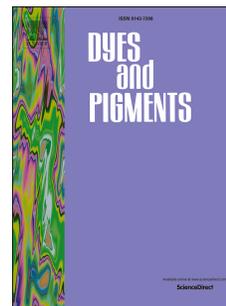


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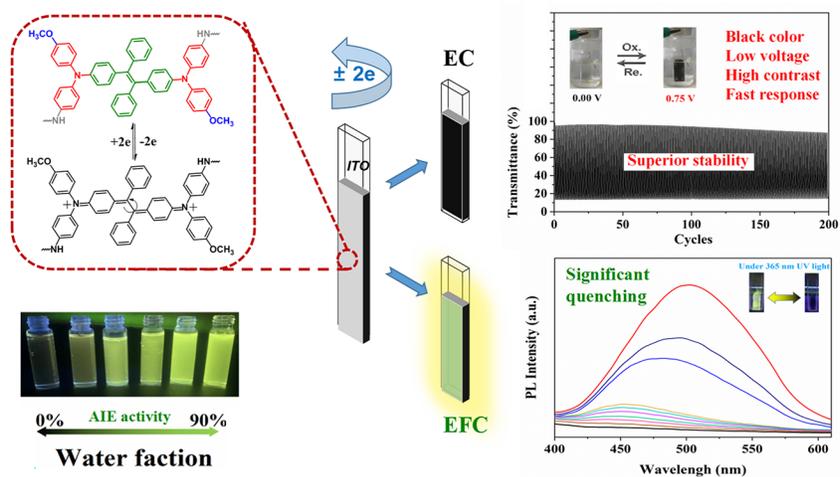
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Yuntao Han: Investigation, Formal analysis, Resources, Writing - Review & Editing.

Hongyan Yao: Writing - Review & Editing, Visualization, Formal analysis, Conceptualization, Supervision.

Zheng Chen: Data Curation, Resources, Investigation.

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Polymeric optoelectronic materials with low-voltage colorless-to-black electrochromic and AIE-activity electrofluorochromic dual-switching properties

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Abstract

In recent years, colorless-to-black electrochromic (EC) and electrofluorochromic (EFC) materials are attracting increasing interest for the fundamental scientific research and potential applications. In order to achieve multiple-response optoelectronic materials with better black conversion and solid-state fluorescence performance (black-color/emission dual-switchable materials), we adopted a novel design strategy to synthesis a diamine monomer named TPE-NH₂, in which the π -core tetraphenylethene (**TPE**) connects with two oxidation centers. All the polyamides/polyimides based on this monomer exhibited good solubility, thermal stability and aggregation-induced emission (AIE) activity. Among these, polyamide

5a not only showed rare EC properties (colorless-to-black) with ultra-low voltage (0-0.75 V), high optical contrasts (up to 87.9% at 692 nm) and fast switching times (2.04/1.45 s) but also demonstrated high fluorescence properties with the introduction of **TPE**. In addition, polyamide 5a showed good continuous switching stability for EC property and acceptable stability for EFC property, which makes it a potential candidate in EC/EFC applications.

Keywords: electrochromic; electrofluorochromic; colorless-to-black; AIE; dual-switching

1. Introduction

Nowadays, stimuli-responsive optical materials including the electrochromic/electrofluorochromic (EC/EFC) materials have attracted great attention on their potential applications of the displays and sensors. The EC/EFC materials combine the advantages of both EC and EFC materials, thus they can be applied for more scenarios. Non-emissive EC materials and emissive EFC materials can exhibit reversible color changes and reversible fluorescence changes under the electrochemical redox reactions with only little energy consumption, respectively [1-11]. However, there are still some problems of the research of high-performance EC and EFC materials, which need to be solved.

To date, the colorless-to-black EC polymer materials are still rare, especially organic polymer EC materials. Compared with the inorganic EC materials, the organic polymer EC materials have several unique advantages such as low voltage, solution

process ability, short switching time and high optical contrast ratios [12, 13]. However, it is difficult to develop black polymer EC materials to reverse absorption in the transparent state and absorb all over the entire visible light in the colored state with a high contrast ratio [14]. Moreover, most reported black EC materials are designed based on the color-mixing theory which multi-chromophores with different absorption wavelengths are incorporated into one polymer to absorb the light of the whole visible spectrum [14-18]. There are some drawbacks to this strategy. First, it is difficult to control all chromophores to achieve appropriate changes at the same time and it always leads to a higher operating voltage of electrochromism which may lead to the decomposition of polymer and also consume more energy [18]. Second, the copolymers containing multi-chromophores always reveal more absorption and show dark color in the transmissive state [19-23]. Another strategy to develop black EC polymers was via donor-acceptor approaches and extending the triarylamine core, however, further extensions inevitably lead to the collapse of the desired color such as impure black or colored in the bleached state [14, 19, 24-28]. The contrast ratio was limited ($<60\%$) and the stability was not desirable [14]. Therefore, it is urgently desired to develop a new strategy to achieve excellent colorless-to-black performance. As for the EFC materials, several polymer materials with excellent redox-switchable fluorescence have been reported [29, 30]. However, the fluorescence quenching problem caused by aggregation (ACQ) weakens the fluorescence intensity of EFC materials and has always hindered its application [31]. Tang et al. first reported that the tetraphenylethene (TPE) derivatives showed a special aggregation-induced

emission (AIE) phenomenon in the solid state due to the specific twist propeller-like conformation of **TPE** [32, 33]. The discovery of AIE provides a chance to break through the limitation of conventional chromophores in EFC field.

Currently, several triphenylamine (**TPA**) based emission/color dual-switchable materials connected with **TPE** structure have been reported to avoid ACQ and enhance fluorescence in the solid state [34-37]. However, few of them utilized the redox reaction of the **TPE** structure. When undergoing the redox reaction, the sterically congested **TPE** derivatives can exhibit remarkable structural changes, which the “C=C” double bond changed to “C-C” single bond as shown in **Fig. 1**. The concomitant rotation of the single bond could induce the disproportionation of cation which may reduce the voltage of complete oxidation [38, 39]. In this context, we have adopted a donor- π -donor design strategy which propeller-like **TPE** as a π -core connected with star-sharp **TPA** and utilized the redox ability of both **TPE** and **TPA**. The electroactive and photoactive unit in the polymer can be easily oxidized to cation radicals with an obvious color change and quenching fluorescence. Therefore, a kind of dual-switching EC/EFC property, that is the colorless-to-black EC materials with AIE enhanced EFC dual-switching property, can be achieved. The twisted configuration in the polymer may reduce the charge transfer complex (CTC) formation and enhance the visible transparency and fluorescence performance in the neutral state in the meantime [40-44]. Under the oxidation, the structural changes of **TPE** core could result in a wide wavelength absorption and high extinction coefficient

to achieve a black color with high contrast. In addition, the disproportionation of the two oxidation centers arisen from **TPE** π -core could reduce the voltage greatly.

In this work, a new diamine monomer (**Fig. 1**), $N^1, N^{1'}-((1,2\text{-diphenylethene-1,2-diyl})\text{bis}(4,1\text{-phenylene}))\text{bis}(N^1\text{-}(4\text{-methoxyphenyl})\text{benzene-1,4-diamine})$ (**TPE-NH₂**) was designed and synthesized. The polyamides (PAs) and polyimides (PIs) as a kind of high-performance polymers with excellent electroactive, chemical stability and processability were prepared from the monomer and named as PA5a, PA5b and PI5a', PI5b'. In this diamine monomer, the electron-donating methoxy groups are introduced at the para-site of the amino group of **TPA** to reduce the oxidation potential and enhance the electrochemical stability of the result polymers [45-51]. The prepared polymers are expected to exhibit unique colorless-to-black electrochromic and AIE-activity electrofluorescent dual-switching behaviors with an ultra-low voltage, good stability, high optical contrasts and fast switching time. The solubility, thermal properties, electrochemical and EFC properties of these polymers are also described herein.

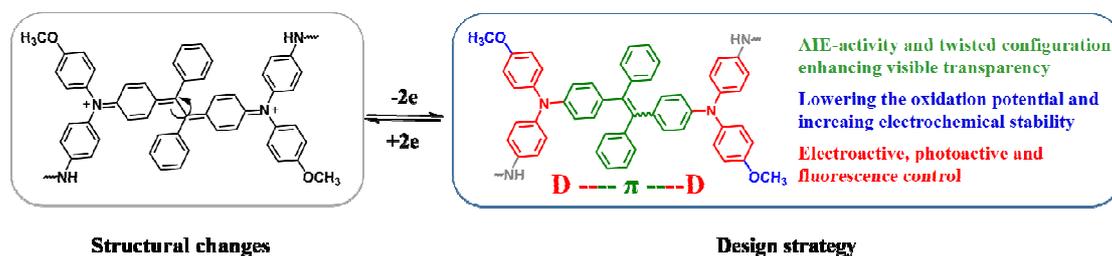


Fig. 1. The design strategy and structural changes.

2. Results and discussion

2.1. Synthesis and characterization of the monomer and the polymers

The synthetic route of the new diamine was shown in Scheme 1. Mass spectroscopic (MS) and nuclear magnetic resonance (NMR) spectrum were used to identify the structures of the compounds. The ^1H NMR spectrum of compound 4 is illustrated in **Fig. S1**. The characteristic resonance signals at 5.6 ppm and 3.72 ppm were belonged to the protons of $-\text{NH}_2$ and $-\text{OCH}_3$, respectively. All of the other signals also could be well assigned to the chemical structure of the monomer. The result of the ^1H NMR spectrum proved the successful synthesis of the target monomer. (The detail of discussion, ^1H NMR and mass spectra was provided in *Supporting Information*.)

All the polymers were prepared via condensation polymerization (as shown in Scheme 1). Fourier transform infrared (FTIR) spectra and NMR spectra were used to characterize the chemical structure of the polymers (**Fig. S3** and **Fig. S4**). The FTIR spectra of PA5a and PA5b exhibited characteristic absorption bands of the amide at around 3311, 1670 cm^{-1} and 3321, 1681 cm^{-1} . The resonance signals at 9.70 and 10.32 ppm in the ^1H NMR spectra also supports the formation of amide linkage in the PAs. The FTIR spectra of PI5a' and PI5b' exhibited characteristic absorption bands of the imide at around 1781, 1720, 1376 cm^{-1} and 1776, 1727, 1371 cm^{-1} . The results of FTIR and NMR spectra proved the synthesis of the polymers. (The detail of FTIR, ^1H NMR spectra was described in *Supporting Information*).

transition temperature from 223 °C to 260 °C (**Fig. S5**). The excellent solubility and thermal stability of the polymers are beneficial to their application for EC/EFC devices.

2.3. Electrochemical Properties

The electrochemical behavior of the as-prepared polymer was investigated by cyclic voltammetry measurements in a three-electrode (The polymer film/ITO substrates were used as the working electrode, Ag/AgNO₃ and platinum wire were used as reference and auxiliary electrodes, 0.1 M TBAP in anhydrous acetonitrile was the supporting electrolyte). All the polymers showed a similar redox feature (**Table. 1**), due to the same electroactive unit which played a major role in the electrochemical properties. The electroactive materials containing a double **TPA** structure usually have two couples of redox peaks [45, 46, 52]. However, all prepared PAs and PIs only showed one reversible peak. As reported, the **TPE** systems undergo oxidation processes will disproportionate one-electron oxidation product to dications, which lead to the virtually degenerated one-electron oxidation product. In addition, the fairly low onset oxidation potentials of the polymers are attributed to the electron-donating methoxy substituent. Compared with PIs, PAs have a little lower redox potentials. The substitution of a strong electron-withdrawing imide structure by an amide group can not only reduce the redox potential, but also improve the redox cycle stability. After 100 cyclic scans, the PAs thin film still maintained good stability with only a 10% decrease in the peak current. However, the PI5a' can not go through 10 cycles and PI5b' can't even withstand two cycles.

Table 1. Electrochemical Properties of Polymers

Polymer	Oxidation ^a (V)			Energy level (eV)	
	E _{onset}	E _{1/2}	E _g ^b (eV)	HOMO ^c	LUMO ^d
PA5a	0.24	0.31	3.08	5.02	1.94
PA5b	0.25	0.30	2.89	5.03	2.14
PI5a'	0.31	0.55	3.14	5.09	1.95
PI5b'	0.33	0.41	2.88	5.11	2.23

a Oxidation potentials since the first time of CV scan. b Calculated from: Energy gap = $1240/\lambda_{\text{onset}}$. c Calculated from the cyclic voltammetry and referenced to ferrocene (4.8 eV; onset = 0.02 V). d LUMO = HOMO - E_g.

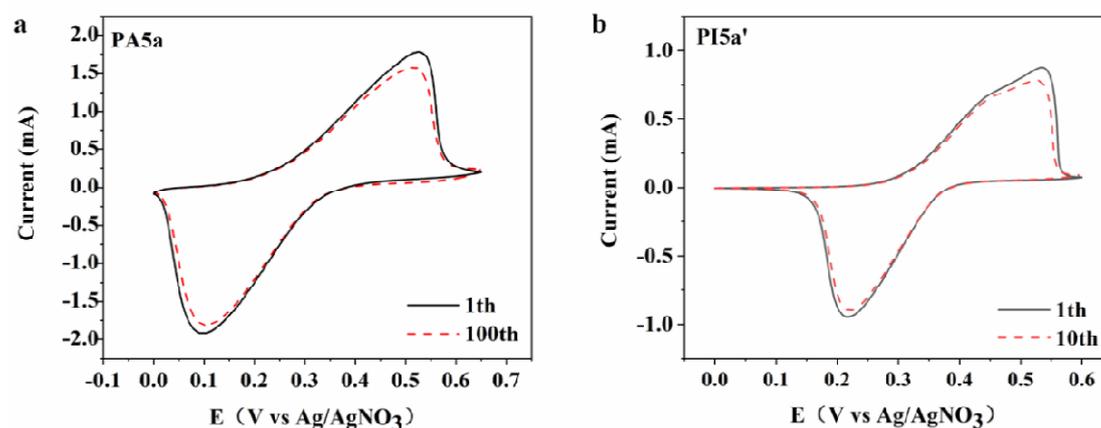


Fig. 2. a) CV diagrams of PA5a from 0.0 to 0.65 V for continuous 100 cycles at a scan rate of 50 mV s^{-1} . b) CV diagrams of PI5a' from 0.0 to 0.6V for continuous 10 cycles at a scan rate of 50 mV s^{-1} .

2.4. Spectro-Electrochemical and Electrochromic Properties.

In the process of CV scanning, the films revealed obvious color changes, thus we researched the EC properties by coupling the electrochemical workstation with UV-vis absorption spectroscopy. The typical EC properties of PA5a at different

applied potentials are depicted in **Fig. 3**. At the neutral state of 0.00 V, the film PA5a exhibited a strong absorption at 314 nm and a slight absorption before 400 nm. This makes the film transparent and almost colorless under naked eyes which could be attributed to the shorter conjugation and the inhibited CTC resulted from the alicyclic twisted non-planar chain structure [19, 20]. Upon gradual oxidation of the polymer film, the absorption at 314 nm gradually decreased due to the π - π^* , while a concomitant enhancement dramatically emerged in the absorption throughout the whole visible region extending up to 1000 nm with two wide absorption bands centered around 460 and 692 nm. This wide-range absorbance in the visible region made the color of the film change from nearly colorless ($L^* = 95$, $a^* = -4$, $b^* = 9$) to truly black ($L^* = 13$, $a^* = 2$, $b^* = 11$). As reported, most of black EC materials need multiple redox centers to achieve broad and intense spectrum absorption and thus a multi-step oxidation process inevitably needs a higher applied voltage. The applied voltage of most EC materials is higher than 1.5 V. Compared with most of EC materials, PAs exhibited ultra-low applied voltage. Among them, the applied voltage of PA5a was as low as 0.75 V, which is the lowest voltage in transmissive-to-black EC materials to best our knowledge [14, 20-25]. Different from these general EC materials, a **TPE** (π -core) connected with two **TPA** (oxidation centers) is the electrochromic active unit, which the disproportion of cation to dications reduces the voltage required to oxidize multiple centers. In addition, the electron-donating methoxy groups also reduce the oxidation potential. As a result, the PAs can change to black color at such a low applied voltage which was a great improvement.

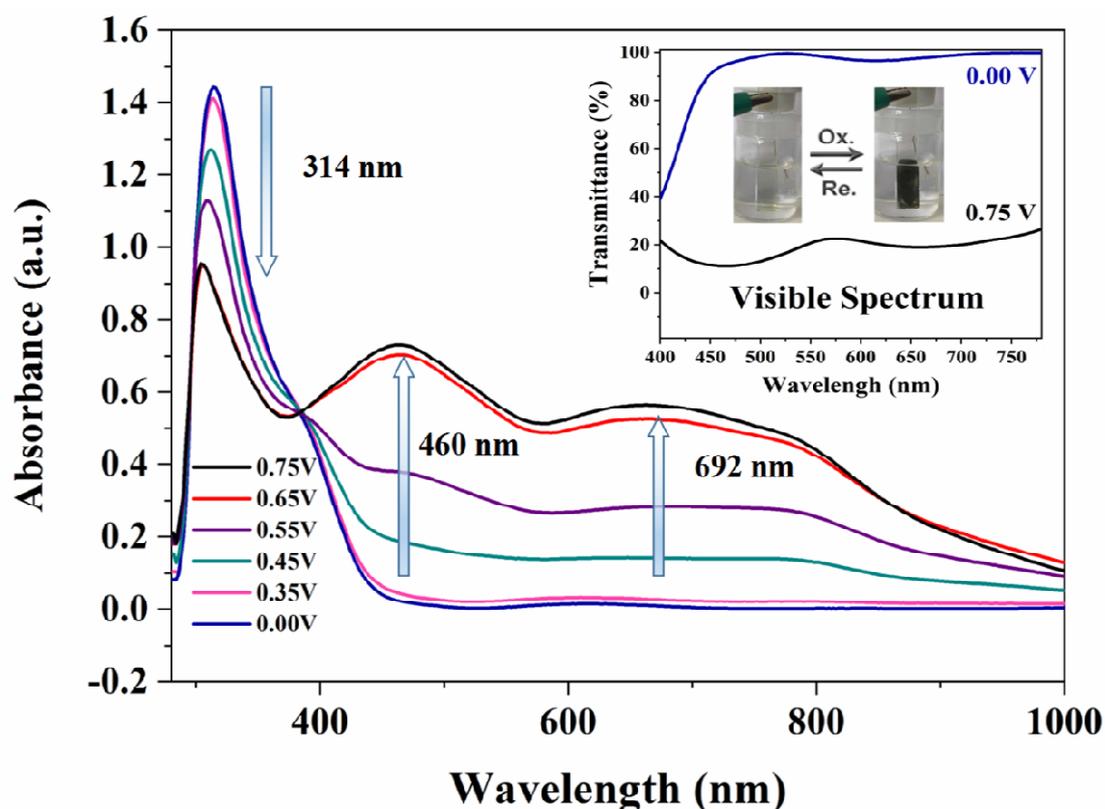


Fig. 3. Absorbance and transmittance spectra of PA5a thin-film on the ITO glass as electrode in 0.1 M $\text{Bu}_4\text{NClO}_4/\text{CH}_3\text{CN}$ at different applied potentials from 0.0 to 0.75 V (vs. Ag/AgNO_3).

Dynamic EC switching behaviors of the polymers was observed by monitoring transmittance at 692 nm when applying step potential between the neutral and the oxidation states. The typical EC behaviors of PA5a are depicted in **Fig. 4**. PA5a showed extremely significant transmittance changes, the integrated contrast ratios ($\Delta\%T$) from 380 to 780 nm was 87.9% which was one of the highest value in literature, that indicated an extremely high optical change and obvious color switching [53]. Moreover, the response time in the 90% transmittance change (colored/blended) was found to be 2.04/1.45 s which is faster than most triphenylamine-based EC

materials. This excellent rapid response speed could be ascribed to that the twisted **TPE** core structure reduced the interchain packing, the looser chain stacking could accelerate the ion transport. The coloration efficiency (CE) of PA5a calculated to be $260 \text{ cm}^2 \text{ C}^{-1}$ at 692 nm. The high CE value means that a small amount of electron injection can bring a huge color change which is favorable to save energy. For practical applications, the long-term stability of EC materials is also the most important parameter. As shown in **Fig. 4a**, PA5a exhibited extremely superior stability. After 200 continuous cycles with a cycling time of 40 s, the stability showed no obvious degradation, because the methoxy group can prevent the intermolecular coupling reaction. Therefore, this new colorless-to-black electrochromic material has great application potential in the display field due to its ultra-low voltage, high contrast, fast switching time, high CE value and good stability.

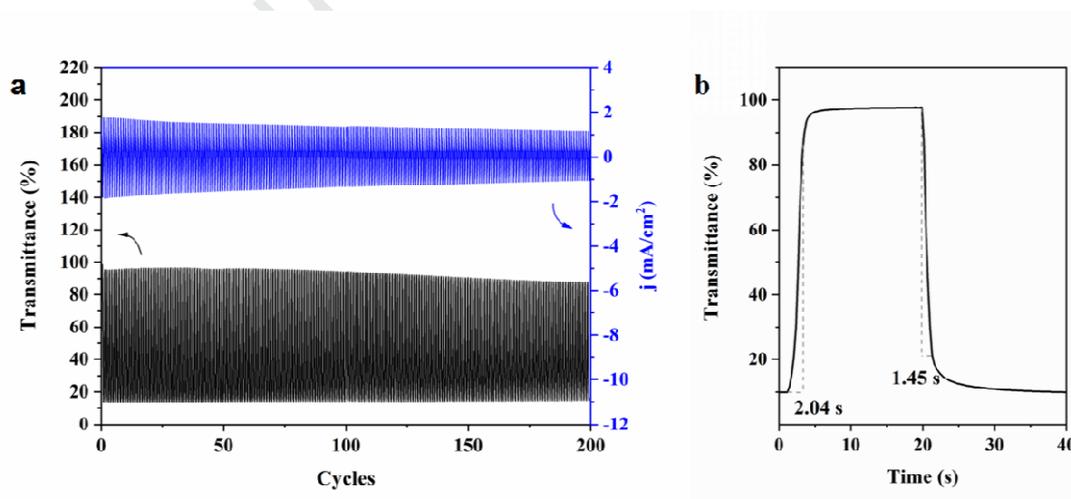


Fig. 4. a) EC switching of PA5a thin film electrode for continuous 200 cycles at the monitored wavelength of 692 nm : transmittance changes (left axis) and electrical current response (right axis). b) Optical switching time at 692 nm.

2.5. Fluorescence and EFC Properties.

All the polymers exhibited fluorescence and AIE properties (**Table. 2**). The fluorescence of compound PA5a and PI5a' was significantly stronger than compound PA5b and PI5b', because the aliphatic structure reduced the CT effect on PA5a and PI5a'. In addition, PIs exhibited a slightly weaker fluorescence than PAs, due to the electron-withdrawing imide structure connected with methoxy para-substituted **TPA**. The donor-acceptor structure enhances the intermolecular CT interaction and weakens the fluorescence of the PIs [54].

Table. 2. Optical Properties of Polymers

Polymer	Solution ^a (nm)			Film (nm)			
	Abs. _{max}	PL _{max} ^b	Φ_F^c (%)	Abs. _{onset}	Abs. _{max}	PL _{max}	Φ_F^c (%)
PA5a	315	545	1.5	440	330	512	14.0
PA5b	300,355	420	0.7	450	320,360	551	2.6
PI5a'	310	530	1.4	430	305	517	10.4
PI5b'	310	418	0.4	450	315	556	1.4

a The polymer concentration was 10^{-5} M in NMP. b They were excited at the Abs._{max} for the solution states. c The quantum yield was tested by using a calibrated integrating sphere.

The introduction of the **TPE** structure endows the polymers with the AIE properties. To further investigate the AIE, we tested the fluorescence of PA5a in the mixed solvent of NMP and water. As shown in **Fig. 5a**, with the increasing proportion of water from 20% to 90% in the mixed solvent, the fluorescence intensity of the PA5a solution enhanced gradually. This reason for the phenomenon is the case that the

TPE structure restricted the intramolecular rotation effect and induced the aggregation of the polymers. Moreover, the twisted structure formed by star-sharp **TPA** with propeller-like **TPE** efficiently hinders the intermolecular π - π stacking interactions that also promoted the enhancement of fluorescence.

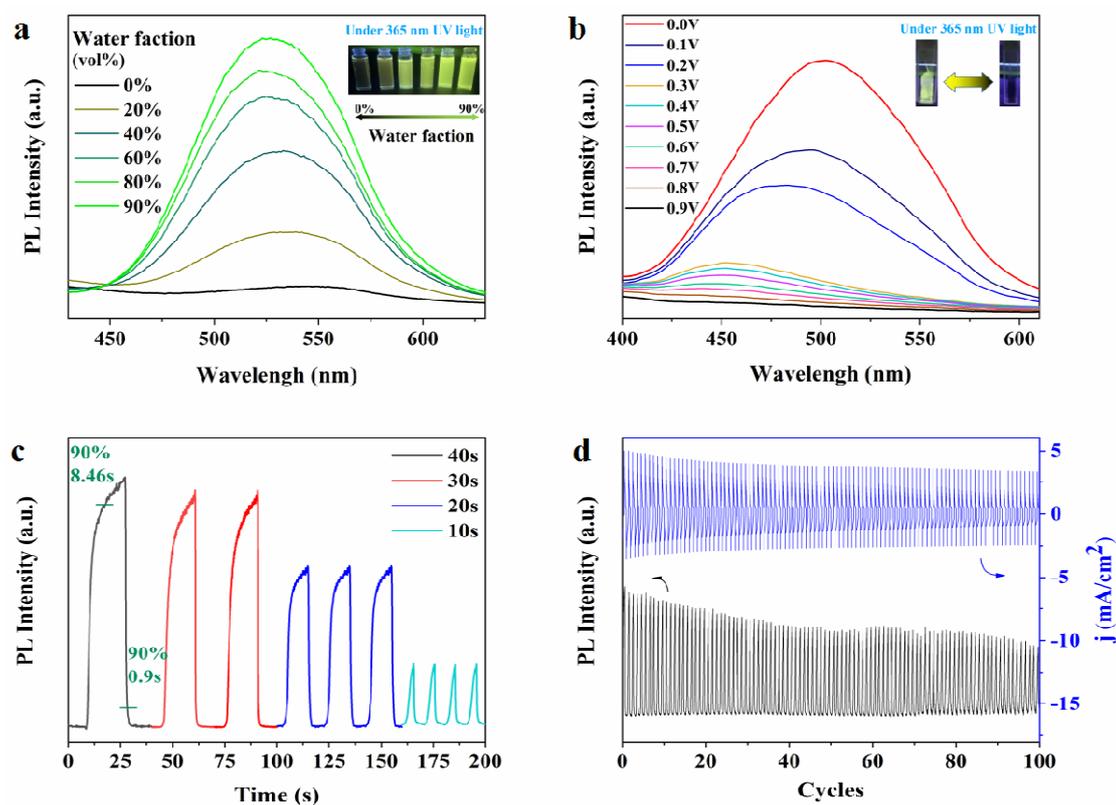


Fig. 5. a) PL spectra based on PA5a in different water/NMP fraction. (Solution concentration: 10^{-5} M). b) PL spectral changes of PA5a thin film electrode at different applied potentials from 0.0 to 0.9 V (vs. Ag/AgNO₃) under excitation at 330 nm. c) EFC switching of PA5a thin film electrode at different step cycle times of 40, 30, 20, and 10 s and the switching time of PA5a at 40 s. d) EC switching of PA5a thin film electrode for continuous 100 cycles at the monitored wavelength of 512 nm.

Considering the high fluorescence intensity and redox stability, the PA5a is expected to show acceptable EFC properties. EFC properties of PA5a were measured

by monitoring the fluorescence emission changes in different voltage at 512 nm. As shown in **Fig. 5b**, as the voltage gradually increased, the emission became weaker and finally quenched. In addition, when a reverse potential was applied, the fluorescence could be recovered. The response time of fluorescence estimated at 90% of the full switching process was 8.46/0.9 s, the very short quenching time indicated that **TPA**⁺ has a significant quenching effect on fluorescence. Moreover, the PL contrast ratio was decreased gradually with decreasing switching cyclic time from 40 to 10 s (**Fig. 5c**), which indicates that the degree of redox is related to during time. If the duration time is too short, the redox can not be completed. Furthermore, long-term stability and reversibility of PA5a were also investigated. As shown in **Fig. 5d**, after 100 cycles, PA5a still showed good stability, even though it was significantly lower than the property of electrochromism. This phenomenon may attribute to the inevitable charge trapping which was induced by disproportionation and through-bond magnetic interaction from **TPE** during the redox process [38, 39]. These trapped charges effect on the quenching of fluorescence is much greater than the absorption of spectroscopy.

2.6. Conclusion

In this work, the electro-/AIE-active polymers were synthesized from a new designed diamine monomer containing **TPA** and **TPE** structure. The electroactive and photoactive structure of π -core **TPE** connected with two **TPA** effectively ensured the wide wavelength absorption, low applied voltage and high solid-state fluorescence for the polymers. The PA5a not only showed rare colorless-to-black EC properties with

ultra-low voltage (from 0 to 0.75 V), extremely high optical contrast (up to 87.9%) and fast switching time (2.04/1.45 s), but also demonstrated AIE-activity EFC properties. This color/emission dual-switchable material also exhibited good switching stability (200/100 cycles for EC/EFC properties). Thus, this work supplies a new design strategy for developing colorless-to-black EC and AIE-activity EFC dual-switching materials.

3. Experimental section

3.1. Materials

4-bromobenzophenone, p-Anisidine, 4-fluoronitrobenzene, TiCl_4 , trimethylamine, 80% hydrazine monohydrate, 10% palladium on charcoal (Pd/C), Tri-tert-butyl phosphine (TPP, 1.0 M) were all purchased from Aladdin. Zinc (Zn), potassium carbonate (K_2CO_3) were from TCI. 1,4-cyclohexanedicarboxylic acid (CHDA), terephthalic acid (PTA), 1,2,4,5-Benzene tetracarboxylic dianhydride (PMDA) and 1,2,4,5-Cyclohexanetetracarboxylic dianhydride (HPMDA) were all from Aladdin and dried before used. Dimethyl sulfoxide (DMSO), N-methyl-2-pyrrolidinone (NMP), o-dichlorobenzene and pyridine (Py) were treated using 4 Å molecular sieves before using. All other chemicals were directly used as received from commercial sources.

3.2. Synthesis of 4-Methoxy-4'-nitrodiphenylamine (1)

Compound 1 was obtained following a reported method in our previous work. ^1H NMR (300 MHz, DMSO- d_6 , δ , ppm): 9.1(s, 1H), 8.05 (d, J= 6 Hz, 2H) 7.18 (d, J= 7.5

Hz, 2H), 6.98 (d, J= 9.0 Hz, 2H), 6.88 (d, J= 9.0 Hz, 2H), 3.76 (s, 3H).

3.3. Synthesis of 1,2-bis (4-bromophenyl)-1,2-diphenylethene (2)

Compound 2 through the McMurry reaction. An ice-cooled (-5°C) suspension of zinc powder (10.0 g, 152.91 mmol) in anhydrous THF (450 ml) was prepared in a three-neck flask, under argon atmosphere and TiCl₄ (14.4 g, 75.92 mmol) was added slowly to the suspension with a syringe. After refluxing the resulting mixture for 3 h, the mixture was cooled to room temperature and added a solution of 4-bromobenzophenone (20.00 g, 76.60 mmol) in THF (50 ml). After refluxing for 12h, the mixture was cooled to room temperature, quenched with 10% K₂CO₃ aqueous solution until no bubble come out. The resulting mixture was filtered and extracted with chloroform for three times. Then the combined organic layer was dried over sodium sulphate and the solvent was evaporated, dried under reduced pressure. The resulting white crude product was purified by chromatography (mixture of Z/E isomers). Compound 2 was obtained as white powder (11.1g, yield= 55.5 %). ¹H NMR (300 MHz, CDCl₃ δ, ppm): 7.25 (m, 4H), 7.13 (m, 4H), 6.98 (m, 4H), 6.87 (m, 4H).

3.4. Synthesis of 4,4'-(1,2-diphenylethene-1,2-diyl)bis(N-(4-methoxyphenyl)-N-(4-nitrophenyl)aniline) (3)

Compound 1 (6.22 g, 25.5 mmol), compound 2 (5.0 g, 10.2 mmol), KOtBu (2.855 g, 25.5 mmol), Pd(OAc)₂ (0.255 g, 1.13 mmol), 0.1M TPP (7 g, 3.42 mmol)

and toluene (250 ml) were added in a 500 ml two neck flask. The reaction mixture was refluxed for 24 h under nitrogen atmosphere. After cooling to room temperature, the solution was filtered and poured into petroleum ether. The resulting mixture was filtered and dried. Then the orange crude product was purified by chromatography. Compound 3 was obtained as orange powder (5.16 g, yield= 62 %). ^1H NMR (300 MHz, DMSO- d_6 , δ ppm), 8.05 (d, $J= 9.0\text{Hz}$, 2H), 7.92 (d, $J= 9.0\text{Hz}$, 2H), 7.09 (Br, 26H), 6.65 (dd, $J= 8.6\text{Hz}$, 4H), 3.75 (m, 6H, -OCH₃). MS (ESI) m/z calculated. For (C₅₂H₄₀N₄O₆): 816.2948, found: 816.4382.

3.5. Synthesis of $N^1, N^{1'}-((1,2\text{-diphenylethene-1,2-diyl})\text{bis}(4,1\text{-phenylene}))\text{bis}(N^1-(4\text{-methoxyphenyl})\text{benzene-1,4-diamine})$ (4)

Compound 3 (5 g, 6.1 mmol), Pd/C (0.34 g) and 1,4-dioxane (70 ml) were added in a 250 ml two neck flask. After heating the mixture to reflux, added 80% hydrazine monohydrate slowly. The reaction mixture was refluxed for 10 h under nitrogen atmosphere. Then filtrated and poured the filtrate into water. Collected the crude product and purified by chromatography. Compound 4 was obtained as orange-brown powder (4.0 g, yield= 80 %). ^1H NMR (300 MHz, DMSO- d_6 , δ ppm), 7.08 (m, 6H), 6.96 (ddd, 8H), 6.83 (m, 8H), 6.70 (d, $J=9.0\text{Hz}$, 4H), 6.52 (m, 8H), 5.6 (s, 4H, -NH₂), 3.72 (m, 6H, -OCH₃). MS (ESI) m/z calculated. For (C₅₂H₄₄N₄O₂): 756.3464, found: 756.3477.

3.6. Synthesis of polyamides (PA 5)

The newly synthesized diamine (compound 4, 1 mmol), dicarboxylic acid (CHDA/PTA, 1 mmol), TPP (1 ml), Py (1 ml), CaCl₂ (0.3 g) and NMP (2.5 ml) were added in a 25 ml two neck flask. Heated for 3h at 120 °C and cooled. The solution was poured into ethyl alcohol. The resultant polyamide solid was collected by filtration and washed with lots of ethyl alcohol and hot water. We named the two polyamides as PA5a (CHDA) and PA5b (PTA).

PA5a: FTIR (KBr), 3311, 1670 cm⁻¹ (amide group). ¹H NMR (300 MHz, DMSO-d₆, δ ppm). 9.70 (s, 2H), 7.50 (s, 6H), 6.45-7.3 (Br, 28H), 3.54 (s, 6H, -OCH₃), 1.2-2.1 (Br, 10H). Number averaged moalr mass (Mn): 66925. Weight averaged moalr mass (Mw): 104849.

PA5b: FTIR (KBr), 3321 and 1681 cm⁻¹ (amide group). ¹H NMR (300 MHz, DMSO-d₆, δ ppm), 10.32 (s, 2H), 8.01(s,3H), 7.73(s, 4H), 6.45-7.2(Br, 31H), 3.72 (s, 6H, -OCH₃). Mn: 69230. Mw: 97575.

3.7. Synthesis of polyamides (PI 5)

The newly synthesized diamine (compound 4, 1 mmol), anhydride (HPMDA/PMDA, 1 mmol), DMAc (10 ml) were added in a 25 ml two neck flask. The reaction mixture was stired at 20□ over night under nitrogen atmosphere. Added Py (2 ml) and acetic anhydride (4 ml) into the solution. Then reaction mixture was heated for 3h at 100°C and cooled. The resultant polyimide solid was collected by filtration and washed with lots of ethyl alcohol and hot water. We named the two polyamides as PI5a' (HPMDA) and PI5b' (PMDA).

PI5a': FTIR (KBr), 1781, 1720 and 1376 cm^{-1} (amide group). ^1H NMR (300 MHz, DMSO- d_6 , δ ppm), 7.5-6.6 (Br, 40H), 3.71 (s, 6H, $-\text{OCH}_3$), 1.92 (d, $J=8.71\text{Hz}$, 2H). Mn: 11899. Mw: 12393.

PI5b': FTIR (KBr), 1776, 1727 and 1371 cm^{-1} (amide group). ^1H NMR (300 MHz, DMSO- d_6 , δ ppm), 7.2-6.2 (Br, 32H), 3.66 (s, 6H, $-\text{OCH}_3$), 3.15 (s, 4H). Mn: 21918. Mw: 29487.

3.8. Measurements

Nuclear magnetic resonance (NMR) spectra were recorded on a BRUKER-300 using deuterated DMSO as the solvent. Mass spectra were recorded on a MALDI-TOF-ESI. Fourier transform infrared (FTIR) spectra were recorded on a Bruker Vector 22 spectrometer. The glass-transition temperature (T_g) of the polymers was measured by using differential scanning calorimetry (DSC) on a METTLER 821e. Thermogravimetric analysis (TGA) was carried out in the temperature range of 100–750 $^\circ\text{C}$ on a Pyris 1 TGA under a flow of nitrogen. Electrochemistry data were acquired with an electrochemical analyzer (CHI 660e) using a three-electrode cell in 0.1 M tetrabutylammonium perchlorate (TBAP) with dried CH_3CN as the supporting electrolyte. The working electrode was the polymer film coated on an ITO glass substrate by drop-coating 50 mg/mL polymer solutions in NMP, and the resulting area of the polymer film was about 1.5 cm^2 . The auxiliary and reference electrodes were platinum wire and Ag/AgNO_3 electrodes, respectively. The UV-vis spectra were recorded with a Shimadzu UV 3101-PC spectrophotometer. Photoluminescence (PL)

spectra and fluorescence quantum yield (by using a calibrated integrating sphere) were acquired with Edinburgh FLS920 fluorescence spectrophotometer. The number and weight averaged molar mass of the polymers were measured by using high temperature gel permeation chromatograph (PL-GPC-220).

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Supporting Information

TableS1. Solubility behaviors of polymers

Polymer	Solvent ^a					
	NMP	DMAc	DMF	DMSO	THF	CHCl ₃
PA5a	++	++	++	+	+ -	+ -
PA5b	++	++	++	+	+ -	+ -
PI5a'	+ -	+ -	+ -	+ -	+ -	+ -
PI5b'	+ -	+ -	+ -	+ -	- -	+ -

a Solubility: ++, soluble at room temperature; +, soluble on heating; +-, partially soluble or swelling; -, insoluble even on heating. The solubility was determined by adding 10 mg sample in 1 mL solvent.

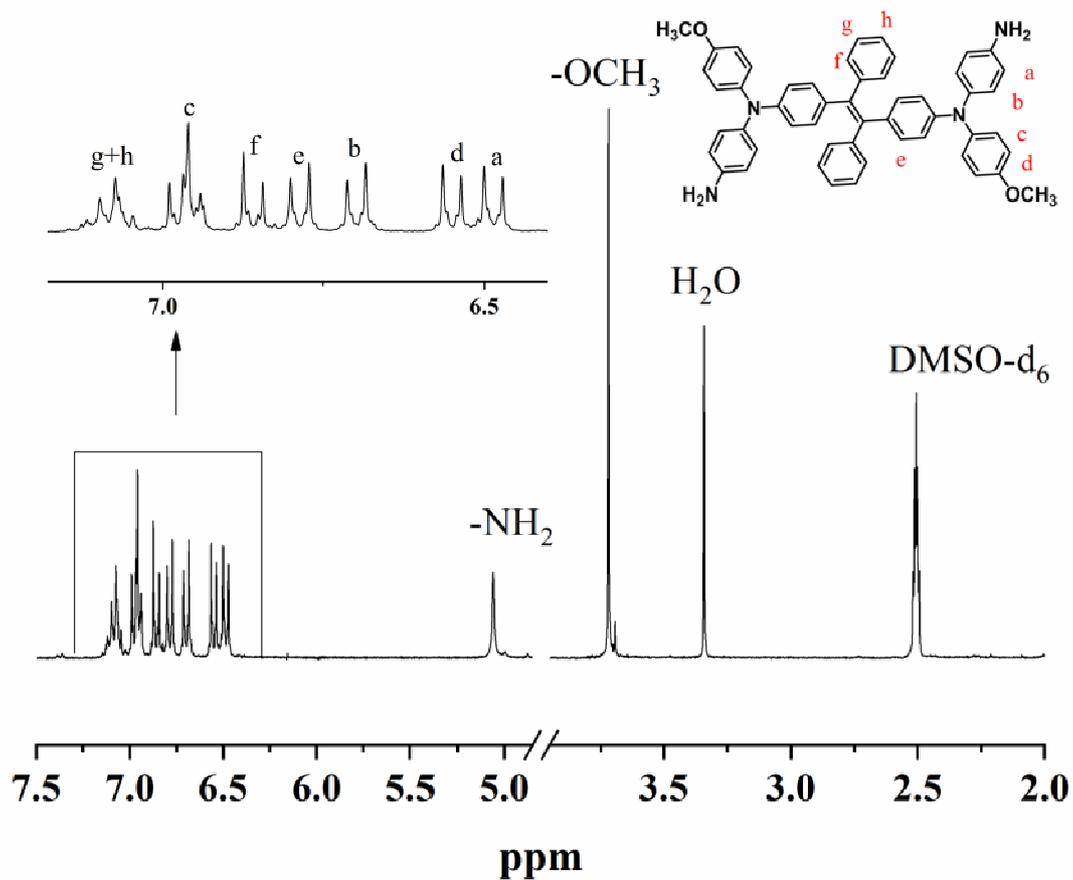


Fig. S1 ^1H NMR spectrum of diamine monomer 4.

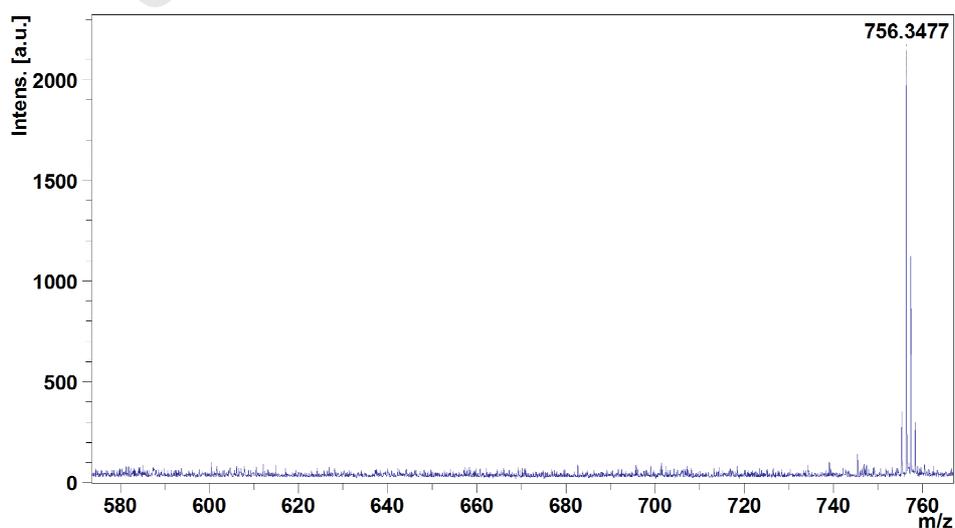


Fig. S2 Mass spectrum of diamine monomer 4.

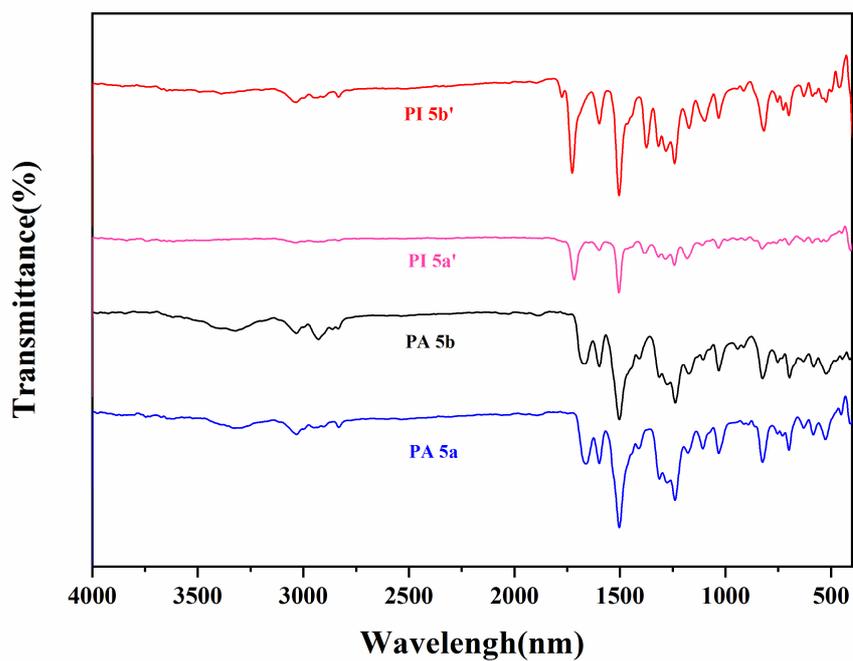
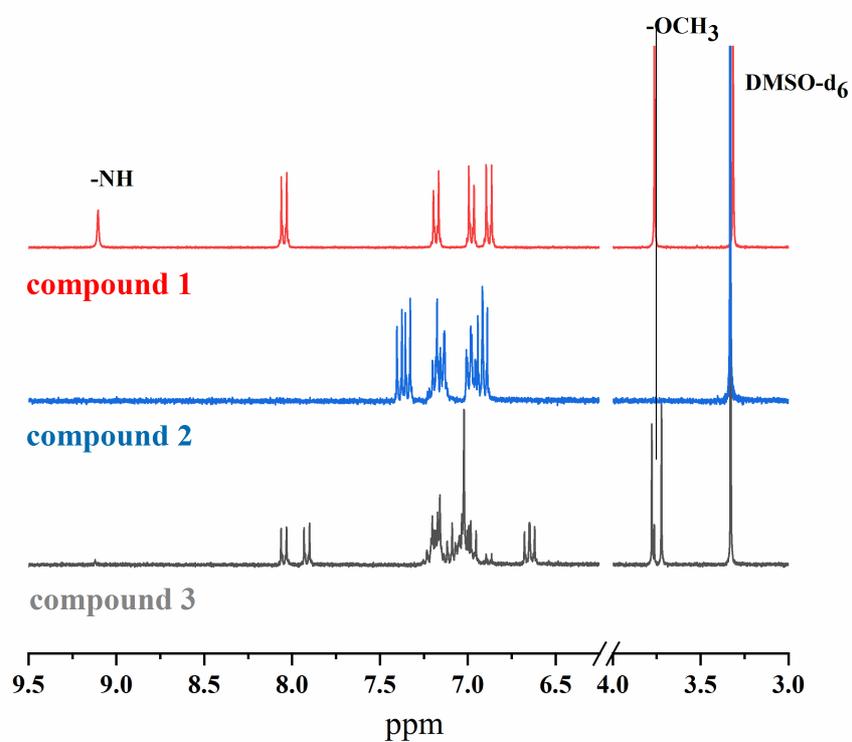


Fig.S3 FTIR spectra of polymers.



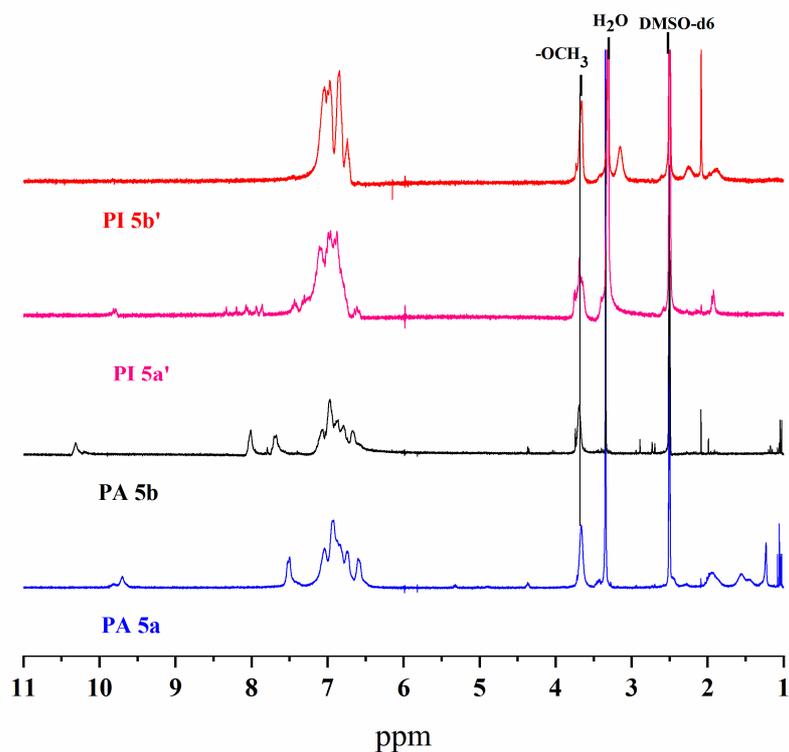


Fig.S4 ^1H NMR spectra of compounds and polymers.

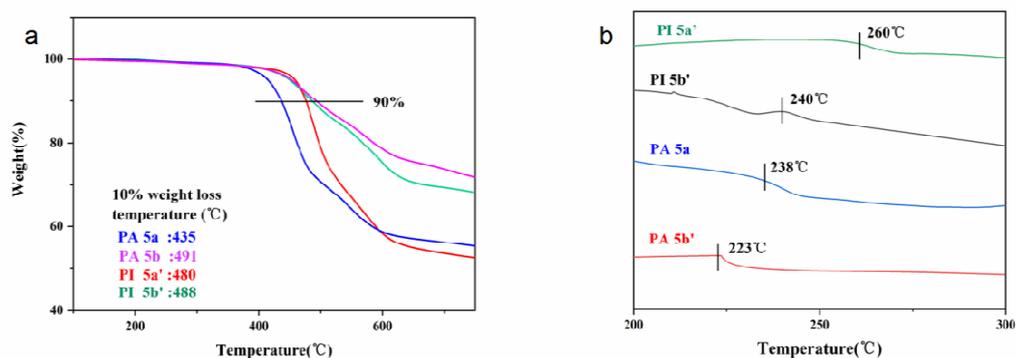


Fig.S5 Thermal properties of the polymers a) TGA and b) DSC measurements.

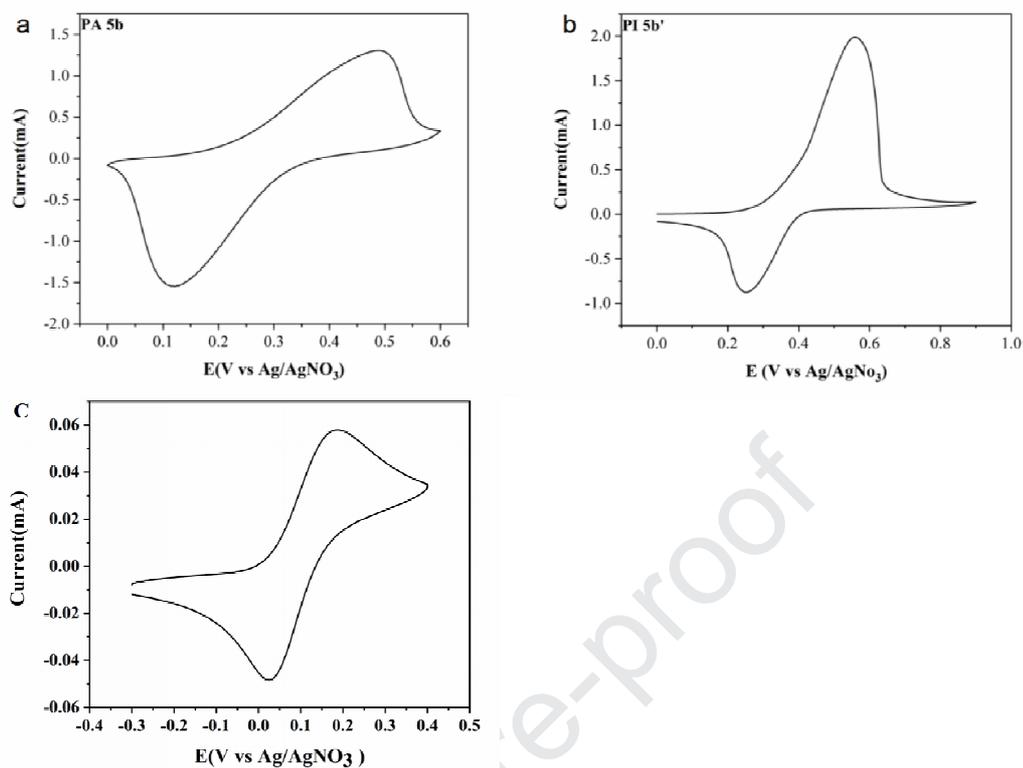


Fig.S6 CV diagrams of a) PA5b from 0.0 to 0.6 V b) PI5b' from 0.0 to 0.9V c) ferrocene from 0.0 to 0.4V at a scan rate of 50 mV s⁻¹.

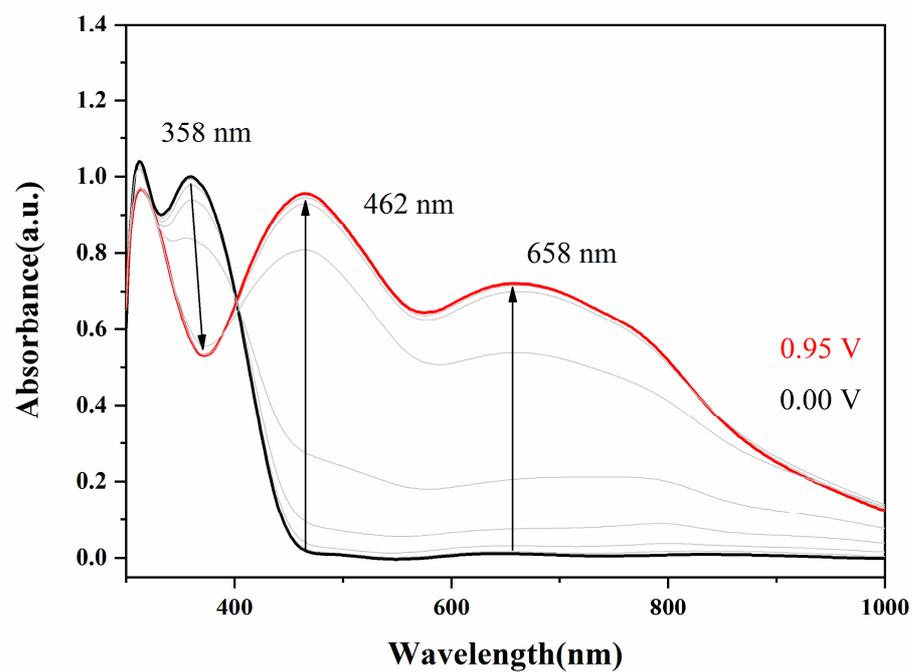


Fig.S8 Absorbance spectra of PA5b thin-film on the ITO glass as electrode in 0.1 M $\text{Bu}_4\text{NClO}_4/\text{CH}_3\text{CN}$ at different applied potentials from 0.0 to 0.95V (vs. Ag/AgNO_3).

Highlights

- Adopted a novel design strategy to use tetraphenylethene as π -core connects with two oxidation centers.
- Four kinds of novel D- π -D Polymers (PA5a, PA5b, PI5a', PI5b') were synthesized with multiple-response optoelectronic properties.
- PA5a not only showed rare colorless-to-black EC properties with lowest applied voltage (0-0.75V), high optical contrast (87.9%) and fast switching time (2.04/1.45 s), but also demonstrated AIE-activity EFC properties with good switching stability (200/100 cycles).

Declaration of interests

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.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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