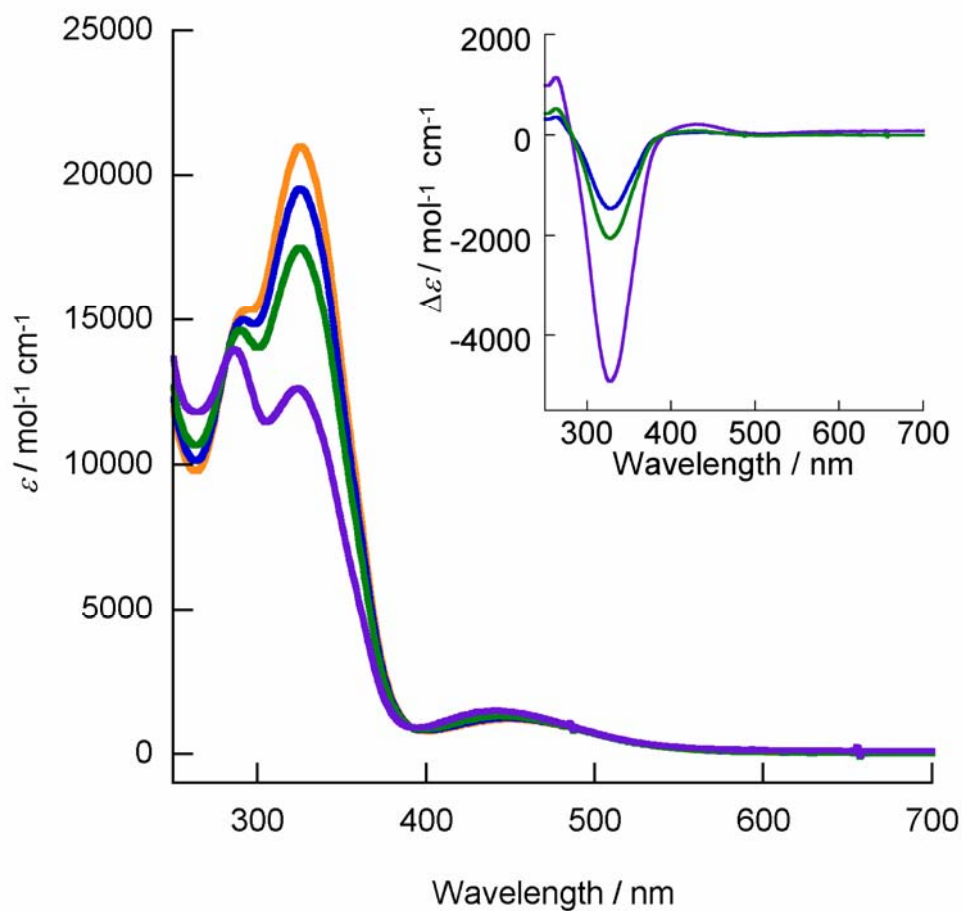


Fig. S1 UV-vis absorption spectrum of **1** (2.8×10^{-5} M) and its 546 nm (green line), 365 nm (purple line) and 436 nm (blue line) photoirradiated spectra. (offset: Differences in the UV-vis absorption spectra between initial spectrum and 546 nm (green line), 365 nm (purple line) and 436 nm (blue line) photoirradiated spectra.)

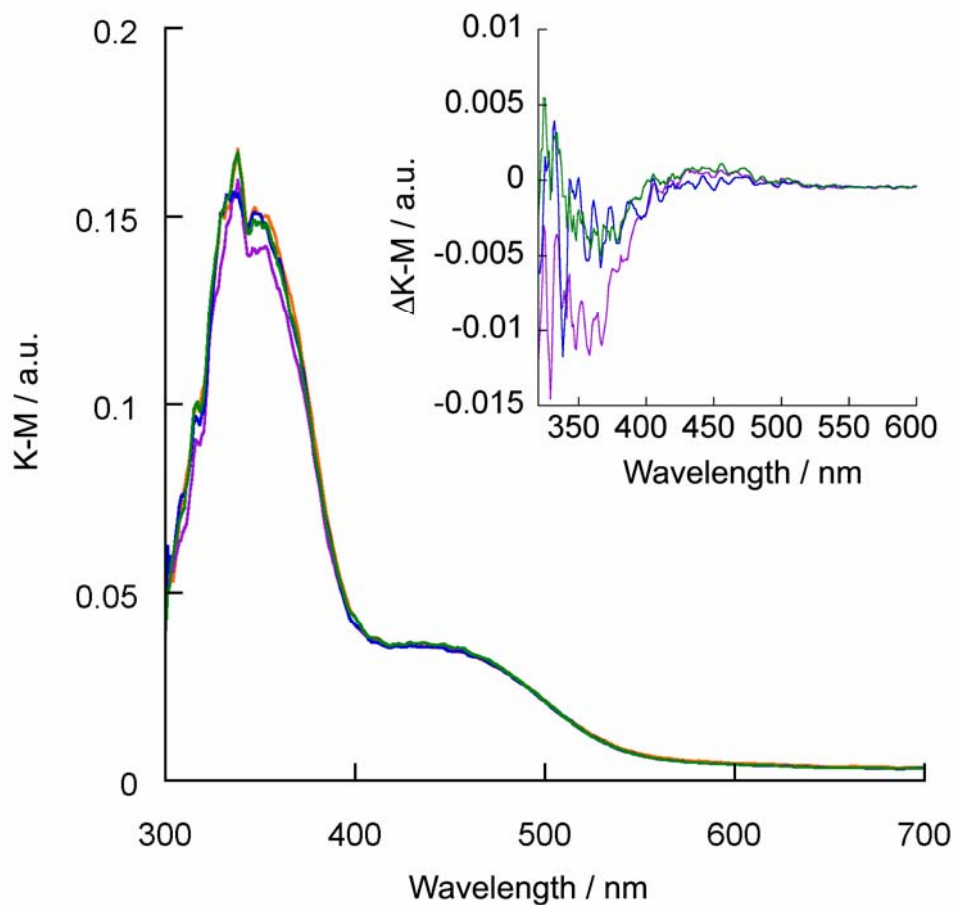


Fig. S2 UV-vis diffuse reflectance spectrum of **1** on ITO nanoparticles as received, and its 546 nm (green line), 365 nm (purple line) and 436 nm (blue line) photoirradiated spectra. (offset: Differences in the UV-vis absorption spectra between initial spectrum and 546 nm (green line), 365 nm (purple line) and 436 nm (blue line) photoirradiated spectra.)

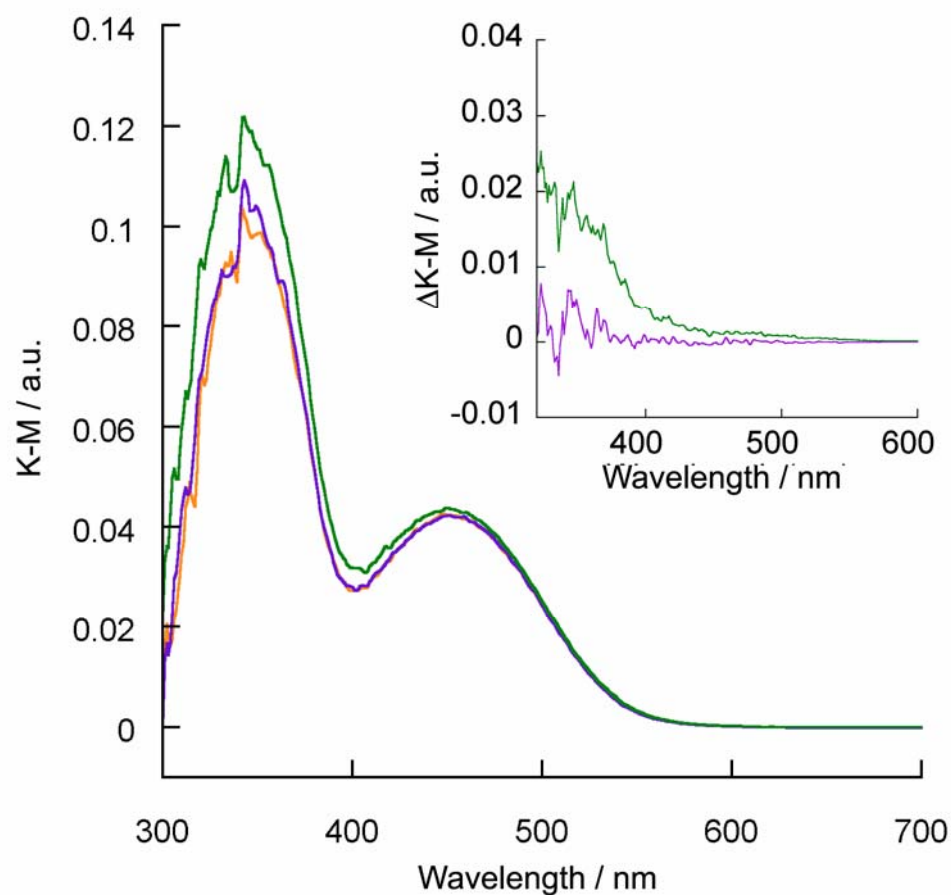


Fig. S3 UV-vis diffuse reflectance spectrum of **1** on ITO nanoparticles with hydrophylization (orange line), and its 546 nm (green line), 365 nm (purple line) and 436 nm (blue line) photoirradiated spectra. (offset: Difference UV-vis absorption spectra obtained by subtracting the initial spectrum from 546 nm (green line) and 365 nm (purple line) photoirradiated spectra.)

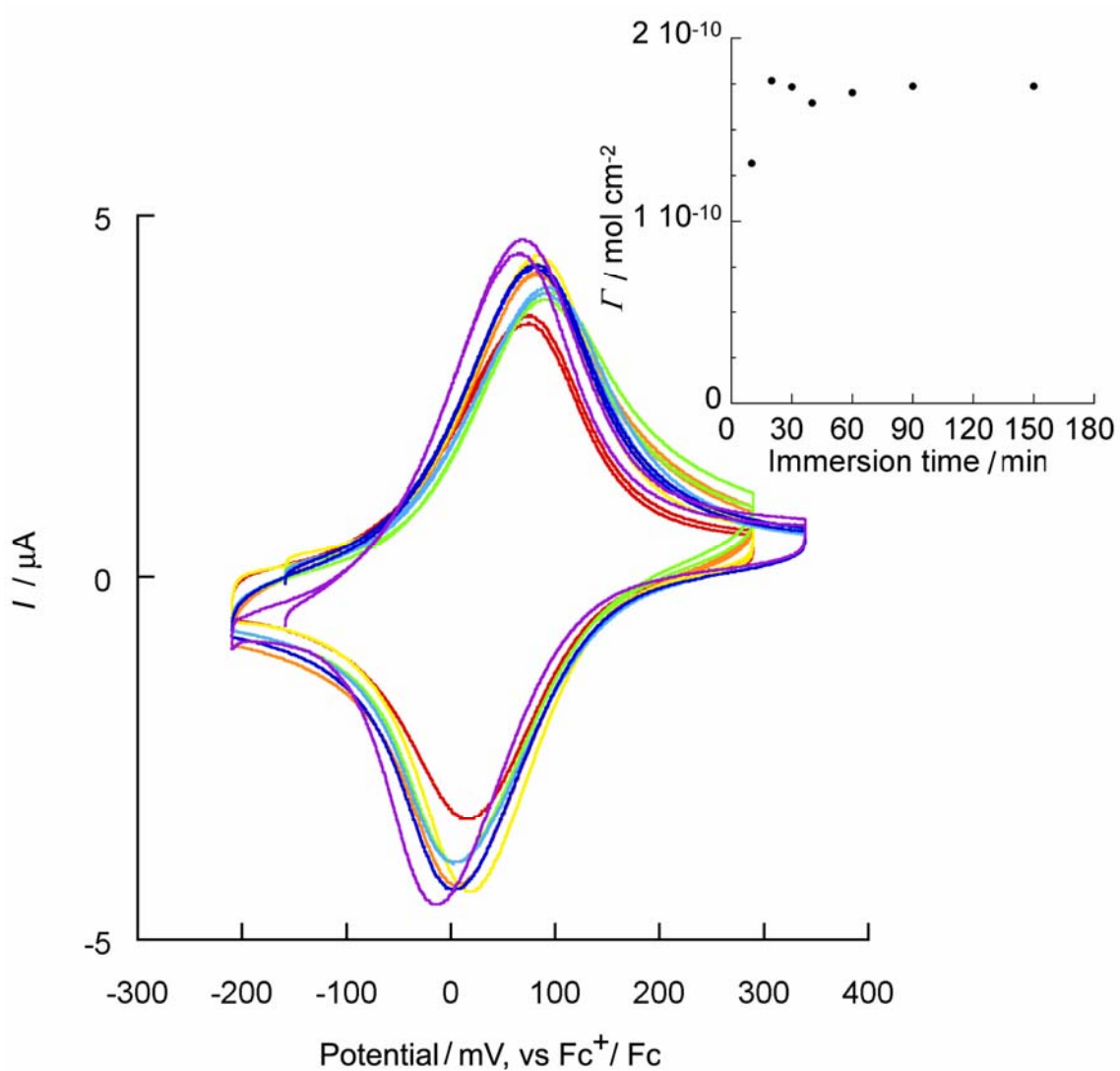


Fig. S4 Cyclic voltammograms of 1/ITO in 0.1 M *n*-Bu₄NClO₄-ethanol vs. Fc⁺/Fc at a immersion time of 10 (red line), 20 (orange line), 30 (yellow line), 40 (green line), 60 (sky-blue line), 90 (blue line), and 150 min (purple line). (offset: Surface coverage vs. immersion time plot of 1/ITO.)

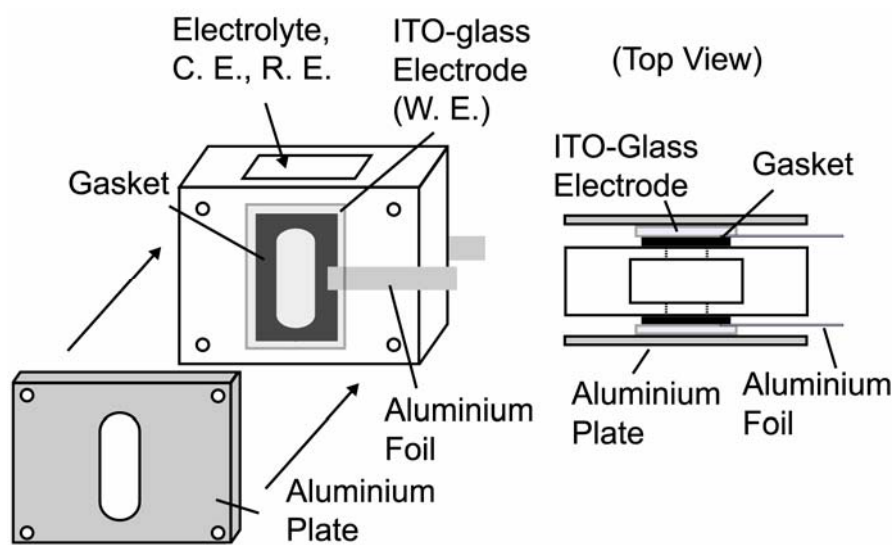


Fig. S5 A sketch of the cell to observe the spectral changes by the redox coupled green light photoisomerization of 1/ITO.

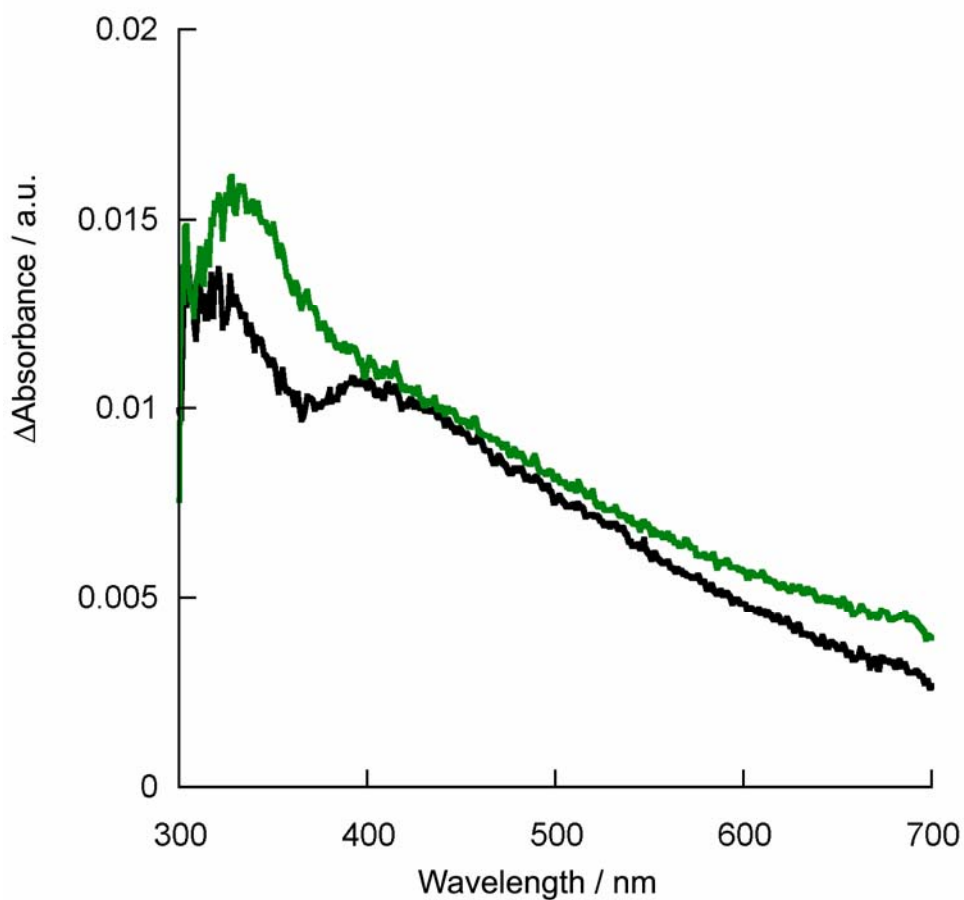


Fig. S6 Difference UV-vis absorption spectra of **1**/ITO obtained by subtracting the initial spectrum (B state in Scheme 1a) from that after 5 min in the dark (“dark” condition) or photoirradiated with 546 nm light (“illuminated” condition) with holding the potential at 0.32 V vs. Fc^+ / Fc and re-reduced with holding the potential at -0.08 V vs. Fc^+ / Fc for 30 s (black line for “dark” condition and green line for “illuminated” condition).