

## *Supporting information*

### **Electrochromic device based on dynamic coordination and dissociation of Fe<sup>2+</sup>/Fe<sup>3+</sup> and leuco dye with improved cycle life**

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## Supplementary figures

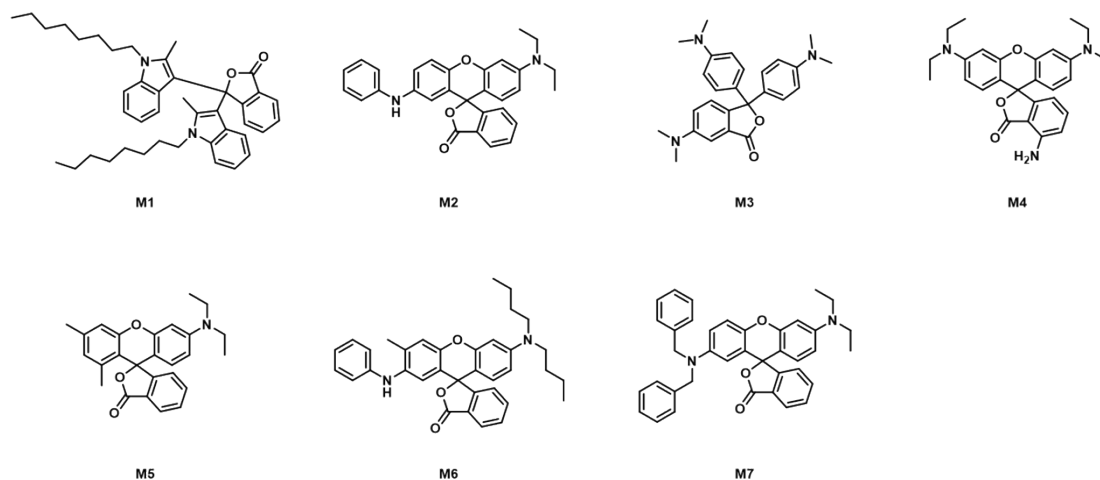


Fig. S1. The chemical structure of M1-M7.

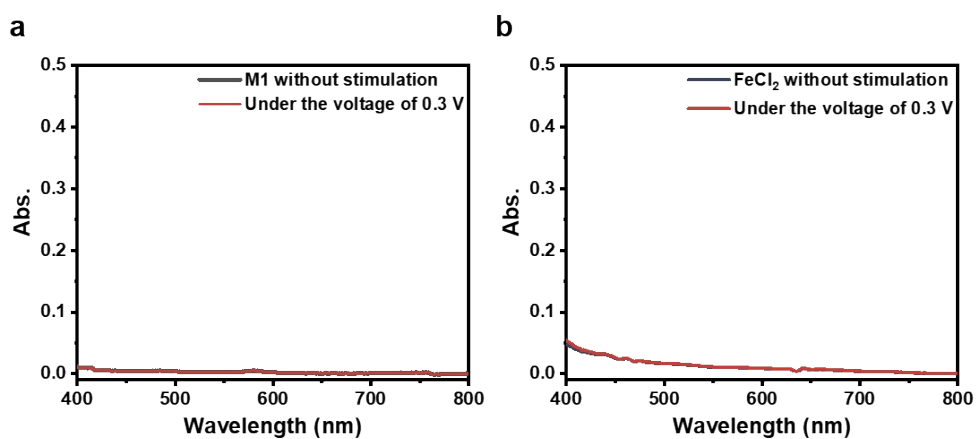


Fig. S2. The absorption spectra of M1 (a) and FeCl<sub>2</sub> (a) without stimulation and under the voltage of 0.3 V. The concentration of M1 and FeCl<sub>2</sub> were  $1.0 \times 10^{-4}$  mol/L in CH<sub>3</sub>CN.

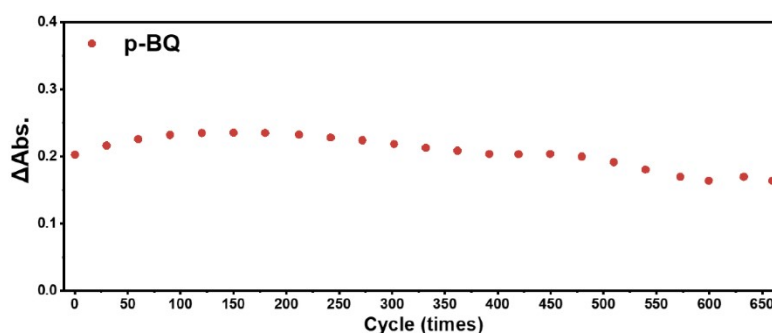


Fig. S3. The absorption changes of the ECD made with p-BQ at 532 nm under stimulation of 1.7 V/-1.0 V.

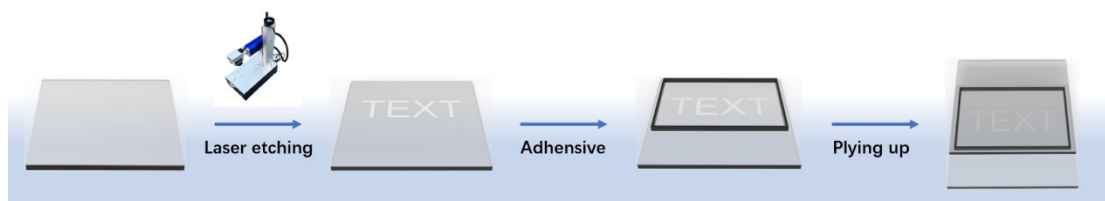


Fig. S4. The process of the preparation of electrochromic device.

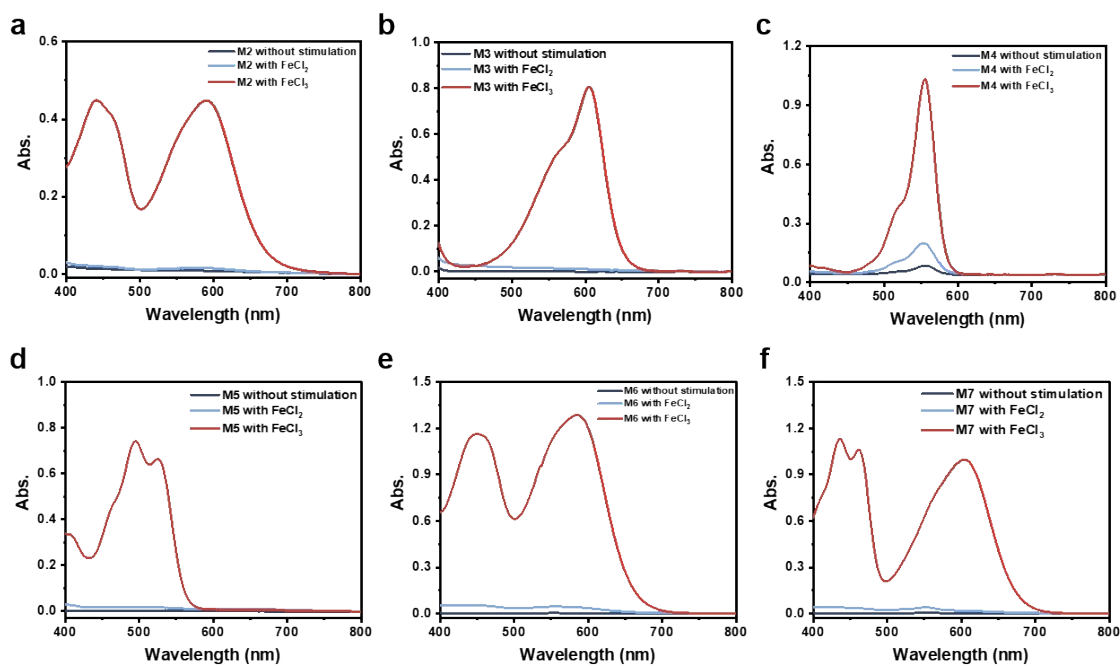


Fig. S5. The absorption spectra of dyes (black curve),  $\text{FeCl}_2$ /dyes (blue curve) and  $\text{FeCl}_3$ /dyes (red curve) in  $\text{CH}_3\text{CN}$ .

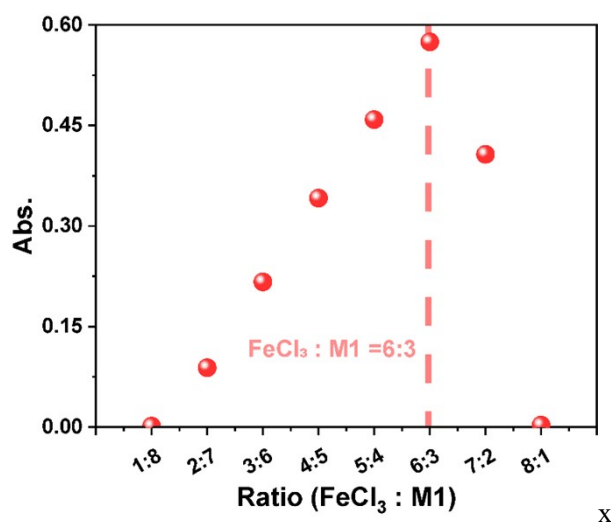


Fig. S6. Jobs plot of  $\text{FeCl}_3$  : M1. To perform this experiment, solution consisted of  $\text{FeCl}_3$  and M1 with different ratio have been prepared, and the total concentration of these solution is the same ( $5.0 \times 10^{-4}$  M). Then, the absorbance of these solutions at 532 nm have been tested. The result of this experiment after subtracting the baseline is shown as Fig. S6. It can be found that the solution

shows highest absorbance at 532 nm when ratio of  $\text{FeCl}_3$  to M1 reach to 6: 3. This result proves that the coordinate ratio between  $\text{FeCl}_3$  and M1 is 2: 1.

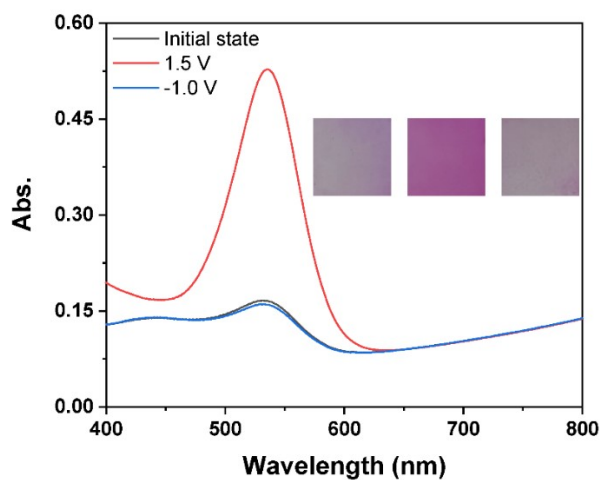


Fig. S7. Photos and UV-vis spectrum of thin-film electrochromic device based on  $\text{Fe}^{3+}$  and M1.



Fig. S8. Photos of different leuco dye (M2-M7) with  $\text{Fe}^{3+}$ .

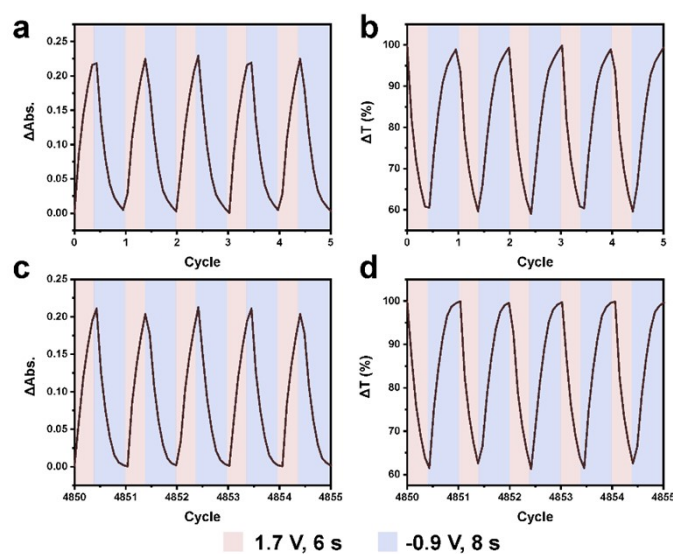


Fig. S9. Absorbance (a and c) and transmittance (b and d) change before (a and b) and after (c and d) cyclic test. Areas with different color show the different electric stimulation during the cyclic test.

# **M1 + FeCl<sub>3</sub>**

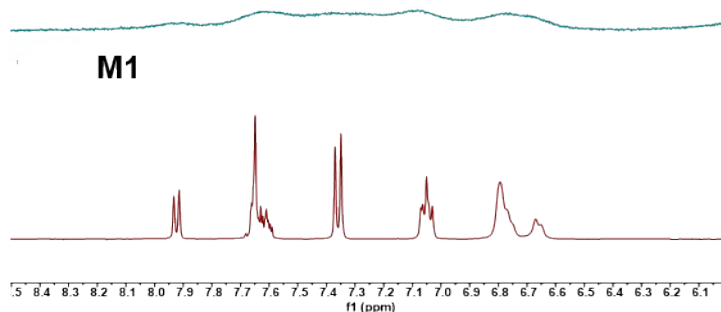


Fig. S10. <sup>1</sup>H NMR spectra of M1 and M1 + Fe<sup>3+</sup>, samples are dissolved in CD<sub>3</sub>CN.

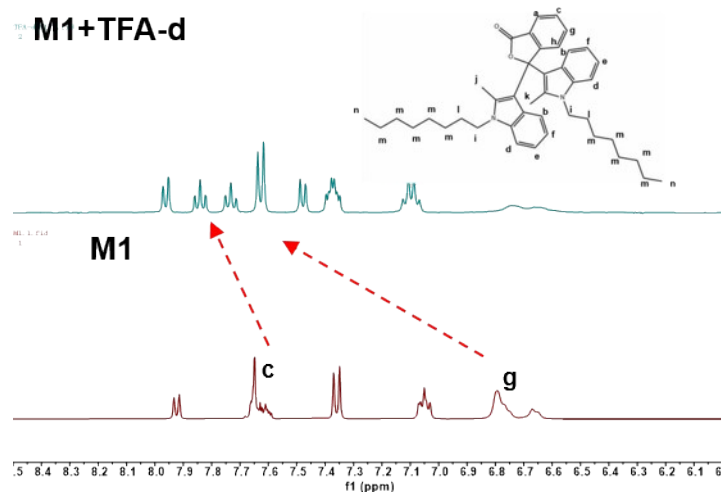


Fig. S11. <sup>1</sup>H NMR spectra of M1 and M1 + TFA-d, samples are dissolved in CD<sub>3</sub>CN.

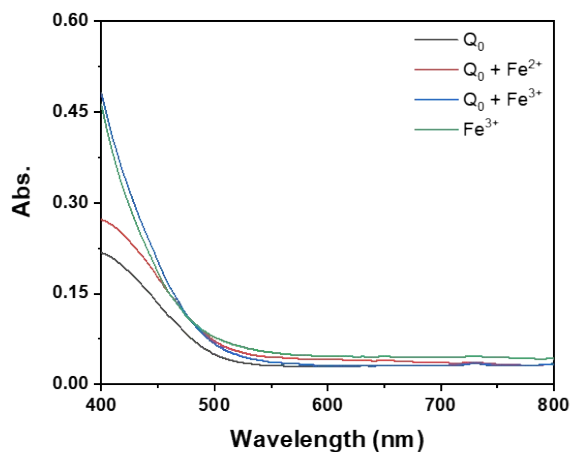


Fig. S12. Absorbance spectrum of Q<sub>0</sub>, Q<sub>0</sub> with Fe<sup>2+</sup> (FeCl<sub>2</sub>), Q<sub>0</sub> with Fe<sup>3+</sup> (FeCl<sub>3</sub>) and Fe<sup>3+</sup> (FeCl<sub>3</sub>), respectively. the result shows that the color of Q<sub>0</sub> will not change when Fe<sup>2+</sup> is oxidized under positive voltage. Considering that Q<sub>0</sub> shows no oxidation peak under 0 V (fig. S10), the color change of electrochromic device cannot be attribute to Q<sub>0</sub>.

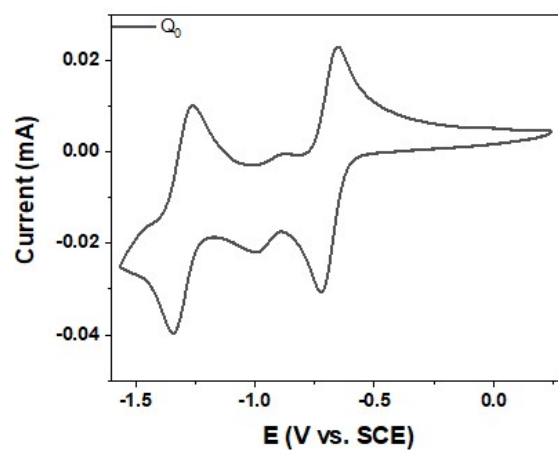


Fig. S13. Cyclic voltammetry test of  $Q_0$

M1, 1, 104

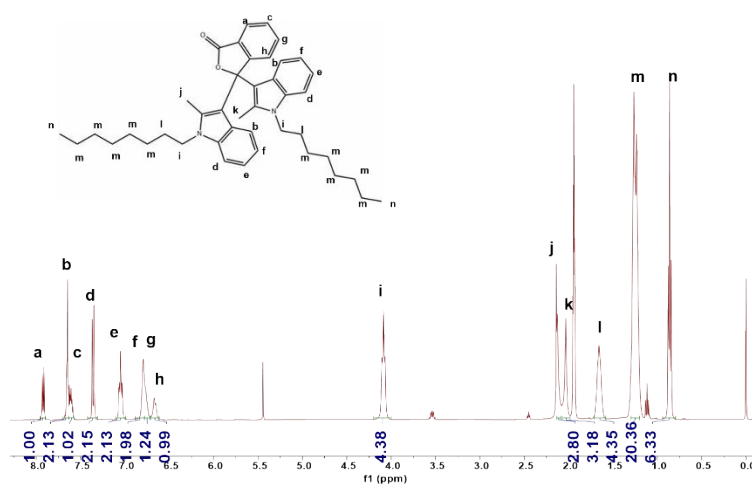


Fig. S14.  $^1\text{H}$  NMR spectra (full spectrum) of M1, samples are dissolved in  $\text{CD}_3\text{CN}$ .