

Contents lists available at ScienceDirect

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journal homepage: http://www.elsevier.com/locate/dyepig

A novel bis(terpyridine) with π -conjugated phenyl viologen and its metallo- supramolecular polymers: Synthesis and electrochromism

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ARTICLE INFO

ABSTRACT

Keywords: Bis(terpyridine) Viologen Metallo-supramolecular polymer Electrochromism A novel phenylene viologen functionalized bis(terpyridine) is synthesized and characterized with ¹HNMR and Maldi-tof-MS. This rod-like and π -conjugated molecule, 1,1'-[4'-(4-phenyl)-2,2:6',2"- terpyridine-4,4'-bipyridine-1,1'-diium dichloride (TPV⁺²2Cl⁻), synthesized by Zincke reaction of 4'-(4-aminophenyl)-2,2:6',2"- terpyridine with 1,1'-bis (2,4-dinitrophenyl)-4,4'-bipyridine,1,1'-diium dichloride, exhibited strong absorption and fluorescence in wide UV and visible wavelength range. It complexes with Fe- and Ru- ions and can self-assemble into metallo-supramolecular polymers in solution, which can be coated on ITO-glass. The electrochemical characteristics of TPV⁺²2Cl⁻ and its Fe-TPV⁺²-BF₄ supramolecular polymer in solution were studied with cyclic voltammetry. Four different color states, colorless (transparent), purple, reddish brown and grayish green, were observed in a cycle of redox reaction during the cyclic voltammetry scanning. A simple liquid electrochromic device with the Fe-TPV⁺²-BF₄ supramolecular polymer film as working electrode, and with LiClO₄ aqueous and K₃Fe(CN)₆, was fabricated. It can be colored/bleached reversibly between purple and green-yellowish colors by switching the applied voltage from 0 to 0.8 V. The π -conjugation among the bis(terpyridine)s and the phenylene viologen leads the subunits electronically and chemically connected. This interesting viologen functionalized bis (terpyridine) dye will find applications in wide ranges.

1. Introduction

Molecular self-assembly is an essential and powerful tool for fabricating molecular materials and molecular-based nanodevices [1]. The coordination of transition metal ions with ligands on designed molecules, such as bis(terpyridine)s, is a useful handle for molecular self-assembly, especially when precisely placing the active components into a molecular-based device or architecture is required. Bis(terpyridine)s have been widely used as the binding modules of such molecular devices for controlling light at molecular level, artificial species or systems for solar energy conversion, due to their high binding affinity toward transition-metals, p-stacking ability, and their distinct photophysical and electrochemical properties [2–6].

Viologens, i.e. 4,4'-bipyridinium ions, are electrochromic dyes that can undergo reversible one- and two-electron reductions. They have been well studied and used for fabrication of electrochromic devices, such as auto-dimming smart windows, anti-glare rear-view mirrors or low power consumption displays, and as the building blocks for the construction of nanosheets, charged covalent organic networks as well

[7–12].

In designing electrochromic materials, in order to achieve multicolor discoloration, combining two or more electro chromophores in one molecule is an often adopted strategy, because a single chromophore can rarely simultaneously exists in more than two different color states [13–21]. Because viologen and bis(terpyridine) chromophores are colored at different voltages in electrochromic reactions, and the bis (terpyridine) can complex with different metals [22,23], the combination of viologen with bis(terpyridine) will lead to molecular materials capable of showing multicolors by only tuning the applied potential. There are a few studies on the bis(terpyridine)s with viologen motifs as a pendent or a non-conjugated chromophore, such as the so called metalloviologen [24–27].

We designed a new bis(terpyridine) dye, TPV^{+2} , in which the two terminal terpyridines are linked and π -conjugated by a phenyl viologen subunit. By complexation with transition metal ions TPV^{+2} is capable of self-assembling into metallo- supramolecular polymers (Scheme 1). Both the bis(terpyridine) and the phenyl-viologen chromophores have been well studied for their electrochromism: the color of bis(terpyridine)s-

https://doi.org/10.1016/j.dyepig.2020.108251

Received 28 November 2019; Received in revised form 27 January 2020; Accepted 28 January 2020 Available online 30 January 2020 0143-7208/© 2020 Elsevier Ltd. All rights reserved.

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metal complex is the metal ion dependent, and the phenyl-viologen shows deep green color at colored state. We report here the synthesis, characterization, optical and the primary electrochromic properties of this viologen functionalized bis(terpyridine) dye and its Fesupramolecular complex. The optical properties of Ru- supramolecular complex are also reported for comparison.

2. Experimental section

2.1. Materials and instruments

All commercially available chemicals and solvents were purchased and used unless otherwise mentioned. 1,1'-bis(2.4-dinitrophenyl)-4,4'bibyridine-1,1'-diium dichloride was synthesized by the reported procedures [28]. 1,4-Bis-(2,2':6',2''- terpyridine-4'-yl) benzene (BTP) and the Fe-BTP were synthesized as descripted in the supporting materials.

Instruments: Bruke AC-200 nuclear magnetic resonance instrument; UV-3802S ultraviolet visible spectrophotometer, Unico (Shanghai) Instrument Co, Ltd; CS350 electrochemical workstation, Wuhan Kesite Instrument Co, Ltd; DC stabilized power supply; FluoroMax-4 fluorescence spectrophotometer, France HORIBA; Agilent HP5973 mass spectrometer for the high resolution matrix assisted laser dissociation time-of-flight mass spectrometer (MALDI-TOF-MS).

2.2. Synthesis of the viologen-conjugated bis(terpyridine) and the metallosupramolecular complex polymer

2.2.1. Synthesis of 4'-(4-nitrophenyl)-2,2:6',2'' -terpyridine (T1)

p-Nitro benzaldehyde (3.78 g, 25 mmol), 10% aqueous sodium hydroxide solution (27.5 mL) and ethanol (125 mL) were added to a 500 ml flask. Under magnetic stirring 2-acetylpyridine (6.65 g, 55 mmol) and

ammonium hydroxide (75 mL, 25–28%) was slowly added in turn. The reaction was carried out at 0 °C for 24 h. The crude product was recovered by filtration, and washed once with water and then with ethanol. It was finally recrystallized from ethanol and dried in vacuo to get a dark brown solid 1.91 g, yield 18.3%. ¹H NMR $\delta_{\rm H}$ (400 MHz, CDCl₃): 7.37(dt, *J* = 4.53, 6.95 Hz 2H), 7.90(td, *J* = 1.51, 7.69 Hz 2H), 8.03–8.07(m, 2H), 8.35–8.5(m, 2H), 8.69(dd, *J* = 7.74 Hz 2H), 8.75(s, 2H), 8.79(dd, *J* = 8.46 Hz 2H).

2.2.2. Synthesis of 4'-(4-aminophenyl)-2,2:6',2"- terpyridine (T2)

T1 (1.6 g, 4.5 mm), SnCl₂ (5.35 g, 28 mmol) and hydrochloric acid (40 mL, 36%–38%) were added in flask and reacted under reflux for 6 h. Then the flask was cooled to room temperature and the product was filtered. Appropriate amount of 10% NaOH aqueous solution then added into the filtrate and stirred for 1 h. After filtration and washing with water and then dried in vacuo, it give a brown solid 1.27 g, yield 79%. ¹H NMR $\delta_{\rm H}$ (400 MHz, CDCl₃): 3.86(d, J = 9.32 Hz, 2H), 6.87(d, J = 8.42 Hz, 2H), 7.41(ddd, J = 1.06, 4.75, 7.42 Hz, 2H), 7.85(d, J = 8.45 Hz, 2H), 7.94(td, J = 1.75, 7.72 Hz, 2H), 8.73(d, J = 7.91 Hz, 2H),8.76 (s, 2H), 8.77–8.81(m, 2H).

2.2.3. Synthesis of 1,1'-[4'-(4-phenyl)-2,2:6',2"-terpyridine-4,4'-bipyridine-1'1-diium dichloride ($TPV^{+2}2Cl^{-}$)

T2 (1.2 g, 3.7 mmol) in ethanol (25 mL) and 1,1'-bis(2,4-dinitrophenyl)-4,4'-bipyridine-1,1'-diium dichloride (0.86 g, 1.5 mmol) in distilled water (26 mL) were mixed in flask and stirred under reflux for 70 h. After rotavap to remove the water and ethanol, the solid was dissolve with a small amount of methanol, and then precipitated with diethyl ether. By washed twice with diethyl ether and dried under vacuo, it gave a red-brown solid product 1.97 g, the counter anions is chloride ion, yield 57%. The samples for ¹H NMR and HRMS



Scheme 1. Bis(terpyridine) and the metallo-supramolecular polymers.

measurements were recrystallized from methanol and diethyl ether. ¹H NMR (400 MHz, (CD₃)₂SO): $\delta_{\rm H}$ ppm⁻¹ = 7.63 (dd, J = 5.52, 6.83 Hz, 4H), 8.14 (dd, J = 7.15, 15.27 Hz, 4H), 8.25 (d, J = 8.35 Hz, 4H), 8.44 (d, J = 8.35 Hz, 4H), 8.79(d, J = 7.73 Hz, 4H), 8.83(d, J = 4.14 Hz, 4H), 8.89 (s, 4H), 9.21 (d, J = 6.42 Hz, 4H), 9.85(d, J = 6.42 Hz, 4H). HRMS (ESI): C₅₂H₃₆N₈ calculated 772.3052, found 772.3051.

2.2.4. Synthesis of Fe-TPV⁺²-BF₄ supramolecular polymer

TPV⁺² 2Cl⁻ (169 mg, 0.2 mmol) was added in water (160 mL) and refluxed under N₂ for 0.5 h. Then ferrous acetate tetrahydrate (49 mg, 0.2 mmol) was added under stirring. The solution turned into a dark purple immediately. It was further refluxed for 12 h, then cooled to room temperature and filtered to remove trace solid. After addition of lithium tetrafluoroborate 0.64 g to the filtration, the purple and flocculent precipitate was formed and the solution gradually became clear. The purple-black solid product was collected by centrifugation, then dried under vacuo, TPV⁺²-Fe-BF₄, 148 mg, yield 68%.

Ru-TPV⁺²-BF₄ **supramolecular polymer** was similarly synthesized with RuCl₂(DMSO)₄ (97 mg 0.2 mmol), yield 56%.

2.3. Preparation of Fe-and Ru-TPV⁺²-BF₄ film

The Fe-TPV⁺²-BF₄ or Ru-TPV⁺²-BF₄ film was prepared by the following step: firstly, preparing 1.0 mg/mL solution of Fe-TPV⁺²-BF₄ in acetonitrile, and then filtrated with a microporous membrane; secondly, a 2 × 2 cm bare area on ITO glass sized 3 × 4 cm was taped with self-adhesive tape and placed on a hot plate at 80 °C; thirdly about 2–4 mL of the Fe-TPV⁺²-BF₄ in acetonitrile solution was sprayed evenly onto the bare area with a mini spray gun. The Fe-TPV⁺²-BF₄ film with size of 2 × 2 cm on ITO glass was obtained after peeling off the surrounding protective tape.

2.4. Preparation of $Fe-TPV^{+2}-BF_4$ device

The device is assembled with the Fe-TPV⁺²-BF₄ film as working electrode, 0.1 mol/L LiClO₄ aqueous as electrolyte solution and 20 mg/mL K₃Fe(CN)₆ as complementary material. The working area of the PV-Fe-BF₄ film was 2 × 2 cm with 0.2 mm thickness controlled by the sealing strip.

2.5. Electrochemical and electrochromic test

Spectroelectrochemical tests of Fe-TPV⁺²-BF₄ and Fe-BTP⁺²-BF₄ supramolecular polymers were carried out in acetonitrile with LiClO₄ as the electrolyte, Pt as the counter electrode and Fe-TPV⁺²-BF₄ or Fe-BTP⁺²-BF₄ as the working electrode, and cyclic voltammetrically scanning between -1.2 V and 1.5 V to obtain the redox curves.

3D- and 2D-fluorescence spectroscopy of TPV^{+2} was recorded with the solution of 0.06 g/L of TPV^{+2} in DMSO by a fluorescence spectrophotometer set at 5 nm slit width, and excitation wavelength in 250–500 nm, emission in 300–800 nm with 10 nm interval wavelength.

The matrix assisted laser desorption ionization-mass spectrometry (Maldi-tof-MS) was performed with α -Cyano-4-hydroxycinnamic acid (CHCA) as matrix to obtain the spectra in a linear mode.

3. Results and discussion

3.1. Synthesis and characterization of TPV^{+2} 2Cl⁻, and its Fe- or Rusupramolecular polymers

The viologen conjugated bis(terpyridine), $TPV^{+2}2Cl^{-}$, was synthesized, as showed in Scheme 2. The building block T1 was prepared in one-step by slightly modifying the reported two-step reaction procedures [29–31] with improved product yield. We found that for our one-step reaction to T1, the reaction temperature greatly affected the product yield, and the optimal temperature for the reaction is about 0



Scheme 2. Syntheses of the viologen conjugated bis(terpyridine), TPV⁺² 2Cl⁻.

 $^\circ\text{C}.$ When the reaction was carried out under reflux almost no T1 product was obtained. Yield could be further improved by extending reaction time.

T2 was synthesized by the reduction of T1 under mild condition as the reported procedure [29]. Finally the TPV⁺² dichloride, TPV⁺² 2Cl⁻, was obtained by Zincke reaction of 4⁻(4-aminophenyl)-2,2:6['],2"-terpyridine with 1,1'-bis(2,4-dinitrophenyl)-4,4'-bipyridine-1,1'- diium dichloride. TPV⁺² 2Cl⁻ is soluble in methanol, DMSO and propylene carbonate, but only slightly soluble in water and ethanol.

The Ru- and Fe-TPV⁺²-BF₄ supramolecular polymers were prepared in water by the complexation reaction of TPV⁺² 2Cl⁻ with the Ru⁺² or Fe⁺² salt at 1:1mol ratio, followed by treating with LiBF₄ to replace the Cl⁻ counter anions with BF₄. The resultant Fe- or Ru- supramolecular polymer complex is soluble in acetonitrile, but not in water, DMSO, methanol and propylene carbonate.

TPV⁺² was characterized by ¹H NMR and high resolution mass spectrometer (HRMS). All the H-atoms of TPV were assigned in the spectra, as showed in Fig. 1a. Under the soft Maldi-tof-MS condition for HRMS the molecular ion of the TVP, $M^+ = C_{52}H_{37}N_8^+$, with the m/z calculated as 772.3052 was found as m/z = 772.3051, as showed in Fig. 1b. The other ions above the M^+ include those ions as M^+ + H₂O, M^+ H⁺ and M + Na⁺.

The Fe-TPV⁺²-BF₄ supramolecular polymer was also checked with Maldi-tof-MS. There is a region of wide m/z distribution beyond m/z = 2500 in the Maldi-tof-MS, as shown in the inset of Fig. S1. The emerged peak at m/z around 3000-6000D can not be easily explained, because the m/z values of ions in MS depend on the number of charges on the ions, which in turn depends on the degree of ionization of the metallo-supramolecular polymers. The detected ions in the ESM processes may also contain some anions. For metallo-supramolecular polymer it is still not clear whether the molecular weight can be directly determined by Maldi-tof-MS [32,33]. The smooth thin film made with the



Fig. 2. a) Pictures of powder and films Fe-/Ru-TPV⁺²-BF₄ metallo-supramolecular polymer and b) UV–Vis absorption spectra of TPV⁺²2Cl⁻.

 $\rm Fe-TPV^{+2}-BF_4$ metallo-supramolecular polymer solution on glass, as depicted in Fig. 2a, is an indication of high molecular mass, because low molecular mass substance, especially with rigid rod-like molecule, can not form smooth thin film by its self.

The powder and films of the $Fe-/Ru-TPV^{+2}-BF_4$ metallosupramolecular polymers are deep colored, as depicted in Fig. 2a. The absorption spectra of TPV⁺²2Cl⁻ in DMSO solution are showed in Fig. 2b. The strong absorption band, with λ_{max} =278 nm and ε = 5.58 × 10⁴ dm³mol⁻¹cm⁻¹, extended from UV to visible region of 200–650 nm. This wide range of absorption is quite characteristic in comparing with the other bis-(terpyridine)s with viologen-like motifs that cut off absorption under 500 nm wavelength [24,34]. It is resultant of the long



Fig. 3. UV–Vis absorption spectra of Fe-/Ru-TPV $^{+2}\mbox{-}BF_4$ supramolecular polymer.

range of π -conjugation through the electro-withdrawing phenylene viologen unit. The absorption shoulder around 321 nm is composed of the absorption of viologen and the pyridine ligand subunits of TPV⁺².

The UV–Vis absorption spectra of the Ru⁺² or Fe-TPV⁺²-BF₄ complex are showed in Fig. 3. The strong absorption bands at visible wavelength range, with λ_{max} =494 nm (ε = 2.85 × 10⁴mol⁻¹dm³cm⁻¹) and λ_{max} = 575 nm (ε = 2.67 × 10⁴mol⁻¹dm³cm⁻¹) for Ru-TPV⁺²-BF₄ and Fe-TPV⁺²-BF₄ complex, respectively, come from the ligands complexed with the metal ions, similar to the of Fe- and Ru-bis(terpyridine)s complexes in absorption wavelength [2,23].

The 3D and 2D-fluorescence spectra of TPV⁺²2Cl⁻ were measured, as

shown in Fig. 4. In the 3D spectra the excitation wavelength sets at the ordinate and emission wavelength at the abscissa, and the fluorescence intensities were indicated by the color apertures. The 2D- luminescence spectra were obtained by excitation at three specific wavelengths. From Fig. 4, it can be seen that $TPV^{+2}2Cl^{-}$ is a fluorescent dye strongly emitting fluorescent covering the entire visible range, from 330 nm to 750 nm, when excited by radiation from 250 nm to 475 nm. The rigid structure of the $TPV^{+2}2Cl^{-}$ molecule makes its luminescence intensified.

The luminescence of the Fe- or Ru-TPV^{+2} supramolecular polymer complex is much weaker than TPV^{+2} , and their fluorescence properties are still under studying.

3.2. Electrochemical and electrochromic behaviors of $TPV^{+2}2Cl^{-}$ and Fe- TPV^{+2} -BF₄ supramolecular

The electrochemical characteristics of $TPV^{+2}2Cl^{-}$ were studied with cyclic voltammetry in DMSO solution containing LiClO₄ as the electrolyte. Pt sheets were used both as the working and counter electrode against the Ag/AgCl reference electrode. In the cyclic voltammetry curve, Fig. 5, the two pairs of redox peaks comes from the redox of the viologen subunit. The two oxidation peaks at -0.41 V and -0.13 V correspond to the oxidation of zero valent TPV^{0} to the radical cation $TPV^{\bullet+1}$, and $TPV^{\bullet+1}$ to TPV^{+2} , respectively. The reduction peaks at -0.37 V and -0.87 V arise from $TPV^{\pm}2$ to $TPV^{\bullet+1}$, and $TPV^{\bullet+1}$ to TPV^{0} , respectively. During the cyclic voltammetry scanning, the Pt working electrode, after reductive scanning to below -0.37 V, was found to have a thin layer of green-colored deposition, like the color of phenyl viologen at the colored state. This deposition came from the $TPV^{\bullet+1}$ radical cations that tend to dimerize in solution [8]. The dimers are less soluble



Fig. 4. a) 3D-dimensional fluorescence spectra of $TPV^{+2}2Cl^{-1}$ in DMSO (the ordinate is the excitation wavelength and the abscissa is the emission wavelength); 2D-luminescent spectra at b) fluorescence spectra exited with photons of b) 310 nm; c) 350 nm; d) 430 nm.



Fig. 5. Cyclic voltammetry curve of $TPV^{+2}2Cl^{-}$ (0.1 mol/L LiClO₄/DMSO solution as electrolyte).

because of their rigid and conjugated structure.

The electrochemical redox reactions of Fe- TPV⁺²-BF₄ supramolecular polymer were similarly studied with cyclic voltammetry in acetonitrile with LiClO₄ as the electrolyte, and the Fe-TPV⁺²-BF₄ film sprayed on an ITO glass as the working electrode and a Pt sheet as the counter electrode, against the Ag/AgCl reference electrode. The cyclic voltammetry curve is shown in Fig. 6, together with that of Fe-BTP for comparison [23]. By comparing the two cyclic voltammetry curves, it can be seen that the cyclic voltammetry curve of Fe-TPV⁺²-BF₄ film is composed of the two redox reactions of TPV^{+2} unit and Fe^{+2} ions. The two peaks at 1.09 V and 0.75 V come from the oxidation of Fe^{+2} to Fe^{+3} and the reduction of Fe^{+3} to Fe^{+2} , respectively. The two peaks at -0.46and -0.23 V arise from the oxidation of the TPV⁺² to TPV^{\bullet +1}, and $TPV^{\bullet+1}$ to TPV^{+2} , respectively. The reductions of TPV^{+2} to $TPV^{\bullet+1}$ and further reduction to TPV⁰ are included in the wide peak that started at about -0.2 V, centered at -0.63 V and ended at about -0.9 V. From Figs. 5 and 6, it can be calculated that the onset of the oxidation peak for the TPV^{\bullet +1} from TPV⁰ is about -0.81 V and -0.53 V for the supramolecular polymer and for TPV^{+2} , respectively, while the onset of reduction of TPV^{+2} to $TPV^{\bullet+1}$, for either the supramolecular polymer or TPV^{+2} is about -0.2 V. In other words, while the lowest unoccupied molecular orbital energy, E_{LUMO} for either TPV^{\bullet +1} of supramolecular polymer or of the bis(terpyridine) does not change much, the highest occupied molecular orbital energy, E_{HOMO} , of TPV^{\bullet +1} decreased about 0.81-0.53 = 0.28 V for the supramolecular polymer relative to TPV⁺².

These changes can be ascribed to the complexation of the TPV^{+2} ligands with metal ions, which makes the orbital energy of the viologen unit lower, or more stable.

Fig. 6b is the images of the color changes of Fe-TPV⁺²-BF₄ film as the working electrode of the electrochemical cell during the cyclic voltammetry scanning. At least four colors can be observed in a cycle of redox reaction. The corresponding states of the chromophores are denoted.

A simple liquid electrochromic device with Fe-TPV⁺²-BF₄ supramolecular polymer film as the working electrode, LiClO₄ aqueous as electrolyte, was fabricated and its electrochromism was spectroelectrochemically studied, as showed in Fig. 7a. To reduce the device driving potential K₃Fe(CN)₆ was added as the complementary material. At 0 V, or without the applied potential, owing to the absorption at about 330 nm and at 575 nm, the supramolecular polymer film on ITO glass is purple-colored. When a positive potential 1.2 V applied it bleached to slight yellow-greenish owing to the oxidation of Fe^{+2} to Fe^{+3} that leads to gradual disappearance of the absorption at 575 nm. When negative potential applied the color of the film changed to brownish, depending on the potential applied, the more negative the potential, the deeper the color, owing to formation of the greenish radical cation TPV $^{\bullet+1}$. Fig. 7b shows the structure and images of the color changes. More electrochromic properties are still under study and will be reported elsewhere.

The electrochemical and electrochromic characteristics of Ru-TPV⁺²-BF₄ are in some way similar to Fe-TPV⁺²-BF₄ supramolecular polymer, and are still under studying.

4. Conclusion

A novel bis(terpyridine) including π -conjugated phenylene viologen is synthesized and studied. It strongly absorbs photons and emits fluorescence in wide UV and visible wavelength range. It complexes with transition metal ions and self-assembles into metallo-supramolecular polymers in solution, which can be sprayed on ITO-glass. The Fe-TPV⁺²-BF₄ supramolecular polymer exhibited electrochromic multicolors, depending on the metal ions coordinated and potentials applied. The π -conjugation among the bis(terpyridine)s and the phenylene viologen makes these subunits electronically and chemically connected that the optical absorption of the coordinated ligands redshifted and the oxidation potential of the viologen unit decreased. This interesting viologen functionalized bis(terpyridine) dye will find applications in wide ranges.



Fig. 6. a) Cyclic voltammetry curve of Fe-TPV⁺²-BF₄ (purple) and Fe-bis(terpyridine) complex (Fe-BTP, blue) in acetonitrile with LiClO₄ as electrolyte; b) Images of the Fe-TPV⁺²-BF₄ film color changes in cyclic voltammetry scanning, denoted with the corresponding states. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article).



Fig. 7. a) Electrochemical spectra of Fe-TPV⁺²-BF₄ supramolecular polymer; b) Structure of Fe-TPV⁺²-BF₄ supramolecular polymer and Images of electrochromic device colour changes. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article).

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Yuchen Qian: Conceptualization, Data curation. Han Yang: Conceptualization, Data curation. Yuechuan Wang: Methodology, Writing - original draft.

Acknowledgment

This work is partly supported by the Project of State Key Laboratory of Polymer Materials Engineering (Sichuan University).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.dyepig.2020.108251.

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