

# **Organic soluble linear metallo-supramolecular polymer based on Iron(II) and terpyridyl ligand with high electrochromic performance**

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## Abstract

Ionic metallo-supramolecular materials possess excellent electrochromic properties due to the coordination of organic ligands and inorganic metal ion. In this paper, we prepared a linear organic soluble metallo-supramolecular electrochromic material named P-FeTPY which was coordinated with terpyridine as organic ligands and Fe(II) as inorganic metal ion. The polymer P-FeTPY whose ligands were modified with alkyl chains could be dissolved in dichloromethane with a solubility of 20 g/L. This indicates the introduction of long alkyl chains is effective to increase solubility of the ionic metallo-supramolecular polymer. The polymer films were spin-coated on the ITO substrate and their electrochemical and electrochromic properties were investigated. P-FeTPY film showed purplish red color with an absorption band at around 580 nm in neutral state due to the metal-to-ligand charge transfer transition, and became colorless due to the oxidization of central metal ion with around 30% change in transmittance. Cyclic voltammetry test demonstrated that P-FeTPY film which showed a couple of redox peaks at 1.15 V and 0.95 V is electrochemically reversible and stable. After 240 switching cycles, 97% of the optical contrast was retained, indicating excellent stability of P-FeTPY film. This work provides an effective path for producing organic soluble ionic metallo-supramolecular materials, which is solution processible and will greatly benefit the large area production in future industrial applications.

**KEYWORDS:** Metallo-supramolecular, Electrochromic, Solution processible.

## Introduction

Electrochromic materials could change colour, contrast and other optical properties[1-2] through electrochemical redox reaction, which have attracted extensive attention of researchers[3-5]. In the past decades, electrochromic materials have exhibited huge application value in smart windows and electronic display devices. Nowadays, electrochromic materials are meeting the demands of the military[6], aerospace, electronics industries[7-8], and many other industrial applications[9-10]. Among the numerous electrochromic materials, metallo-supramolecular polymers electrochromic materials have shown great stability, various color changes, adjustable characteristics and fast switching times due to the combination of organic and inorganic properties and they come into the sight of researchers[11-12].

Ionic metallo-supramolecular electrochromic materials are constructed by the coordination of metal ion and organic ligands. These hybrid polymers usually exhibit multiple colors at different oxidation states resulting from the metal-to-ligand charge transfer (MLCT)[13-16], and the color of this kind of polymers also can be regulated by changing the central metal ion and ligands[17]. Masayoshi and co-workers[18-20]studied the influence on color changes of metallo-supramolecular polymer by changing different central ion, such as  $\text{Fe}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ru}^{2+}$  and so on, and those reported polymers showed excellent electrochromic properties with multi-colors. Zhong[21-23] had done a lot of work in modifying ligands of 2,2':6',2''-terpyridine and its derivatives, and the obtained coordination compounds showed favorable electrochromic properties in the near-infrared region. These studies have greatly promoted the development of

inorganic and organic hybrid electrochromic materials. However, these metal materials are generally unmanageable to make films due to their insolubility in low boiling point and volatile solvents which were often used as spin coating solvent such as dichloromethane (DCM), chloroform and tetrahydrofuran (THF). At present, electrochromic metal complex films were often obtained by layer-by-layer self-assembly method[24], and the electrochromic nanosheets which were refloated by liquid–liquid interface self-assembly method were also employed[25-26,31]. And layer-by-layer spin coating ligands and metal ion to be film was a normal method in preparing films[37]. These reported metal complex films usually present excellent electrochromic performance, indicating their huge potential values as electrochromic materials. However, there were inevitably some limitations of these film forming methods due to the poor solubility of the polymer, which will limit the practical applications of these materials. To increase the solubility of the metallo-supramolecular polymers, modifying the ligands were commonly used by researchers[33-35]. However, these modified metallo-supramolecular polymers kept a poor solubility in methanol and ethanol which would be classified into high polar solvent that properties are similar to water. Hence, processing polymers in methanol or ethanol solution resulting to the prepared films were very thin which limited the optical transparent  $\Delta T$  (%) significantly. Therefore, to design and synthesize ionic metallo-supramolecular polymers that kept good solubility in DCM, THF and other commonly used organic solvents to make thin films by solution processible methods are needed urgently.

In this paper, we designed and synthesized a terpyridyl ligand with long alkyl

chains, which coordinating with Fe(II) to undergo polymerization to form the ionic metallo-supramolecular electrochromic materials. The final product which can be easily dissolved in low boiling point and volatile organic solvents such as DCM and THF, which could prepare films by directly spin coating on the ITO with the desired thickness after modifying the solvents and concentration. The metallo-supramolecular polymer present here exhibited high electrochromic contrast in the visible region between colored and discolored states, and showed favorable stability both in electrochemistry and optics, which provides a guideline to prepare organic soluble metallo-supramolecular polymer for electrochromism application.

## 1 Experimental Section

### 2.1 Synthesis of metallo-supramolecular polymer (P-FeTPY)

**Materials:** All the reagents were commercial products without further purification. 2,5-Dibromobenzene-1,4-diol, 4-formylphenylboronic acid, 2-acetylpyridine and iron(II) tetrafluoroborate hexahydrate were purchased from Aladdin (Shanghai). Indium tin oxide (ITO) glass substrates ( $RS \leq 10 \Omega^{-1}$ , area: 4 cm  $\times$  0.9 cm) were purchased from CSG HOLDING Co. ITO was cleaned by ultrasonic treatment in a series of solvents including distilled water, ethanol and acetone solution for 20 min, respectively.

#### *Synthesis of 1,4-dibromo-2,5-bis((2-octyldodecyl)oxy)benzene (1):*

1.06 g (4 mmol) of 2,5-dibromobenzene-1,4-diol, 3.62 g (10 mmol, 2.5 eq.) of 9-(bromomethyl)nonadecane and 2.76 g (20 mmol, 5 eq.) of potassium carbonate were mixed in a 100 mL round bottom flask, 30 mL DMF was added. The mixture was heated to reflux and stirred continuously for 18 h in  $N_2$  atmosphere. After cooling to room temperature (RT), the crude product was extracted with DCM, then the organic layer was washed with brine and dried with  $MgSO_4$ , and purified by column chromatography (petroleum ether as eluent) to obtain the product as a colorless oil (2.6 g, yield 78%).  $^1H$  NMR (500 MHz,  $CDCl_3$ ),  $\delta$  7.07 (d,  $J = 9.8$  Hz, 2H), 3.83 (d,  $J = 5.6$  Hz, 4H), 1.80 (m, 2H), 1.37-1.19 (m, 64H), 0.93-0.85 (m, 12H).

*Synthesis of 2',5'-bis((2-octyldodecyl)oxy)-[1,1':4',1''-terphenyl]-4,4''-dicarb-  
aldehyde (2):*

1.20 g (8 mmol, 4 eq.) of (4-formylphenyl)boronic acid, 2.76 g (20 mmol, 10 eq.) of potassium carbonate, and 20 mg tetrakis(triphenylphosphine)palladium were mixed in a 50 mL round bottom flask. The reaction mixture was degassed with N<sub>2</sub> for three minutes. Then 1.66 g (2 mmol) of compound 1, 20 mL water and 1,4-dioxane (volume ratio = 2:3) were added, the reaction was kept overnight at 120 °C. After cooling to RT, the mixture was extracted by DCM and water, and then washed with brine for several times. The organic layer was purified by column chromatography (DCM : petroleum ether = 1:3) to obtain the product as a colorless oil. (1.20 g, yield 70%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>), δ 10.08 (s, 2H), 7.95 (d, *J* = 8.2 Hz, 4H), 7.78 (d, *J* = 8.2 Hz, 4H), 7.01 (s, 2H), 3.84 (d, *J* = 5.3 Hz, 4H), 1.80 m, 2H), 1.37-1.19 (m, 64H), 0.93-0.85 (m, 12H).

*Synthesis of 4',4''''-(2',5'-bis((2-octyldodecyl)oxy))-[1,1':4',1''-terphenyl]-4,4''-diyl)di-2,2':6',2''-terpyridine (3):*

The product was synthesized using Krohnke method[32,39], 440 mg KOH was dissolved in 80 mL ethyl alcohol. After stirring for 20 min at RT, 2-acetylpyridine (976 mg, 8 eq.) and product (3) (879 mg, 1 mmol) were added into the solution, and the reaction was continuously stirred for overnight. When the solution changed to wine red, 20 mL ammonium hydroxide was added in three times. Afterwards, the mixture was kept reacting for two days. The product was then filtered and washed by water and alcohol alternately for several times, a white powder was obtained (730 mg, yield 56%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>), δ 8.85 (s, 4H), 8.77 (d, *J* = 4.2Hz 4H), 8.71 (d, *J* = 8.0 Hz, 4H), 8.02 (d, *J* = 8.3 Hz, 4H), 7.91 (m, 4H), 7.79 (d, *J* = 8.3 Hz, 4H), 7.38 (m, 4H), 7.09 (s, 2H), 3.88 (d, *J* = 5.3 Hz, 4H), 1.8 (m, 2H), 1.37-1.19 (m, 64H), 0.93-0.85(m,

12H).  $^{13}\text{C}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  156.39, 155.87, 150.63, 149.95, 149.15, 136.83, 130.48, 130.19, 126.77, 123.77, 121.37, 118.74, 115.86, 72.37, 38.09, 31.87, 31.49, 30.06, 29.66, 29.34, 26.86, 22.64, 14.07. MALDI-TOF-MS (m/z) 1285.377 for  $\text{C}_{88}\text{H}_{112}\text{N}_6\text{O}_2^+$ .

***Preparation of linear metallo-supramolecular polymer (P-FeTPY):***

128 mg of ligand (3) (0.1 mmol) was added to a 50 mL flask which was degassed with  $\text{N}_2$  for three minutes, then 20 mL DCM was added to dissolve the powder[38]. After that, 33.7 mg iron(II) tetrafluoroborate hexahydrate dissolved in 2 mL methyl alcohol was added dropwisely. The reaction was stirred for overnight. After cooling to RT, the crude product was treated by recrystallization in 200 mL petroleum ether, a dark powder was obtained by filtration and washed with petroleum ether to remove the extra ligands and washed with water to remove the iron(II) tetrafluoroborate hexahydrate.

***Preparation of the P-FeTPY film:*** The polymer P-FeTPY film was prepared by spin-coating its DCM solution on ITO which was treated by ozone for 20 min. Concentration of polymer P-FeTPY was  $10 \text{ mg}\cdot\text{mL}^{-1}$ , and the spin-coating speed was  $1000 \text{ rpm}\cdot\text{s}^{-1}$ .

***Fabrication of electrochromic device:*** The electrochromic device was prepared as follows. Polymethylmethacrylate (PMMA) was completely swelled in propylene carbonate solution at  $75^\circ\text{C}$ . Lithium perchlorate ( $\text{LiClO}_4$ ) dissolved in the ACN was added to the mixture. And then the above mixture was mixed together with sufficient stirring at room temperature for 5 h to obtain a homogeneous solution. The solvent was evaporated at  $80^\circ\text{C}$  for 2 h to form the gel electrolyte. The electrochromic device was



prepared by using the metallo-supramolecular polymer P-FeTPY film as working electrode, the above gel as electrolyte and blank ITO as the counter electrode.

## 2.2 Characterization

$^1\text{H}$  NMR (500 MHz) spectra of the synthesized compounds were recorded on a Bruker AVANCE III instrument (Bruker, Switzerland), and electrochemical properties of the coordination films were performed on a CHI660E electrochemical analyzer (Chen hua, China).

The structure investigation of the films were carried out by a Nicolet 6700 Fourier transform infrared spectrometer (FT-IR) (Thermo Fisher Nicolet, USA) with KBr pellets and S-4800 scanning electron microscope (SEM) (Hitachi, Japan), respectively. Spectroelectrochemistry test, optical contrast and switching time were investigated by Shimadzu UV-1800 spectrophotometer (Shimadzu, Japan) integrated with the CHI660E electrochemical analyzer.

## 2 Results and Discussion

### 3.1 Structure of polymer P-FeTPY and surface morphology of polymer film

As shown in Scheme 1, ionic metallo-supramolecular polymer (P-FeTPY) was synthesized by the coordination of Fe(II) ion and terpyridyl ligand in solvent at the reflux temperature[27].

Fig. 1a shows the  $^1\text{H}$  NMR spectrum of P-FeTPY. The chemical shift at around  $\delta$

= 9.16, 8.06, 7.90 ppm should be attributed to terpyridine, which reveals the formation of coordination bonds between terpyridine and Fe(II) ion, indicating the polymer P-FeTPY was successfully prepared. To further confirm the ligand and metal ion were successfully connected, we also characterized the material by FT-IR. As shown in Fig. 2b, the peak at  $1568\text{ cm}^{-1}$  belonging to the C = C stretching vibration of ligand, shifts to  $1585\text{ cm}^{-1}$  for the P-FeTPY due to the coordination of the ligand and Fe(II), which is consistent with those of the reported Fe(II)-terpyridyl coordination compounds[25]. In addition, the broad peak at around  $1100\text{ cm}^{-1}$  also indicates the insertion of  $\text{BF}_4^-$  and further proves the correct structure of P-FeTPY[24], demonstrating the ions of  $\text{BF}_4^-$  from the  $\text{Fe}(\text{BF}_4)_2$  were inserted to be the counter ions in the polymer.

Fig. 2 present fluorescence emission spectrum of terpyridyl ligand (black) and ligand- $\text{Fe}^{2+}$  in different molar ration, red (5:1), blue (5:2), dark cyan (5:3), magenta (5:4), dark yellow (5:5), navy (5:6), wine (5:7), respectively. As shown in Fig. 2a, the terpyridyl ligand has strong emission at the 439 nm. With the addition of the  $\text{Fe}^{2+}$  ion to the ligand solution, a decrease of the intensity of the band at around 439nm occurred because of the coordination of the ligand and the ion. Till the molar ration increased to ligand :  $\text{Fe}^{2+}$  = 5:5 (1:1), the fluorescence completely quenched, indicating the formation of P-FeTPY and demonstrating correct stoichiometry of the polymer assembly. Fig. 2b shown the UV-vis spectrum of the ligand- $\text{Fe}^{2+}$  in different molar ration. In this figure, the absorption at around 580 nm was increasing with the addition of  $\text{Fe}^{2+}$ , which is result from the MLCT due to contributions from transitions centered at Fe atoms[36], indicating the gradual coordination of the ligand and the ions.

Obviously, the maximum intensity of absorption at 580 nm was ligand : Fe<sup>2+</sup> = 5:5 (1:1), which is determined by the coordination reaction, manifesting the equally consumption of ligand and ion. To further prove the ration of N and Fe, energy dispersive spectrometer was also measured, as shown in table S2, the atomic ratio of N and Fe is 6.3:1, which is very close to 6:1, indicating the number of ligand and ion are equal of the polymer. The ITO covered with P-FeTPY by spin-coating method was studied by SEM, and the thickness of the film tested by Atomic-Profilier was around 90 nm. As shown in Fig. 3a, the film presented a flat surface in total. The smooth surface could indicate the P-FeTPY was uniformly distributed on the ITO. Fig. 3b show the AFM image of the film, as shown in the image, the roughness in this image show less than 30 nm, indicating smooth surface of the film further.

Cyclic voltammetry curves were measured to study the electrochemical properties of this material. The P-FeTPY films were used as the working electrode with Pt wire as the counter electrode and Ag/AgCl as the reference electrode. The Fig. 4a shows a couple of reversible redox peaks of P-FeTPY film with the oxidation peak at around 1.15 V, and the reduction peak at around 0.95 V at a scan rate of 100 mV·s<sup>-1</sup>. The symmetrical redox peaks which might belong to the oxidation of Fe(II) to Fe(III) in the polymers[26], indicated this ionic polymers possessed an excellent electrochemical reversibility. To further study the electrochemical kinetics, cyclic voltammetry tests with different scan rates of the films were conducted at 10, 20, 50, 100 and 200 mV·s<sup>-1</sup>, respectively. As the curves in Fig. 4b presented, the scan rate (v) dependence of the anodic and cathodic peak currents (i<sub>p</sub>) shows that the amounts are linearly proportional

to the scan rate as illustrated. This dependence certified that their electrochemical processes are not diffusion controlled and this behaviors are completely reversible, which is necessary to achieve the excellent electrochromic performance.

### ***3.2 Spectroelectrochemistry and electrochromic properties of P-FeTPY film***

The spectroelectrochemistry measurement of the spin-coated P-FeTPY films were carried out in aqueous solution containing 0.1 M LiClO<sub>4</sub> as the supporting electrolyte and the Ag/AgCl as the reference electrode. As shown in Fig. 5, the purplish red film of P-FeTPY exhibited a strong absorption in the visible light region at 580 nm in the neutral state, which is consistent with its DCM solution sample. As the voltage was increased to 1.0 V, P-FeTPY started to be oxidized mainly resulting from the oxidation of Fe(II) to Fe(III)[19]. The maximum absorption peak located at around 580 nm began to decrease, which is due to the consumption of Fe(II) ion and the increase of Fe(III) as well. Up to the potential of 1.4 V, the absorption disappeared and the film became colorless owing to the complete oxidation of Fe(II)[25].

Colorimetry quantifies the color of the polymer, therein the corresponding L\*a\*b\* represents the lightness L\* (0 = black and 100 = white) and a\* (+ve = red and -ve = green) and b\* (+ve = yellow and -ve = blue)[25,28]. Fig. 6a presents the change of L\* values at the potential from 0 V to 1.4 V. Following the potential increase to 1.1 V, the L\* values of the film improved gradually, indicating the increase of brightness of the film. When the potential was added to 1.4 V, the L\* value reached the maximum, which was consistent with the results of oxidation of the film from purplish red to colorless. The colorimetry plot (a\*b\*) was shown in Fig. 6b, the a\*b\* values of the

organic soluble ionic metallo-supramolecular polymer is  $a^* = 4.19$ ,  $b^* = -5.76$  at 0 V, and  $a^* = -2.00$ ,  $b^* = 9.98$  at 1.4 V, the difference between colors points was calculated as the equation bellow

$$\Delta E_{ab}^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$$

Where  $\Delta E_{ab}^*$  represents the difference between neutral and oxidized state, with values below 2.3 indicating differences that are not noticeable to the eye. We calculated a  $\Delta E_{ab}^*$  to be 18.07, indicating an obvious color difference on the neutral and oxidized state, the color changes moving from red and blue (purplish red) areas to the yellow (transparent) areas with the increasing voltage is noticeable to the eye.

Fig. 7a presents the kinetics test including optical contrast and switching time of P-FeTPY film. The optical contrast was monitored at 580 nm and the switching time was calculated as the time required to reach 95% of the full switching of the transmittance. The film was tested at the applied voltage between 1.4 V for 20 s and 0 V for 10 s, respectively, for complete oxidation and reduction. The repeated step potential curves displayed the switching time of coloring and fading is 2.6 s and 9.6 s, respectively, which is lower than those of some reported organic electrochromic polymer materials[29-30], but faster than most inorganic metal oxides[31]. This consequence results from the function of organic and inorganic hybridization in this polymer, promoting the development of hybrid electrochromic materials. The optical contrast at 580 nm was calculated to be 30% according to the film changes from purplish red to colorless. Besides, the electrochemistry stability was characterized by the step potential method under the same condition in aqueous solution with 0.1 M

LiClO<sub>4</sub> at 0 V for 5 s and 1.4 V for 20 s as shown in Figure S1a. The coloration efficiency was calculated to be 296.5 cm<sup>2</sup>·C<sup>-1</sup> according to the chronoamperometry curves as shown in Figure S1b and the equation. The coloration efficiency is illustrated by equation  $CE = \Delta OD/Q_d$ , where  $Q_d$  represents the injected charge density as a function of electrode area of the full optical switch.  $\Delta OD$  can be obtained from the equation  $\Delta OD = \log(T_{bleached} / T_{colored})$ , where  $T_{colored}$  and  $T_{bleached}$  are the transmittance values in the oxidized and neutral states, respectively[24]. In the light of Fig. 7b, the film retains 97% optical contrast after 240 cycles, demonstrating the excellent optical stability of this organic soluble ionic metallo-supramolecular electrochromic material.

### ***3.3 Spectroelectrochemistry and electrochromic properties of the devices***

In order to better show its electrochromic performance, the electrochromic device of P-FeTPY was also prepared. Fig. 8a shows the transmittance spectra of device which used P-FeTPY covered ITO as the working electrode and blank ITO as the counter electrode. As presented, the oxidation state (black line) and neutral state (red line) both exhibited absorption at 580 nm. It is considered that the remaining absorption at oxidized state may be caused by the blank ITO due to the blocked ion transportation inside, which is different from the electrolyte solution. Another reason is that there may still be some ACN in the gel electrolyte which could dissolve little of the P-FeTPY. Fig. 8b displays the oxidation state and neutral state of the device (1.8 × 2.5 cm). Obviously, the device displayed purplish red at fading and transparent at coloring, Figure S2 show the cycling stability of the devices made by gel electrolyte with applied potential at -1.5 V (neutral state) and 2.3 V (oxidized state) for 10 s respectively. Obviously, the

device kept a great stability, even in gel electrolyte which was including a lot of ACN, indicating the potential application in real life. Further, a large device of  $5 \times 5$  cm was prepared as shown in Figure S3, indicating the potential application.

### 3 Conclusions

In summary, an alkyl modified terpyridyl ligand was synthesized and utilized to construct an organic soluble linear ionic metallo-supramolecular material (P-FeTPY) with Fe(II) as the coordination center. The ionic polymer was characterized by NMR, FT-IR and UV-vis spectra to determine the structure. The spin-coated film showed a smooth surface in the SEM, and its electrochromic properties were studied by electrochemical workstation and UV-vis spectrometer in situ. The P-FeTPY electrochromic polymer film presented a strong absorption at 580 nm and showed over 30% contrast and fast switching time of 9.6 s and 2.6 s for oxidation and reduction respectively. Besides, the film exhibited excellent stability with 97% optical contrast retained after 240 cycles. These results demonstrate that alkyl chains linked ionic metal-organic polymer can be directly spin coated the polymer solution on the ITO that simplified the preparation method of thin film. As the solubility of the material is improved, the method of preparing the film is more convenient, and the material retains excellent electrochromic properties. This work provides an effective path to prepare organic soluble ionic metallo-supramolecular materials, which is necessary for large area production in practical applications.

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## Figure captions

Scheme 1. Synthesis routes of P-FeTPY. Reagents and condition: (i)  $K_2CO_3$ , DMF, reflux; (ii)  $K_2CO_3$ ,  $H_2O$ , 1,4-dioxane,  $Pd(PPh_3)_4$ , 110 °C; (iii) NaOH, EtOH,  $NH_4OH$ ; (iv) DCM, reflux.

Scheme 1/1

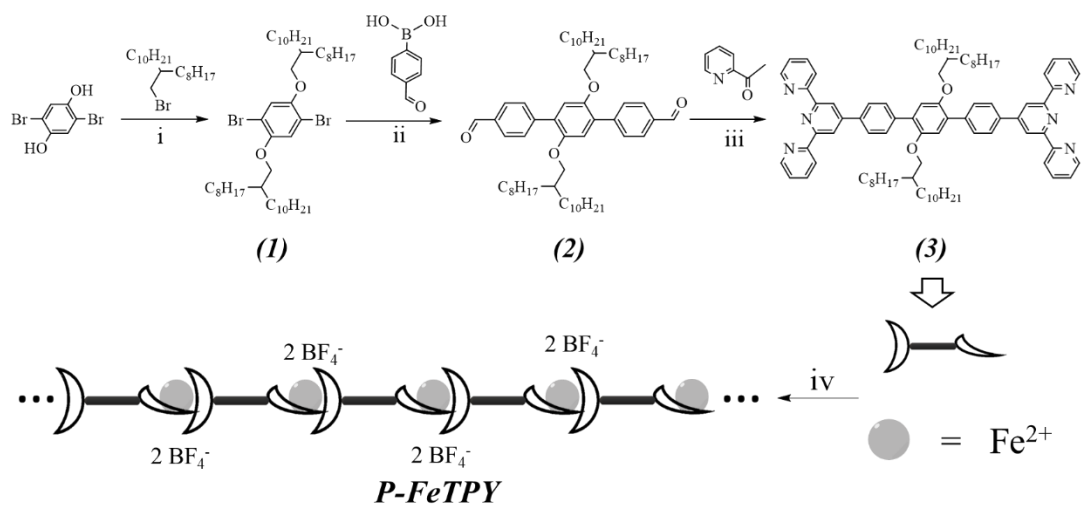


Figure 1. a) <sup>1</sup>H NMR spectrum of terpyridyl ligand (red) and P-FeTPY (black); b) FT-IR spectrum of terpyridyl ligand (red) and P-FeTPY (black).

Figure 2. a) Fluorescence emission spectrum of terpyridyl ligand (black) and ligand-Fe<sup>2+</sup> in different molar ratio. b) UV-vis absorption spectra of terpyridyl ligand (black) and ligand-Fe<sup>2+</sup> in different molar ratio.

Figure 3. a) SEM image of P-FeTPY film on ITO. b) AFM image of the film.

Figure 4. a) Cyclic voltammograms of the P-FeTPY on ITO obtained at different scan rates of 10, 20, 50, 100, 200 mV·s<sup>-1</sup>, respectively. b) The variation of anodic and cathodic peak currents as a function of the scan rates.

Figure 5. UV-vis absorption spectra of electrochromic P-FeTPY on ITO at different states with voltage from 0 to 1.4 V.

Figure 6. a) Lightness values. b) Colorimetry plot (a\*b\*) of P-FeTPY from the neutral (0 V) to the oxidized states (1.4 V).

Figure 7. a) Square-wave potential-step chronoabsorptometry of P-FeTPY film (monitored at  $\lambda_{\max} = 580$  nm, switching potential range: 0 to 1.4 V). b) Electrochromic stability measured on voltage from 0 to 1.4 V (monitored at  $\lambda_{\max}$ , switching potential range: 0 to 1.4 V).

Figure 8. a) Transmittance spectra of electrochromic P-FeTPY device at oxidized and neutral states. b) Image of electrochromic P-FeTPY device (1.8 × 2.5 cm) at oxidized (2.3 V) and neutral stated (-1.5 V).

Fig. 1/8

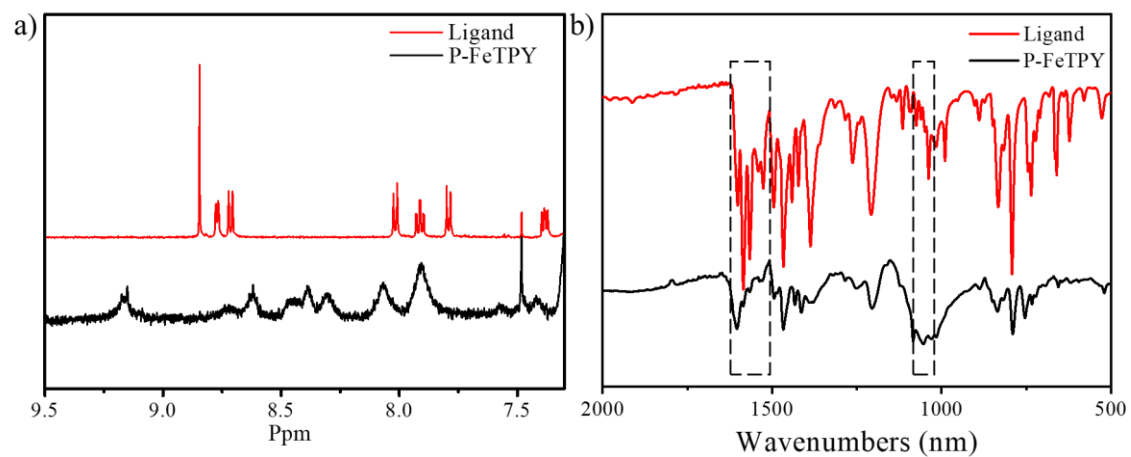




Fig. 2/8

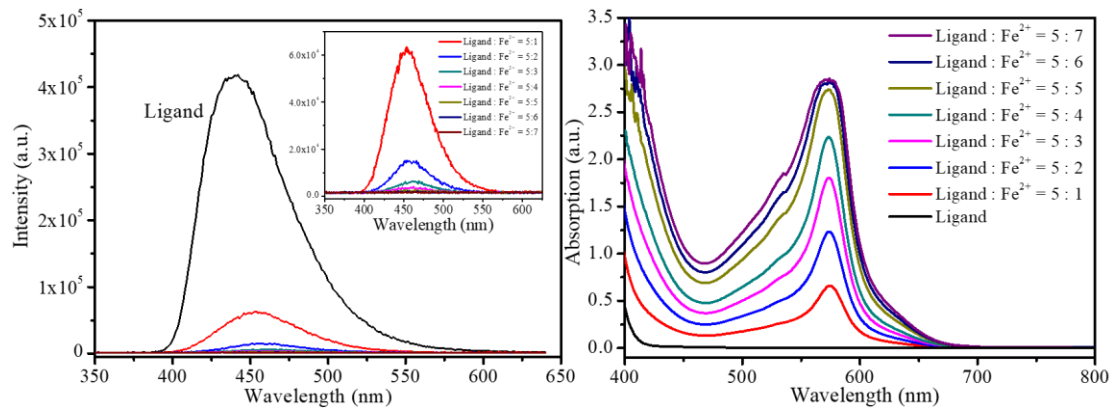


Fig. 3/8

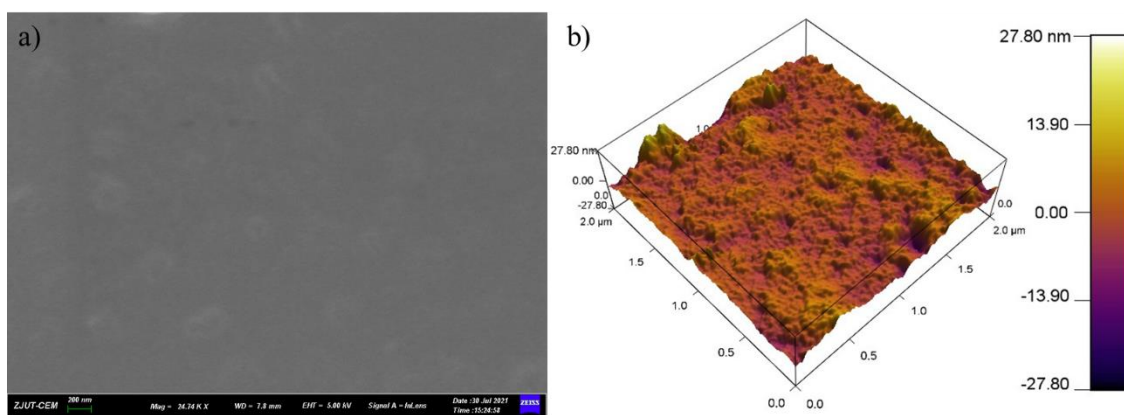


Fig. 4/8

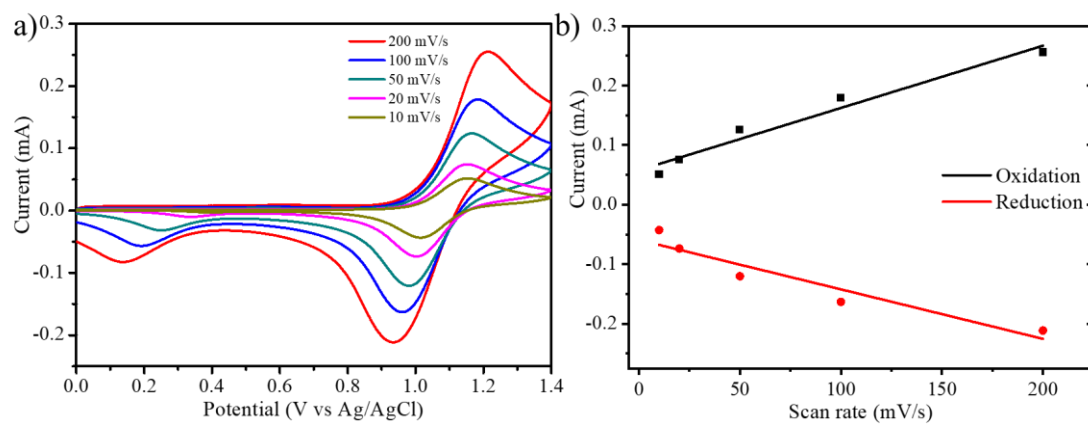


Fig. 5/8

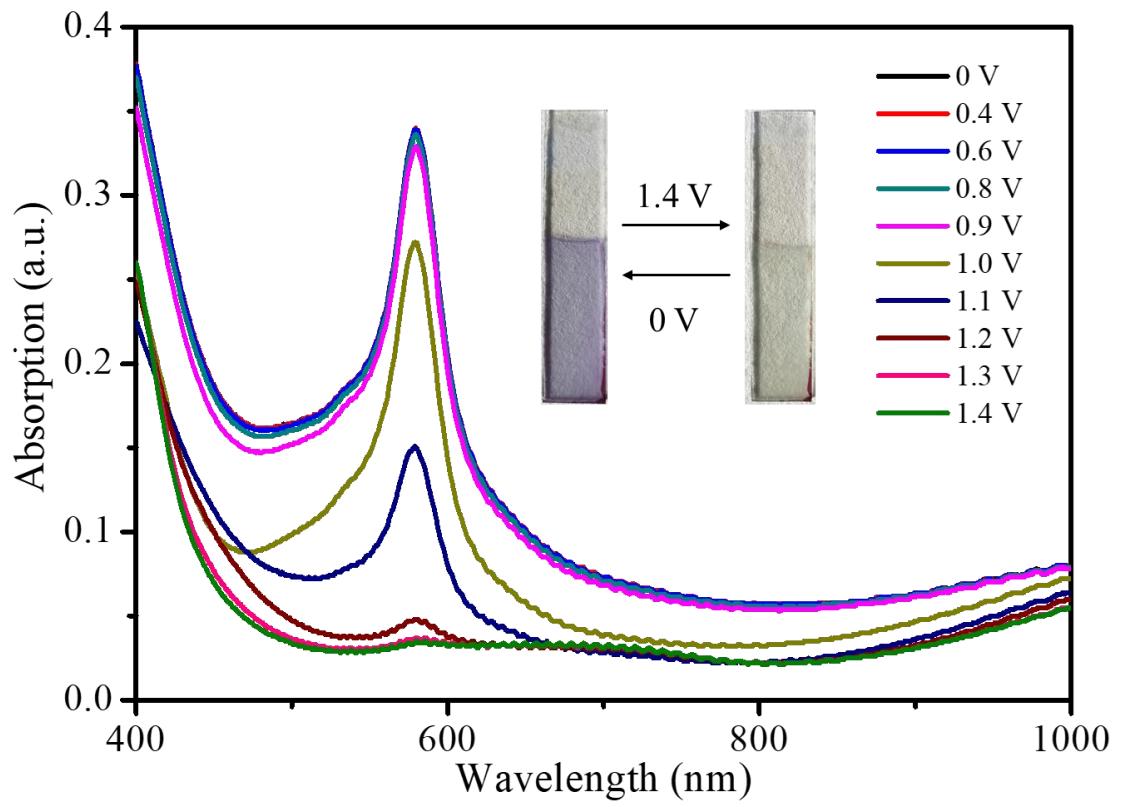


Fig. 6/8

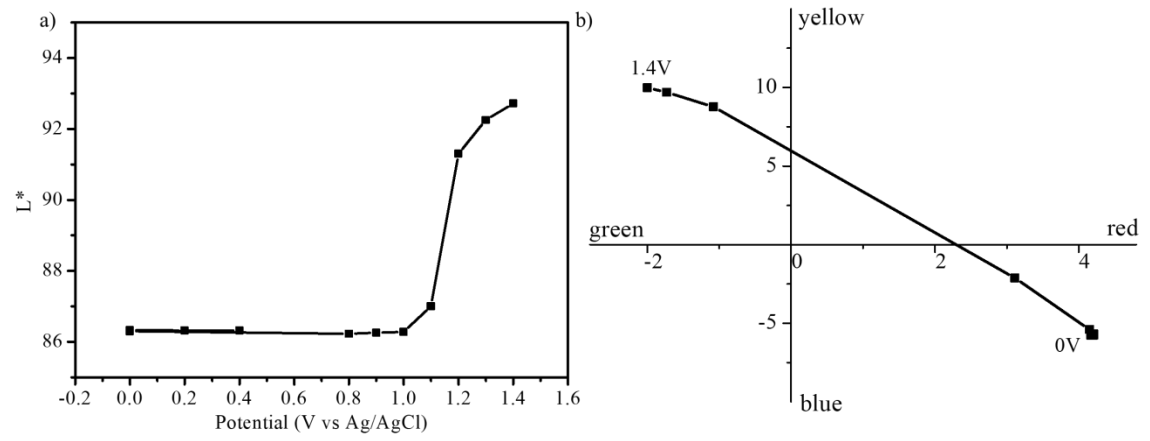


Fig. 7/8

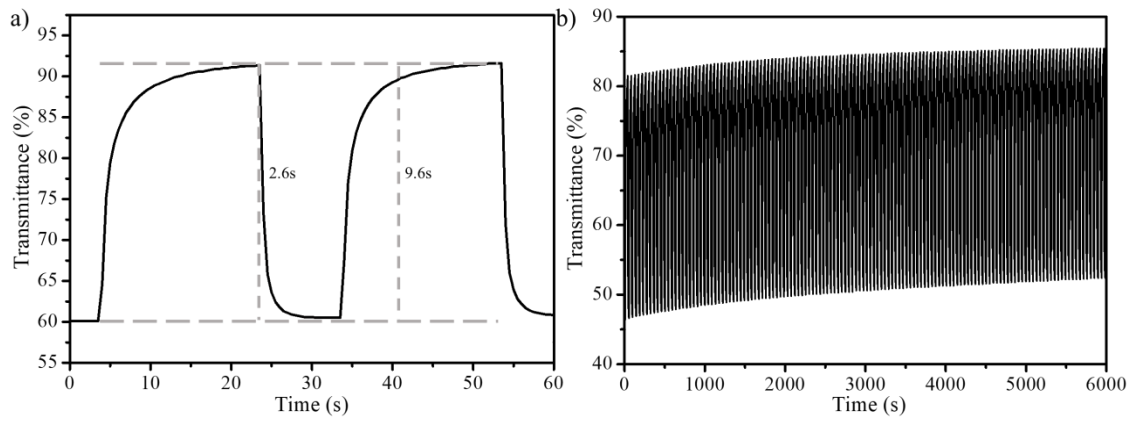
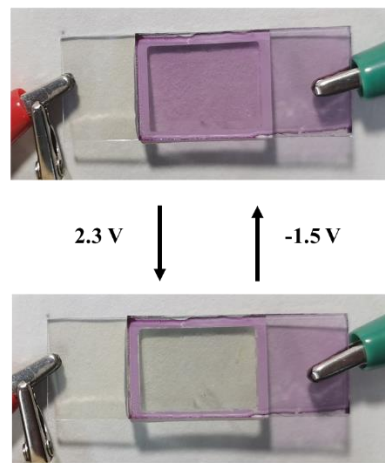
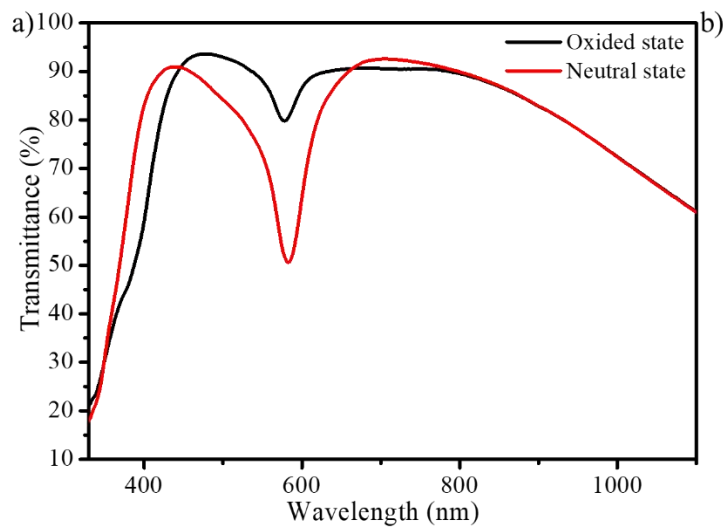
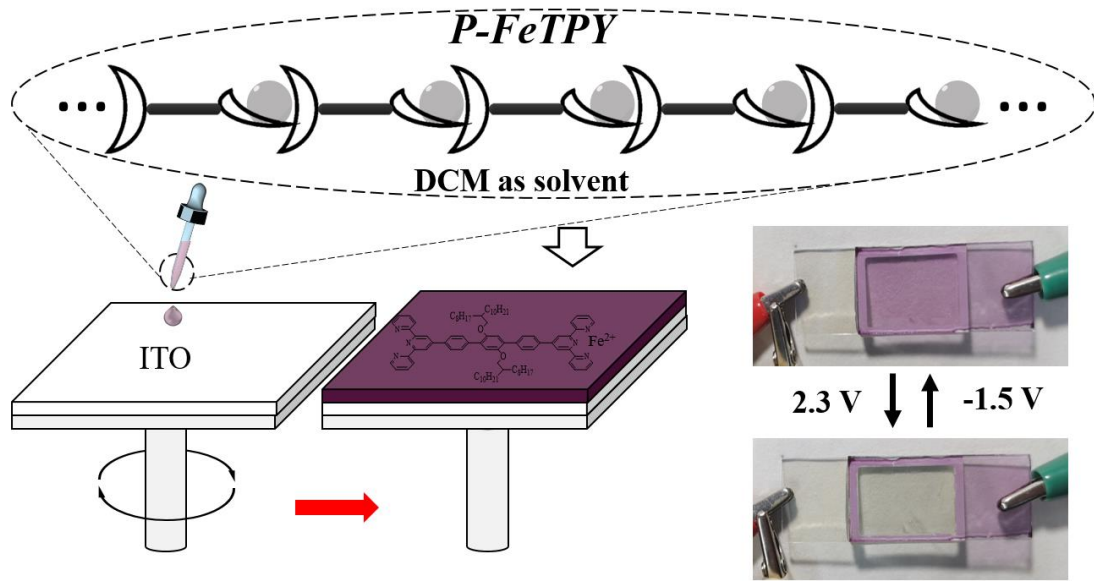


Fig. 8/8



## Table of Content





Supporting information

**Organic soluble linear metallo-supramolecular polymer  
based on Iron(II) and terpyridyl ligand with high  
electrochromic performance**

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Table S1. Properties of the Electrochromic Materials Based on TPY Prepared by Different Methods

EC materials	Solvents	methods	Thickness	$\Delta T$ (%)	Refs
P-FeTPY	DCM	Spin coating	90 nm	30-40	This work
Poly-FeL <sub>n</sub>	MeOH	Casting	-	< 20	33
FeL <sub>n</sub> -MEPE	Ethanol	Dip coating	-	< 30	34
Fe-Tt	Mixed solvents of HFP and ACN	Casting	30-40 nm	29-65	35
TPA-TPY	DCM/water	Liquid/liquid interface	70 nm	$\approx$ 25	26
Metallo- organic bilayers	DCM-MeOH	layer by layer spin coating	310 nm	< 30	36

Table S2. Energy Dispersive Spectrometer

Element	Mass Norm. [%]	Atom. [%]
C	12.45	33.40
O	13.18	26.54
Na	1.91	2.68
Mg	1.13	1.50
Si	17.05	19.56
Ca	1.28	1.03
In	36.55	10.25
Pt	14.86	2.45
Fe	0.61	0.35
N	0.97	2.23
	100.00	100.00

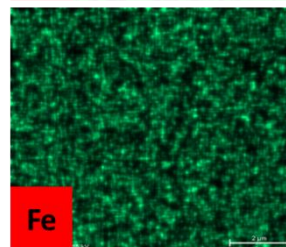
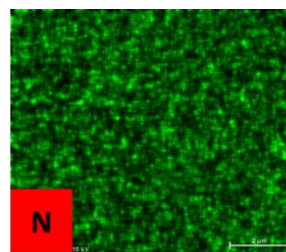


Fig .S1 a) Electrochromic stability measured on voltage from 0 to 1.4 V of the film (monitored at  $\lambda_{\text{max}}$ , switching potential range: 0 to 1.4 V). b) Chronoamperometry curves of the film.

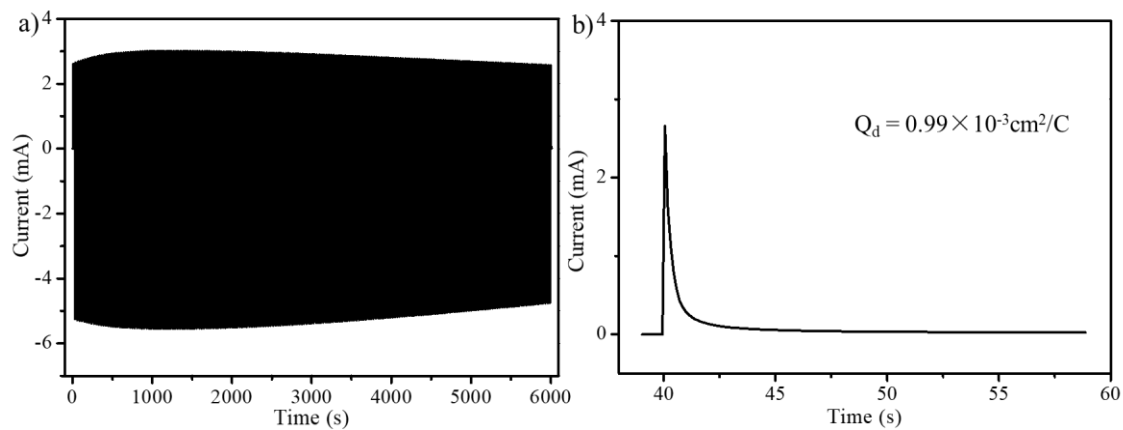


Fig .S2 Electrochromic stability measured on voltage from -1.5 to 2.3 V of the device (monitored at  $\lambda_{\max}$ , switching potential range: -1.5 to 2.3 V).

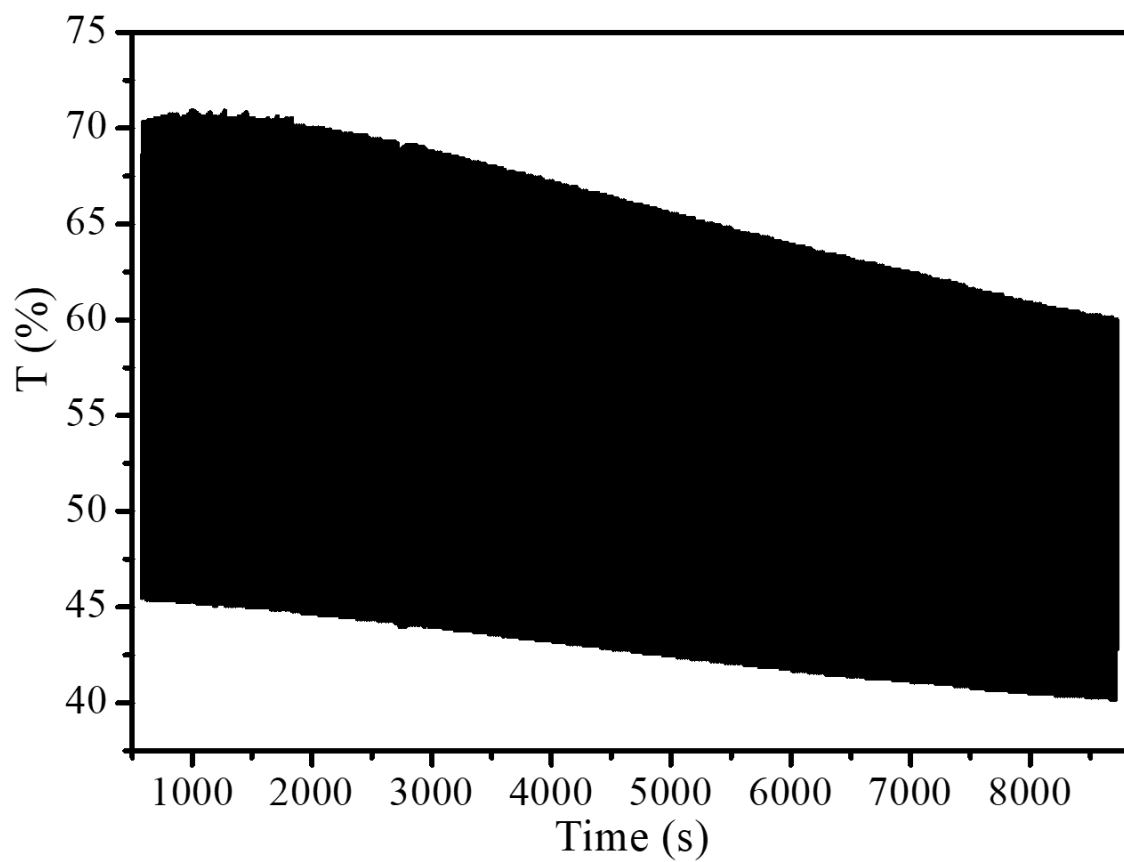


Fig .S3 Image of electrochromic P-FeTPY device ( $5 \times 5$  cm) at oxidized (2.3 V) and neutral stated (-1.5 V).

