

Supporting information

Highly Durable Colour/Emission Switching of Fluorescein in Thin Film Device Using “Electro-acid/base” as In-Situ Stimuli

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Experimental details

1.1 Materials

Chromatographic grade acetonitrile, Poly(methyl methacrylate) (PMMA), Propylene carbonate, Tetrabutylammonium hexafluorophosphate (TBAPF₆), p-Benzoquinone, Fluorescein, Nickel nitrate, and Lithium hydroxide were purchased from Aladdin. Polydimethylsiloxane (PDMS) was purchased from Dow Corning (Sylgard 184). TBAPF₆ was recrystallized three times from ethanol and dried under vacuum at 50 °C. Other chemicals were used as received except for those mentioned.

1.2 Instrument characterization

UV-Vis absorption spectra were measured using a Shimadzu UV-2550 PC double-beam spectrophotometer.

Fluorescence spectra were obtained with a Shimadzu spectrofluorimeter RF-5301PC.

Cyclic voltammograms were obtained from Bio-logic electrochemical work station. Experiments were performed under protection of argon in acetonitrile containing TBAPF₆ (0.1 mol/L) as supporting electrolyte. The three-electrode cell consisted of a glass-carbon working electrode (Chenhua, China), a Pt-wire counter electrode (Chenhua, China) and Ag wire reference electrode (Chenhua, China).

IR spectra studies were performed on Vertex 80/80V FT-IR spectrometer with LN-MCT Mid DC detector over the range of 4000-800cm⁻¹ using a KBr plate.

X-ray Photoelectron Spectroscopy (XPS) measurements were carried out under condition of 15 kV and 17 mA using a Thermo ESCALAB 250 spectrometer with a twin-anode Al K α (1486.6 eV) X-ray source.

1.3 Spectroelectrochemical Characterization

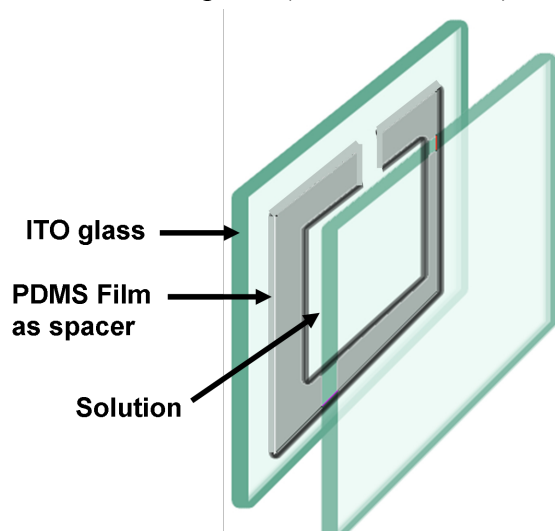
Change of emission (at 535 nm) and absorption (at 515 nm) of mixture solution was measured in situ during the potential sweep using self-made spectroelectrochemical cell (shown as follow).

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In order to measure the emission/absorption spectra and the emission/absorption lifetime of ITO device under in-situ voltage application, the direct current mode was applied to the cell by Bio-logic electrochemical work station.

Preparation of the ITO cells of liquid film:

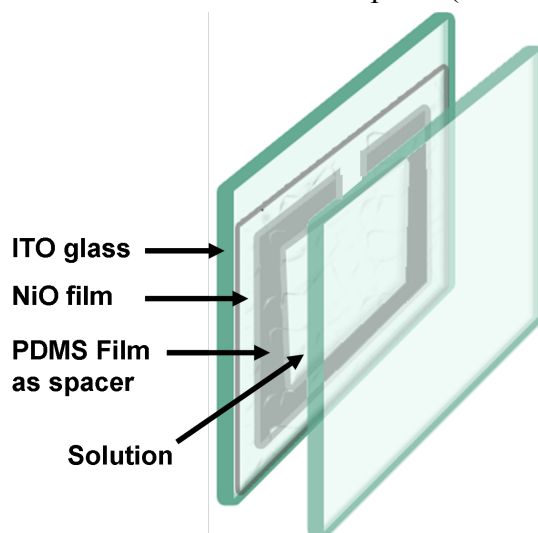
A two electrodes cell was constructed with ITO glass electrodes. The mixture solution containing p-Benzoquinone, Fluorescein, and TBAPF₆ was sandwiched between ITO electrodes. PDMS film was used as spacer (shown as follow).



Preparation of the NiO film coated ITO cells of liquid film:

NiO film on ITO-glass electrode was synthesized according to literature procedures.^[1]

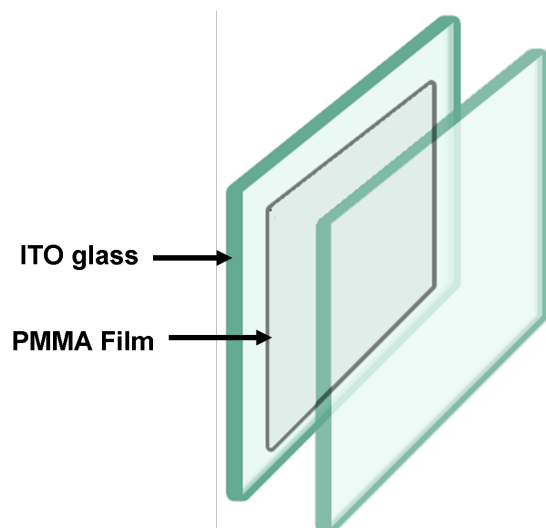
A two electrodes cell was constructed with NiO film-coated ITO electrode as the counter electrode and the ITO electrode as the working electrode. The mixture solution containing p-Benzoquinone, Fluorescein, and TBAPF₆ was sandwiched between ITO electrodes. PDMS film was used as spacer (shown as follow).



Preparation of the ITO cells of PMMA film:

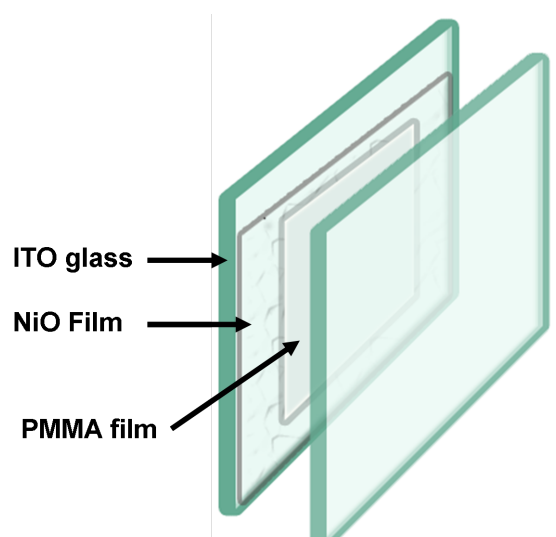
A mixture of 30 wt% of PMMA, 70 wt% of PC, 10⁻³ M p-Benzoquinone, and 10⁻⁵ M Fluorescein was stirred for 24 h. Then a homogeneous phase, with electrochromic properties, was obtained.

A two electrodes cell was constructed with ITO glass electrodes. The PMMA film was laminated between two ITO electrodes. The thickness was set to about 0.1mm (shown as follow).



Preparation of the NiO film coated ITO cells of PMMA film:

A two electrodes cell was constructed with NiO film-coated ITO electrode as the counter electrode and the ITO electrode as the working electrode. The PMMA film was laminated between two ITO electrodes. The thickness was set to about 0.1mm (shown as follow).



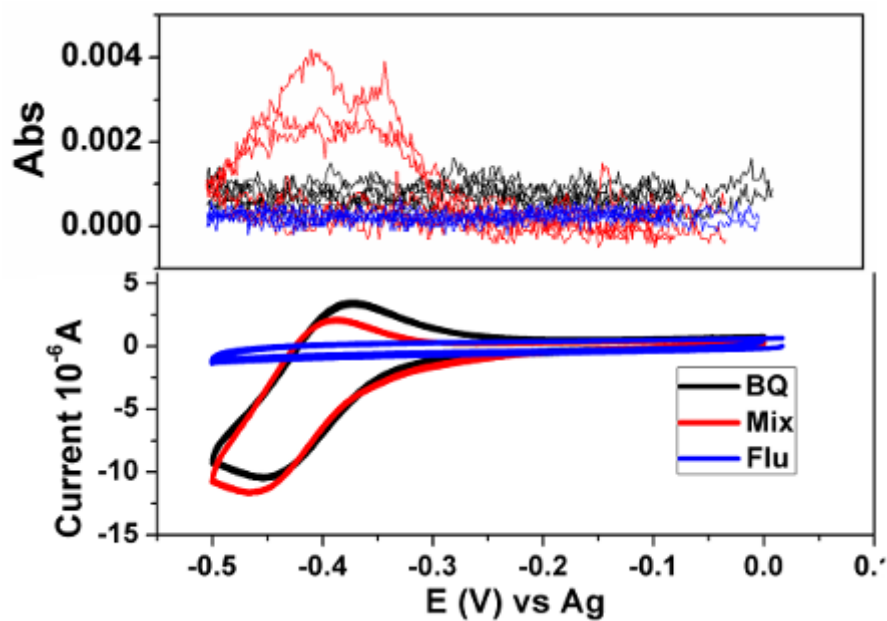


Fig. S1 Changes in absorption at 515 nm (top) and cyclic voltammograms (bottom) of BQ (5.0×10^{-4} M), fluorescein (5.0×10^{-5} M) and BQ/fluorescein (5.0×10^{-4} M/ 5.0×10^{-5} M) in acetonitrile with 0.1 M TBAPF₆ on glassy carbon electrode ($d = 3$ mm). Scan rate: 20 mV/s.

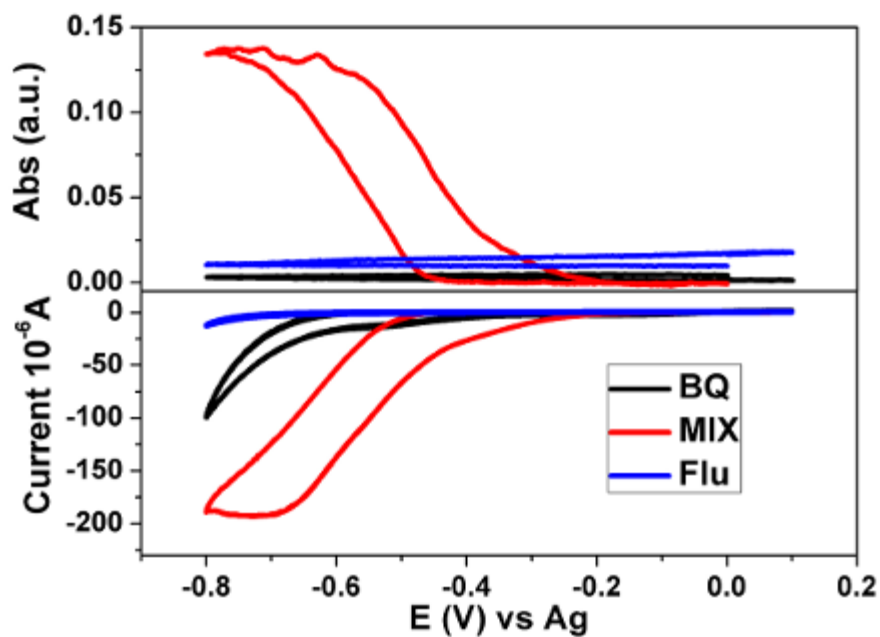


Fig. S2 Changes in absorbance at 515 nm (top) and cyclic voltammograms (bottom) of BQ (5.0×10^{-4} M), fluorescein (5.0×10^{-5} M) and BQ/fluorescein (5.0×10^{-4} M/ 5.0×10^{-5} M) in acetonitrile with 0.1 M TBAPF₆ on ITO. Scan rate: 20 mV/s.

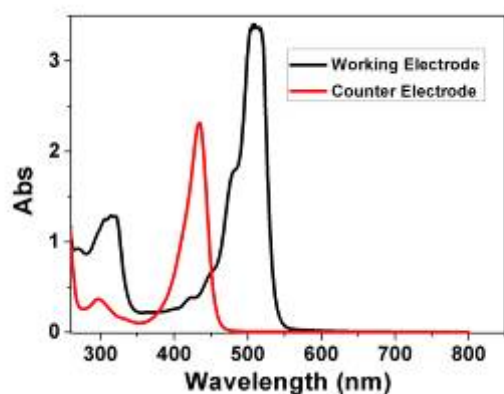


Fig. S3a: Absorption spectra of a mixture of fluorescein(5×10^{-5} M) and benzoquinone(5×10^{-4} M) in acetonitrile electrolyzed in the working electrode (black curve) and the counter electrode (red curve) using H-type cell under a bias voltage of -1.5 V about 60 min.

Note: the maximum absorption of counter electrode was at 432 nm, and the maximum absorption of working electrode was at 515 nm.

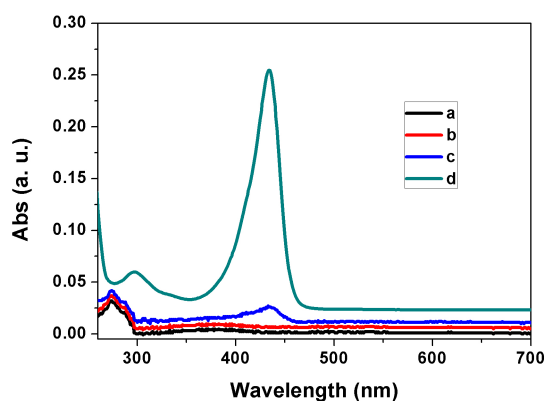


Fig. S3b: Absorption spectra of fluorescein (1.0×10^{-5} M) in the presence of CF_3COOH (black line: 0eq, a; blue line, 1 eq, c) in acetonitrile. Absorption spectra of a mixture of fluorescein (5×10^{-5} M) and benzoquinone(5×10^{-4} M) in acetonitrile electrolyzed in the counter electrode of H-type cell (red line: using NiO coated-ITO electrode, b; green line: using ITO electrode, d) under a bias voltage of -1.5 V about 5 min.

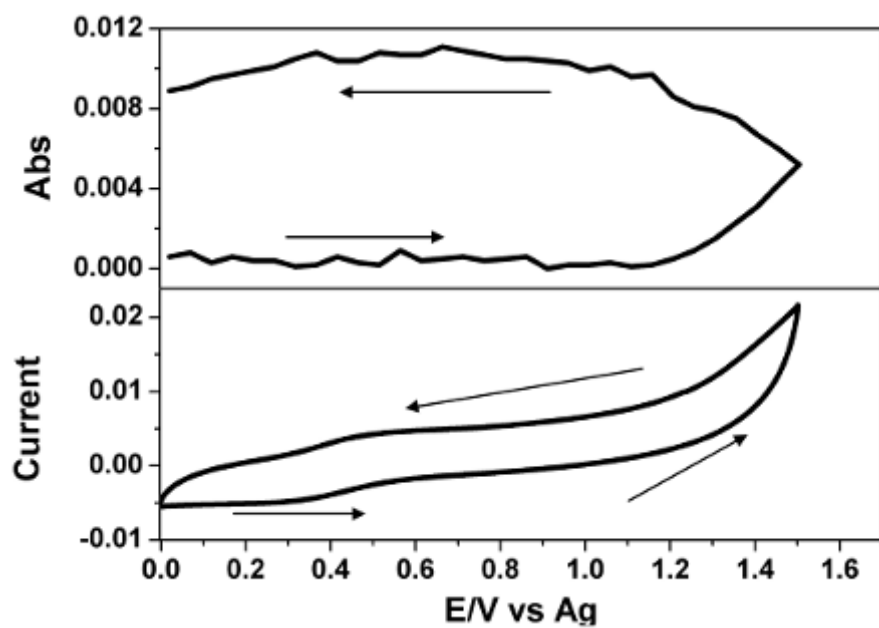


Fig. S3c Changes in absorbance at 432 nm (top) and cyclic voltammograms (bottom) of fluorescein (5.0×10^{-5} M) in acetonitrile with 0.1 M TBAPF₆. Scan rate: 20 mV/s.

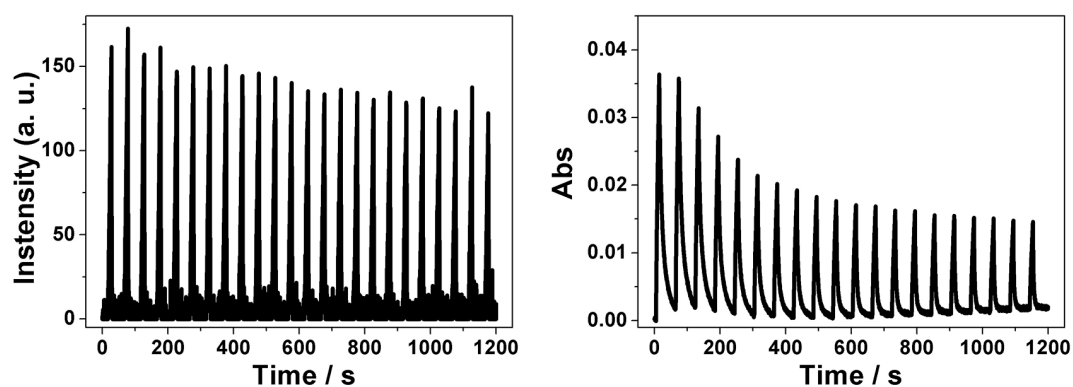


Fig. S4 Absorbance (at 515 nm) and emission (at 535 nm, excited by 515 nm) variation with the switch cycles by alternative -1.5 V (10s) and 1.0 V (40s) using ITO electrode without NiO film.

B. Ou, M. Hampsch-Woodill, and R. L. Prior, *J. Agric. Food Chem.* 2001, **49**, 4619; The degradation of fluorescein was found from switch performance of ITO electrode without NiO film (Fig. S4) compared with NiO film coated-ITO electrode (Fig. S5).

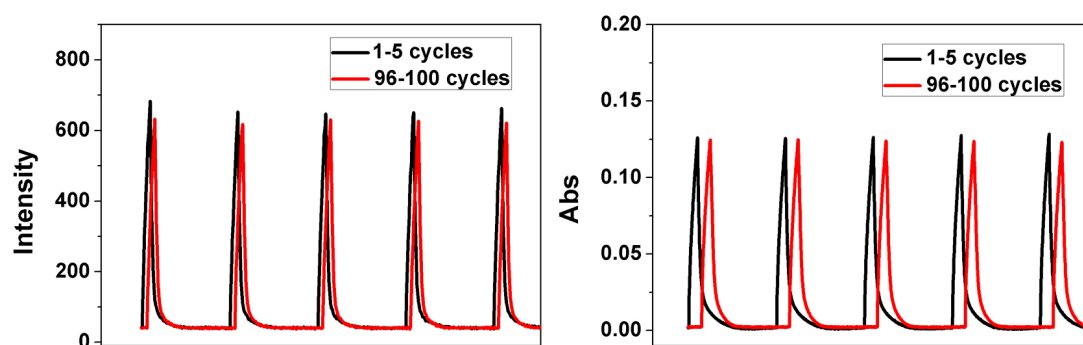


Fig. S5 Absorbance (at 515 nm) and emission (at 535 nm, excited by 515 nm) variation with the switch cycles by alternative -1.5 V (3s) and 1.0V (5s) using ITO electrode with NiO film.

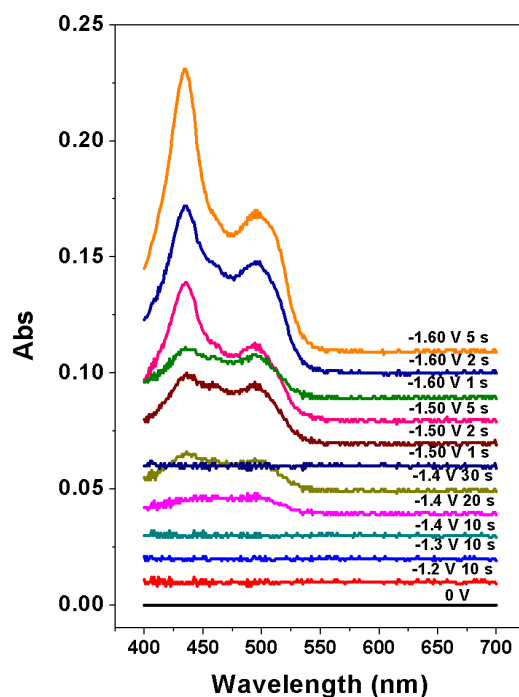


Fig. S6 UV-Vis spectroscopic monitoring of ITO device containing BQ/fluorescein (5.0×10^{-4} M/ 5.0×10^{-5} M) solution under different electric field.

The turn-on and turn-off voltages of ITO device were determined by CV performances of solid and liquid devices, which were exhibited in Supporting Information (Fig. S6 and S7 for ITO device containing BQ/fluorescein, Fig. S10 and S11 for activated NiO electrode in PMMA film). Those turn-on and turn-off voltages were different from CV performances characterized by glassy carbon electrode (Fig. 2).

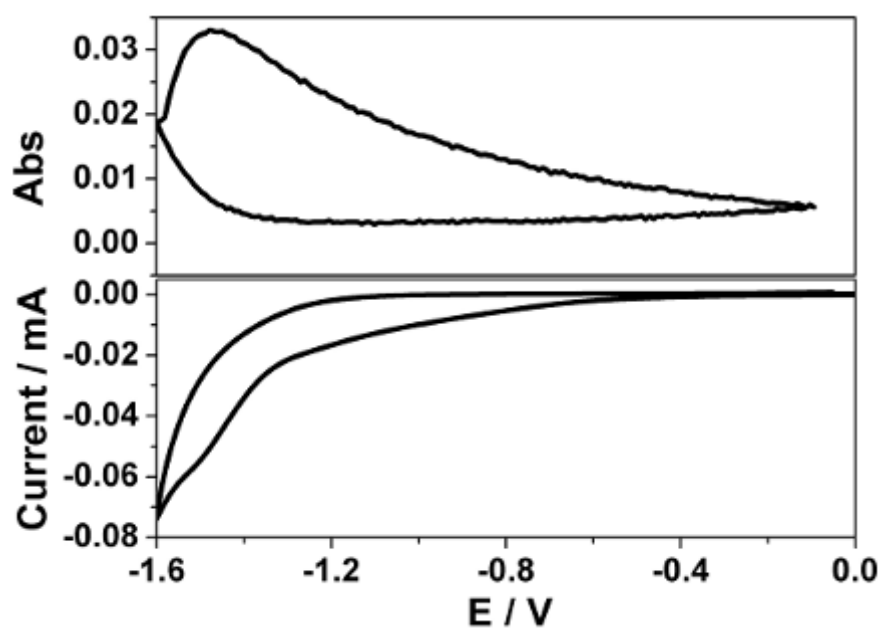


Fig. S7 Change in absorbance (top, 515 nm) and CV response (bottom) of ITO device containing BQ/fluorescein (5.0×10^{-4} M/ 5.0×10^{-5} M) solution.

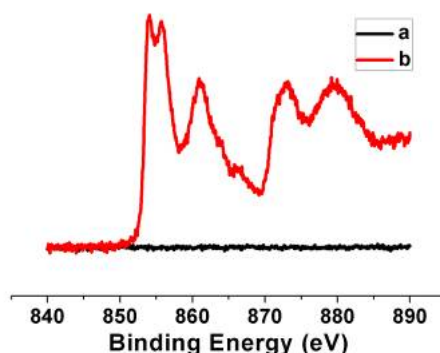


Fig. S8 XPS spectra of the Ni 2p region for ITO electrode without NiO film (a) and NiO film coated-ITO electrode (b).

Y. Watanabe, K. Imaizumi, K. Nakamura and N. Kobayashi, *Solar Energy Materials & Solar Cells*, 2012, **99**, 88; NiO film was characterized by X-ray photoelectron spectroscopy analysis (XPS), shown as Fig. S8. NiO film also have the electrochromic properties in an aqueous solution, but no electrochromic properties were observed in CH₃CN solution.

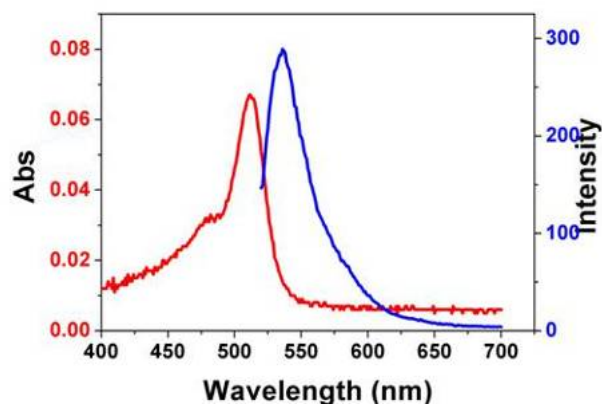


Fig. S9 Absorption spectrum (red curve) and Emission spectrum (blue curve) of a mixture of fluorescein and benzoquinone using activated NiO electrode in PMMA film under -1.5 V.

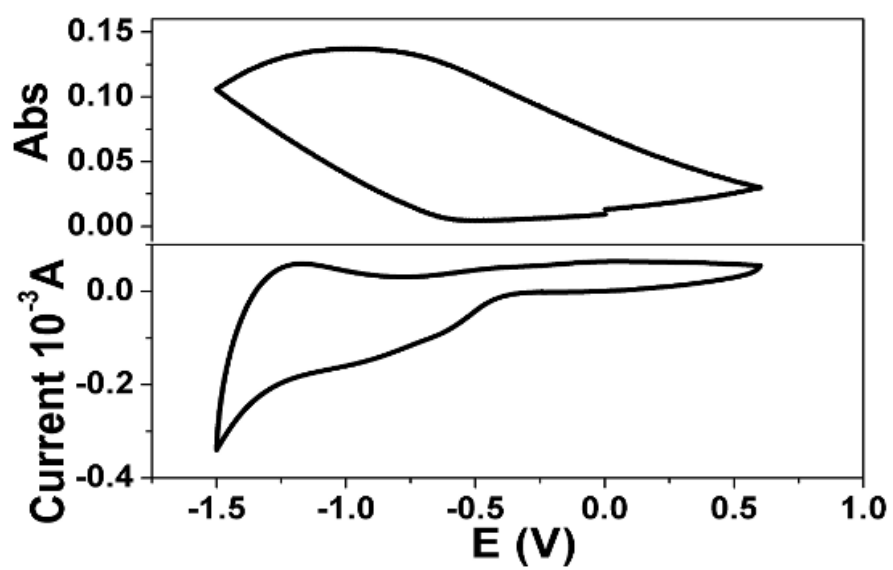


Fig. S10 Change in absorbance (top, 515 nm) and CV response (bottom) of electrochemically activated NiO electrode in PMMA film.

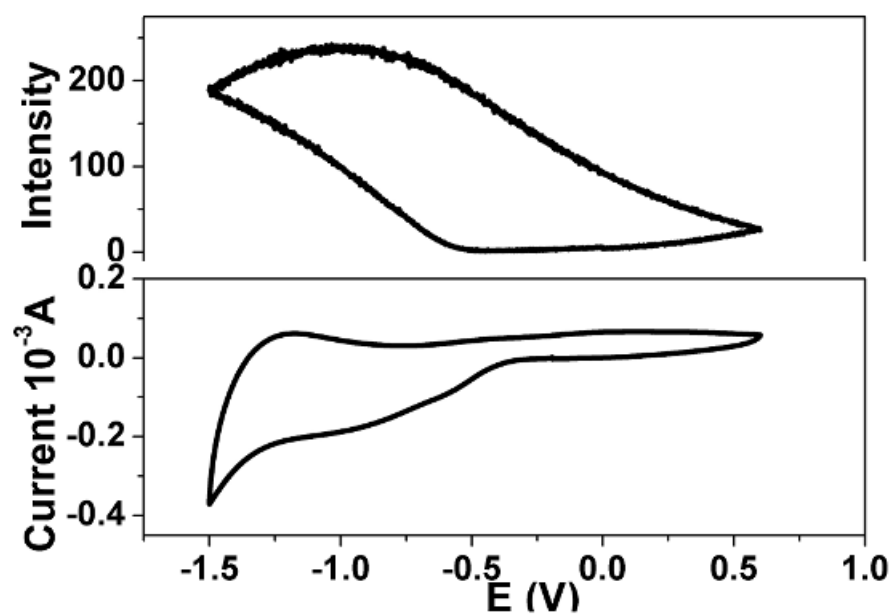


Fig. S11 Change in emission (top, 535 nm) and CV response (bottom) of electrochemically activated NiO electrode in PMMA film.

Experimental results indicate that electric field can switch the emission of fluorescein at 535 nm (the maximum emission wavelength of di-anionic form of fluorescein) only when the both BQ and fluorescein coexist in solution, and the intensity of the emission at 535 nm is dependent on the redox state of BQ. In order to support this conclusion of di-anionic form of fluorescein being generated by the electro-base, literature report (see Ref 12 of the manuscript) is cited herewith, and more results (Fig. S12, S13 and S14) are also provided as follows.

As indicated from Fig. S12 and S13, the fluorescence and the absorption of the open-fluorescein, obtained by adding 8 equiv of potassium tert-butoxide to fluorescein solution, is similar to that of fluorescein stimulated by -1.5 V with BQ. And the open structure of fluorescein obtained by adding 8 equiv base is a di-anionic form of fluorescein, which is proved by ^1H -NMR in Fig. S14.

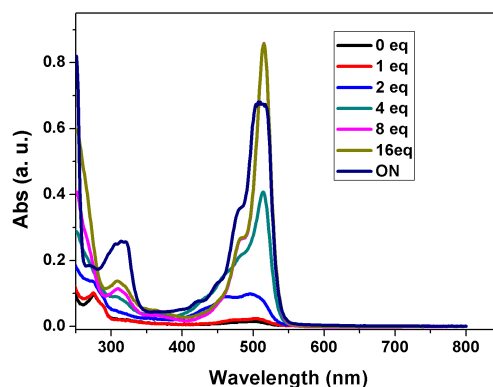


Fig. S12 Absorption spectra of fluorescein (1.0×10^{-5} M) in the presence of potassium tert-butoxide (0eq, 1eq, 2eq, 4eq, 8eq, 16eq) in acetonitrile. And absorption spectra of a mixture of

fluorescein(5×10^{-5} M) and benzoquinone(5×10^{-4} M) in acetonitrile electrolyzed electrolyzed in the working electrode using H-type cell under a bias voltage of -1.5 V about 5 min (blue curve, ON).

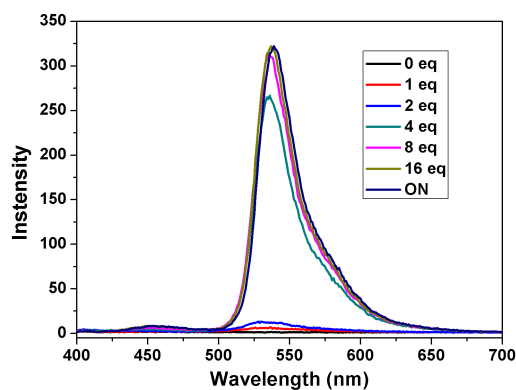


Fig. S13 Fluorescence response of fluorescein (1.0×10^{-5} M, excited by 365 nm) in the presence of potassium tert-butoxide (0eq, 1eq, 2eq, 4eq, 8eq, 16eq) in acetonitrile. And emission spectra of a mixture of fluorescein(5×10^{-5} M) and benzoquinone(5×10^{-4} M) in acetonitrile electrolyzed in the working electrode using H-type cell under a bias voltage of -1.5 V about 5 min (blue curve, ON).

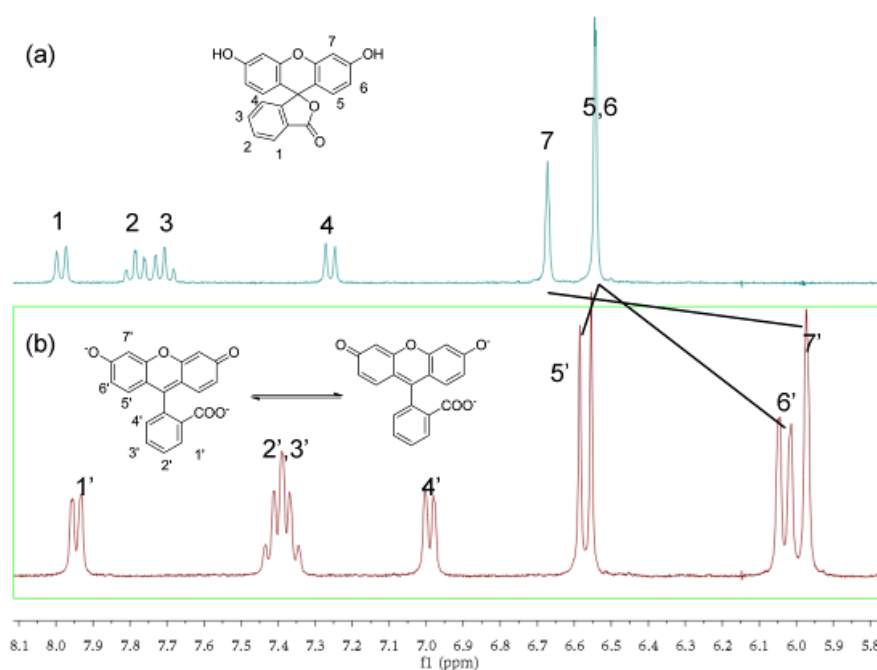


Fig. S14 ^1H NMR spectra of (a) **fluorescein** in DMSO-d_6 ; (b) the open structure of **fluorescein** obtained by adding 8 equiv of potassium tert-butoxide.

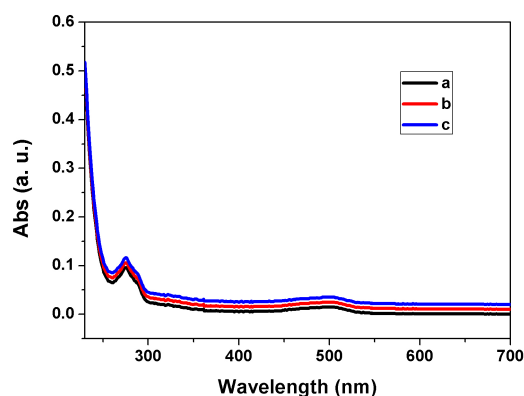


Fig. S15 Absorption spectra of BQ/fluorescein solution before (black curve, a) and after irradiation with UV light (254 nm, 3W, 1h, red curve, b) and after irradiation with a 250 W mercury arc lamp (1h, blue curve, c) in acetonitrile.

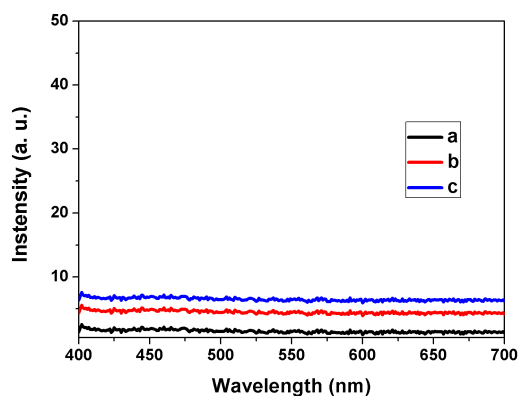


Fig. S16 Fluorescence response of BQ/fluorescein solution before (black curve, a) and after irradiation with UV light (254 nm, 3W, 1h, red curve, b) and after irradiation with a 250 W mercury arc lamp (1h, blue curve, c) in acetonitrile.

[1] Y. Watanabe, K. Imaizumi, K. Nakamura, N. Kobayashi, *Solar Energy Materials & Solar Cells*, 2012, **99** 88.