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Introduction

Electrochromism refers to the reversible changes in the optical properties of a material upon being electrochemically oxidized or reduced.^{1,2} Electrochromic (EC) materials have attracted significant attention and have been studied extensively. For example, the conducting polymers used as EC materials offer various advantages including rapid color switching, excellent stability, high coloration efficiency, ease of large-scale production, and the ability to fine-tune colors through chemical modifications.^{3–9} Triphenylamine (TPA)-containing polymers were also developed as EC materials with the advantages of a colorless neutral state, good EC behaviors, and easy processing. As a result, they have received considerable attention and

Concept of triphenylamine side chains with four electroactive nitrogen centers toward record-high stable electrochromic polyamides*

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Addressing the challenge of long-term electrochromic stability for polymer-based materials is the fundamental key to practical application. To date, numerous examples of electrochromic triarylaminebased polymers have been reported. However, the structure-electrochromic stability relationships are still poorly understood and mostly unexplored. Herein, the side-chain engineering concept of multiple electroactive nitrogen atoms by designing a new triphenylamine-based diamine monomer (4) is successfully incorporated into a series of novel polyamides (PAs) (5) and demonstrated the remarkable enhancement in electrochromic stability. Compared to all other triarylamine-based polymers reported to date, the studied polymer, 5a, presents the highest electrochromic stability of only 8.8% and 9.9% decay of its coloration efficiency (CE) at 1404 nm and 440 nm after 24000 and 20000 switching cycles at the first oxidation stage, respectively, as well as multiple color changes, and a high contrast of the optical transmittance change. The record-high electrochromic stability of 5a could be ascribed to the capability of the stabilizing polaron, originating from a charge of the cation radical dispersed by resonance in between the different redox states and evidenced clearly by the more extended wavelength absorption in the near-infrared (NIR) region. Our described concept confirms that the key to determining the electrochromic stability of the materials is the resonance by the electrons delocalized over all the redox centers rather than the electronic coupling between the different redox centers.

become necessary organic electrochromic materials.^{10–21} In the past few years, developing EC materials capable of operating in the NIR range has been a particular focus owing to the significant attention to their potential applications in optical communication, data storage, and thermal control in buildings and spacecraft.^{22–24} For example, Wan has explored that EC materials with quinone moieties exhibit strong NIR absorption during electrochemical reduction.²⁵ Reynold reported that the conjugated polymers exhibited multicolor properties in the neutral state and transmission in the oxidized state.^{26,27} Liou also reported that TPA-based polymers presented an interesting anodic electrochromic system for NIR applications due to their particular intramolecular electron transfer in the oxidized states.¹¹

In 1967, Robin and Days classified mixed-valence (MV) compounds containing two or more oxidation centers into three categories. The N, N, N', N'-tetraphenyl-*p*-phenylenediamine (TPPA) cation radical has been reported as a symmetrical delocalized class III structure with an intensive electronic coupling (the electron could be delocalized over the two redox centers).²⁸ Nelson and Adam *et al.* demonstrated that the unsubstituted TPA moieties undergo dimerization to tetraphenylbenzidine after the formation of the cation radical.^{29,30} When electron-donating

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substituents incorporated the phenyl groups at the *para*-position of TPA, the dimerization could be effectively prevented, affording stable cationic radicals.^{31,32} Although the reason for the influence of the substituents on the EC stability of materials has been reported, the critical mystery of interconnection between the chemical structure and electrochemical stability for TPA-based polymers is still doubtful.

In developing EC materials, several critical factors are considered, including the electrochemical stability, high coloration efficiency, rapid switching speed, and a significant change in optical transmittance during operation. It is worth emphasizing that the EC stability is crucial for any purpose.³³ Although TPA-based EC materials have been developed for decades, most suffer terribly with electrochemical reversibility. For example, most TPA-based polymers revealed that their electroactivity was retained at 90% after only 2000 switching cycles.¹²⁻¹⁹ However, TPA-based polymers derived from only two specific diamines have demonstrated significantly better electrochromic stability, with their electroactivity decaying by less than 10% even after 10000 switching cycles.^{10,11} Consequently, achieving high EC stability of the triarylamine-based polymers remains a challenge, and research in the future is required to address this issue effectively.

This research aims to develop organo-soluble polyamides (PAs) with high electrochemical stability, fast switching speed, high CE, and multiple coloring changes. The stability of EC materials is a crucial factor for their practical application; thus, this study provides strategies, including introducing multiple electroactive nitrogen centers and electron-donating methoxy substituents, to enhance the electrochemical stability of the resulting PAs. Consequently, we focused on specifically designed TPA-based PAs containing para-substituted methoxy and four electroactive nitrogen centers to investigate the physical properties, such as thermal stability, electrochemical stability, and spectroelectrochemical behaviors, and elucidate the effects of substituents and the number of electroactive nitrogen centers on the electrochemical stability of the PAs. We also aim to obtain fundamental information on the relationships between the cation radical stability and the EC stability of PAs in this work for comparing some EC behaviors with previous studies reporting on the TPA-based polymers of **P1** and **P2**.^{11,34} Their chemical structures are presented in Scheme 1.

Results and discussion

Monomer synthesis

Four steps were employed to synthesize the new diamine 4 from N-(4-aminophenyl)-N'-(4-nitrophenyl)-1,4-phenylenediamine, as shown in Scheme 1a. The C-N coupling reaction was performed between N-(4-aminophenyl)-N'-(4-nitrophenyl)-1,4-phenylenediamine and 4-iodoanisole in the presence of copper to afford compound 1. Then, 1 was hydrogenated to generate compound 2. An aromatic nucleophilic substitution reaction of 2 with 4-fluoro-nitrobenzene was applied in DMSO in the presence of cesium fluoride as a catalyst, generating the dinitro compound 3, which was hydrogenated to yield the new diamine 4. FTIR and NMR spectroscopic techniques were used to identify the structures of the intermediate compounds (1, 2, and 3) and the target diamine monomer 4. The FTIR spectra of the synthesized compounds are depicted in ESI[†] Fig. S1 and S2. Compound 3 exhibited two characteristic bands at around 1579 cm⁻¹ and 1309 cm⁻¹ due to nitro asymmetric and symmetric stretching, respectively. After reduction to the diamine monomer 4, the characteristic absorption bands of the nitro group disappeared and revealed the primary amino characteristic bands at 3446 cm^{-1} and 3365 cm⁻¹ (N-H stretching). ¹H and ¹³C NMR spectra of compounds 1, 2, and 4 are illustrated in Fig. 1a and Fig. S3-S5 (ESI[†]), and agree well with the proposed molecular structures. The signal appearing at 4.93 ppm is particular to the amino group of monomer 4 (Fig. 1a). ESIMS data of compounds 1, 2, and 4 are also provided in Fig. S6-S8 (ESI⁺). NMR, IR, and ESIMS spectra were used to confirm all compounds reported herein.

Polymer synthesis

According to the phosphorylation method described by Yamazaki,^{35,36} a series of new PAs **5a–5c** were synthesized from the diamine monomer **4** with aromatic dicarboxylic acids



Scheme 1 (a) Synthesis of compounds 1, 2, 3, and 4. (b) Synthesis of PAs 5a-5c and illustration of (c) P1 and P2.



Fig. 1 (a) ¹H of monomer **4** and (b) polymer **5a**. (d-solvent: pyridine- d_5)

(Scheme 1b). All polymerization reactions proceeded homogeneously and yielded inherent viscosities of the obtained PAs 5 in the range of 0.32–0.45 dL g^{-1} (Table S1, ESI[†]). All of the polymers could produce transparent and flexible films *via* solution casting. The thickness and surface morphology of the thin films were measured and are depicted in Fig. S9 (ESI[†]). IR and ¹H NMR spectroscopy confirmed the formation of PAs. A typical IR spectrum of **5b** exhibited characteristic absorption bands of the amide group at around 3311 cm⁻¹ (N–H stretch) and 1662 cm⁻¹ (amide carbonyl) (Fig. S2, ESI[†]). Additionally, the NMR spectrum confirmed the chemical structures of **5a–5c**, and the assignment of the proton peaks is shown in Fig. 1b and Fig. S10 and S11 (ESI[†]).

Solubility and thermal property

The solubility of PAs was tested in various solvents, and the results are summarized in Table S1 (ESI[†]). The PAs 5 series revealed good solubility in the tested solvents, and were soluble in *N*-methyl-2-pyrrolidone (NMP) and *N*,*N*-dimethylacetamide (DMAc), which can be attributed to the bulky long side chains, leading to a decrease in intermolecular forces and packing ability of the resulting polymers. The resulting solubility makes these PAs a potential candidate for practical applications through spin-coating or inkjet-printing processes to produce thin films for optoelectronic devices.

Thermal analysis was measured by DSC and TGA, and the thermal properties are listed in Table S2 (ESI[†]). Dynamic thermogravimetry demonstrated the relatively good thermal stability of the PAs. Typical TGA curves of representative polymers in both air and nitrogen atmospheres are summarized in Fig. S12 (ESI[†]). All PAs 5 exhibited good thermal stability with an insignificant weight loss of up to 400 °C. Their 10% weight-loss temperatures in nitrogen and air were recorded at 421–425 °C and 464–470 °C, respectively. In DSC measurements (as shown in Fig. S13, ESI[†]), all PAs 5 revealed distinct baseline shifts on their heating traces. Glass transition temperatures (T_g) , defined as the temperature at the midpoint of the baseline shift, for all PAs were high T_gs (>178 °C). The lowest T_g value (178 °C, measured by DSC) belongs to 5a, which has the flexible ether linkage in its diacid component.

Electrochemical properties

The electrochemical behaviors of the PAs 5 were investigated using cyclic voltammetry (CV) measurements, with the polymer film on an ITO as the working electrode and 0.1 M tetrabutylammonium perchlorate (TBAP) in anhydrous acetonitrile (MeCN) as the supporting electrolyte. The typical CV diagrams of PA 5a exhibit four quasi-reversible redox couples, corresponding to the successive removal of electrons from four different nitrogen centers (Fig. 2a). The electrochemical properties of polymers 5 are summarized in Table 1. During the electrochemical oxidation of the PAs 5, the color of the polymer film changed from colorless to yellow, dark green, blue-green, and blue. The first electron removal occurred at the electroactive nitrogen center attached to the one p-methoxyphenyl group due to the highest electron density among the three nitrogen atoms (Fig. 3b). As shown in Fig. 2b, the CV scans from -0.20 to 0.58 V reveal a highly stable redox process over



Fig. 2 (a) Cycle voltammetric diagrams of **5a** at a scan rate of 0.05 V s⁻¹. (b) Cyclic stability and (c) absorption reversibility of **5a** after different cycles of CV scanning. (d) Nyquist plots of electrochemical impedance spectroscopy of **5a** at the 1st cycle measurement and after 25000 cycles measurements. The measurements were conducted with **5a** thin film (thickness = 160 ± 10 nm) coated on an ITO glass substrate with 0.8 × 2.5 cm² active area. 0.1 M TBAP in MeCN as supporting electrolyte.

Table 1 Optical and electrochemical properties of PAs

	Solution/film (nm)				E _{1/2} ^c					
Polymer	$\lambda_{\max}{}^a$	$\lambda_{\text{onset}}^{a}$	$E_{\rm g}^{\ b}$	E_0	First	Second	Third	Fourth	$HOMO^d$	LUMO ^e
5a	339 (340)	416 (420)	2.95	0.27	0.43	0.62	0.90	1.1	4.79	1.84
5b	322 (322)	417 (426)	2.91	0.29	0.44	0.64	0.97	1.08	4.80	1.89
5 c	322 (326)	423 (423)	2.93	0.28	0.43	0.64	0.96	1.09	4.79	1.86

^{*a*} UV/vis absorption measurement in NMP (1×10^{-5} M) at room temperature, values in parentheses are the polymer film state. ^{*b*} The data were calculated from polymer films by the equation: $E_g = 1240/\lambda_{onset}$ (energy gap between HOMO and LUMO). ^{*c*} From cyclic voltammograms *versus* Ag/ AgCl in MeCN. $E_{1/2}$: average potential of the redox couple peaks. ^{*d*} The HOMO energy levels were calculated from cyclic voltammetry, and were referenced to ferrocene (4.8 eV; $E_{1/2} = 0.44$ V). ^{*c*} LUMO = HOMO – gap.

25 000 cycles, with only a slight decrease in the peak current. After different cycles of CV scans, an absorption spectrum at the neutral state was investigated to evaluate the decay of the **5a** thin film. The reversibility was also calculated by dividing the remaining absorbance after CV scans by the initial absorbance. As depicted in Fig. 2c, an outstanding reversibility of 94.2% was confirmed over 25 000 cycles. A slight increase in electrochemical impedance from 27.9 Ω to 30.2 Ω after 25 000 CV cycles also indicates the high stability of the material after a long-term experiment (Fig. 2d). The first redox process exhibits excellent electrochemical stability due to the low redox potential and resonance stabilization of the cationic radical (Scheme 2).

The redox potentials of PAs 5, their respective highest occupied molecular orbital (HOMO), and lowest unoccupied molecular orbital (LUMO) (*versus* vacuum) were calculated and are summarized in Table 1. The HOMO level of polymers could be estimated from the $E_{1/2}$ values of their oxidation in CV experiments as 4.79–4.80 eV (on the basis that ferrocene/ ferrocenium is 4.8 eV below the vacuum level with $E_{1/2} = 0.44$ V). Comparing homologs **5a** and **P1** containing TPA moieties, we note that their E_{onset} and $E_{1/2}$ values at the first stage oxidation decrease as the number of nitrogen on the TPA moieties increases (**5a**: $E_{\text{onset}} = 0.27$ V, $E_{1/2} = 0.43$ V; **P1**: $E_{\text{onset}} = 0.36$ V, $E_{1/2} = 0.48$ V). **5a** exhibits lower E_{onset} and $E_{1/2}$ than **P1**, which is attributed to the fact that the π -electron on the phenyl and the unshared electron pair of the nitrogen on TPA form



Scheme 2 Resonance stabilization forms of the cation radical

multiple conjugated bonds. Resonance effects are transmitted well between the electroactive nitrogen centers. As a result, the polymers containing more electroactive nitrogen centers exhibit higher electron density of nitrogen on their TPA moieties due to the electron-donating effect of TPA. Furthermore, the higher electron density results in their lower E_{onset} and $E_{1/2}$.

Spectroelectrochemical properties

For the spectro-electrochemical study, spectra of the polymer film coated on an ITO substrate were collected *in situ* by a UVvis spectrophotometer under the controlled potentials of an electrochemical analyzer. The typical spectroelectrochemical spectra of PA **5a** are presented in Fig. 3a. In the neutral form (0 V), the film exhibited strong absorption at around 350 nm, characteristic of triarylamine, but it was almost transparent in



Fig. 3 (a) Electrochromic behavior of PA film 5a from 0.0 to 1.2 V (thickness = 160 ± 10 nm, 0.1 M TBAP in MeCN as supporting electrolyte). (b) Postulated oxidation order of the nitrogen centers.

the visible region. Upon oxidation (increasing applied voltage from 0 V to 0.5 V), the intensity of the absorption peak at 350 nm gradually decreased, while a new peak at 440 nm and a broad band centered around 1404 nm in the NIR region gradually increased in intensity. The spectral change in the visible-light range is attributed to the formation of a stable monocation radical $(5a^+)$ on the side chain. The electron delocalization over the two electroactive nitrogen centers leads to an intervalence charge transfer (IV-CT) absorption in the NIR region. With the potential adjusted to 0.7 V, corresponding to $5a^{2+}$, the absorption bands (350 nm and 440 nm) gradually decreased, and the absorption band at 1404 nm gradually increased. With the potential adjusted to 1.0 V corresponding to $5a^{3+}$, the absorption bands at 1404 nm gradually decreased, accompanied by the emergence of new bands centered at around 788 nm.

Similarly, adjusting to 1.2 V to achieve complete oxidation of the three nitrogen centers resulted in the gradual decrease of the absorption band at 1404 nm, while the absorption band at 788 nm increased. The disappearance of the NIR absorption band can be attributed to the further oxidation of the $5a^{3+}$ species to the formation of $5a^{4+}$. As seen in the inset in Fig. 3, the polymer film changed from colorless in the neutral state to yellow for the first oxidation state, dark green for the second oxidation state, blue-green for the third oxidation state, and blue for the fourth oxidation state. Polymer **5a** shows good contrast in the visible and NIR region, exhibiting a high optical transmittance change (ΔT (%)) of 58% and 91% at 1404 nm at the first and second oxidation stages, respectively.

Electrochromic switching properties

The electrochromic switching stability and response time were investigated by monitoring the absorption changes when applying potential steps in the kinetics studies. Switching data for the representative PA 5a are presented in Fig. 4a, b, and Fig. S14 (ESI[†]). The coloring efficiency (CE) ($\eta = \Delta OD/Q$) and injected charge after various switching cycles were monitored and are summarized in Tables S3–S5 (ESI^{\dagger}). The results for ΔT , CE, and percentage of CE decay in the NIR region are illustrated in Fig. 4c and d. During the first electrochromic switching between 0.0 and 0.5 V, 5a exhibited remarkably high switching stability with almost complete reversibility, experiencing only an 8.8% decay of its CE at 1404 nm after 24000 continuous cycles and a 9.9% decay of its CE at 440 nm after 20000 continuous cycles (as shown in Fig. 4a and Fig. S14, ESI†). This exceptional stability can be attributed to the stable redox property of 5a, and the excellent adhesion between the polymer film and the ITO substrate. A detailed discussion of the relationship between the chemical structure and switching stability is covered in the subsequent section of this article. For the second EC switching between 0.0 and 0.7 V, 5a also displayed high switching stability and near-full reversibility, with only 7.6% decay of its CE at 1404 nm after 4500 continuous cycles (as depicted in Fig. 4d). Furthermore, 5a exhibited a high CE of 204 cm² C⁻¹ at 1404 nm for the first electrochromic process.



Fig. 4 Potential step absorptometry and current consumption of PA **5a** by applying a potential step: (a) $0.0 V \leftrightarrow 0.5 V$, (b) $0.0 V \leftrightarrow 0.7 V$. (c) Plots of ΔT , CE, and the decay percentage of PA **5a** for the first oxidation state at 1404 nm, (d) for the second oxidation state at 1404 nm, with 20 s of cycling time. Potential step absorptiometry during the continuous cycling test of PA **5a** by switching potentials step: (e) $0.00 V \leftrightarrow 0.50 V$, (f) $0.0 V \leftrightarrow 0.7 V$ with a cycle time of 5 h and 5 min for coloring and bleaching processes, respectively. All of the above experiments were conducted in 0.1 M TBAP in MeCN as the supporting electrolyte.

Additionally, the response time of **5a** (coloring/blenching) calculated at 90% of the full optical changes was found to be 10/2.4 s and 7.7/3.7 s at 1404 nm for the first and second electrochromic processes, respectively. The PAs **5** switched quickly at the first and second stages. Moreover, Fig. 4e, f and Fig. S15 (ESI†) illustrate the long-term stability of **5a** measured by maintaining each coloring process for 5 h at the applied potentials of 0.5 V and 0.7 V, revealing that highly stable electrochemical behaviors were observed. For the first oxidation stage, the novel PA **5a** exhibits the highest EC switching stability to the best of our knowledge compared to all other TPA-based EC polymers. These novel polymers also exhibit high electrochemical stability compared with other EC polymers.^{33,37-39}

Relationship between the chemical structure and switching stability

Due to the different number of redox centers, the IV-CT absorption band in the NIR region of materials shows changes during the oxidation process. To confirm the relationships between the NIR absorption band and the number of electroactive nitrogen centers, UV-vis-NIR absorbance curves correlated to the **5a**, **P1**, and **P2** electrode potentials are presented in Fig. S16 (ESI[†]). The λ_{max} and absorption range in the NIR region at the first stage oxidation for **5a**, **P1**, and **P2** are summarized in Table S6 (ESI[†]). Comparing the NIR absorptions of TPA-based PAs in Table S6 (ESI[†]) reveals that the λ_{max} and

Table 2	Long-term	stability	of	polymers
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Polymer	Potential (V)	$\eta^a \left(\mathrm{cm}^2 \ \mathrm{C}^{-1} ight)$	Cycles ^b	$ riangle T^c$ (%)	$Decay^{d}$ (%)	Ref.
5a	$0.0 \leftrightarrow 0.50$	111	20 000	53.4	9.9	This study
P1	$0.0 \leftrightarrow 0.70$	388	10 000	54.0	4.9	11
P2	$0.0 \leftrightarrow 0.40$	195	15000	54.0	4.9	34

^{*a*} Initial coloration efficiency. ^{*b*} Times of cyclic scan by applying a potential step. ^{*c*} Initial contrast of the optical transmittance change at 440 nm for **5a**, 433 nm for **P1**, and 422 nm for **P2**. ^{*d*} Decay of the coloration efficiency after cyclic scans.

absorption range increase as the number of the electroactive nitrogen centers increases (5a > P2 > P1). 5a has the longest $\lambda_{\rm max}$ and most extended absorption range among those TPAbased PAs (Table S6, ESI[†]). Robin and Day reported that the TPPA cation radical, a symmetrical delocalized class III, leads to an IV-CT absorption band in the NIR region where the electron is delocalized over the two redox centers.²⁸ Notably, all three 5a, P1, and P2 are symmetrical delocalized class III. The results confirm that the polymers containing more electroactive nitrogen centers exhibit longer wavelength absorption in the NIR region at the first oxidation stage due to delocalization from a neutral TPA center to the TPA cation radical center. Longer wavelength absorption in the NIR region means a weaker electronic coupling between the different redox states. The weak electronic coupling is attributable to the fact that a charge of cation radical could be dispersed by resonance. As a result, polymers containing more electroactive nitrogen centers exhibit longer wavelength absorption in the NIR region.

The stability of cation radicals primarily influences the electrochemical stability of TPA-based polymers. Nelson and Adam *et al.* reported that electron-donating substituents like the methoxy group stabilize the cation radicals. In contrast, electron-withdrawing groups, such as the nitro group, have the opposite effect.^{31,32} Two crucial factors affecting the stability of cation radicals are identified. Firstly, the electron-donating or electron-withdrawing effect of substituents contributes to stability. The electron-donating substituents adjacent to the benzene ring attached to the electroactive nitrogen center stabilize cation radicals.

Since cation radicals are considered to be electron-deficient, we would expect an electron-donating group to stabilize cation radicals. Any time a charge of the cation radical can be dispersed or delocalized by inductive effect or resonance, the system could be stabilized. Secondly, the resonance effect of electron delocalization over the electroactive nitrogen centers contributes to stability. The TPPA cation radical is a symmetrical delocalized class III; the electron could be delocalized over the two redox centers.

In this study, PAs 5 with four electroactive nitrogen centers were synthesized to compare the electrochemical stability between PAs 5 and the other TPA-based PAs containing *p*-methoxyphenyl groups, such as **P1** and **P2**, which are summarized in Table 2. Comparing 5a, **P1**, and **P2**, their electrochromic stability at the first stage of oxidation increases as the number of electroactive nitrogen centers increases ($5a^+ > P2^+ > P1^+$), as depicted in Table 2. The differences in stability are

attributed to the differing numbers of electroactive nitrogen centers in the polymers. For instance, 5a with four electroactive nitrogen centers allows the formulation of four resonance structures for the $5a^+$ cation radical. P2, with three electroactive nitrogen centers, forms three resonance structures for the P2⁺ cation radical. P1 with two electroactive nitrogen centers forms only two resonance structures for the P1⁺ cation radical. More resonance structures contribute to more extensive resonance stabilization in a hybrid system. Consequently, 5a exhibits the highest electrochromic switching stability at the first oxidation stage (only decays 8.8% at 1404 nm after 24 000 switching cycles with a high contrast ratio of 57.9%) compared with P1 and P2. The highest stability in 5a is attributable to having the most electroactive nitrogen centers among the three polyamides. The electron delocalization over all electroactive nitrogen centers is suggested to stabilize cation radicals significantly. Incorporating multiple redox centers into the polymer chain significantly enhances its EC stability. Notably, the redox stability of the cation radical center on TPA-based polymers could be governed by the electron-donating or electron-withdrawing effect of substituents and the resonance capability of electron delocalization over the electroactive nitrogen centers.

The stability of the polymer for long-term switching between the oxidized and neutral states is essential for practical application.³⁸ To confirm the relationships between the EC stability and the number of electroactive nitrogen centers, switching cycles correlated to the number of the electroactive nitrogen centers of triarylamine-based polymers with 10% decay of its CE in over 500 continuous cycles at the first oxidation stage are presented in Fig. 5. As shown in Fig. 5, the polymers containing more electroactive nitrogen centers exhibit higher electrochromic stability at the first oxidation stage. For example, their stabilities increase as the number of electroactive nitrogen centers increases $(5a^+ > P2^+ > P1^+)$ at the first stage oxidation. Moreover, these polymers contain the electron-donating methoxy substituents adjacent to the benzene ring attached to the electroactive nitrogen center, stabilizing the cation radicals. PA 5a exhibited the highest electrochromic stability compared to all other reported triarylamine-based polymers. 5a and P3 contain the same number of electroactive nitrogen centers. Both 5a and P3 show high electrochromic stabilities after over 10000 continuous cycles. However, they exhibit different electrochromic stability due to their different chemical structures. As a consequence of the above trends, introducing electron-donating groups and multiple electroactive nitrogen centers is an effective way to increase the electrochromic stability of the resulting polymers.

Mixed-valence (MV) materials containing two (or more) redox centers can be classified into three categories:²⁸ class I with practically no coupling between the different redox states, class II with moderate electronic coupling, and class III with strong electronic coupling (the electron could be delocalized over the two redox centers). A critical feature of classes II and III is the appearance of IV-CT absorption bands in the NIR region. Class III, with stronger electronic coupling, exhibits shorter wavelength absorption in the NIR region than class II.^{16,40} The polymer, derived from class III diamine (N,N'-bis(4-aminophenyl)-N,N'-di(4-methoxyphenyl)-1,4-phenylenediamine), exhibits significantly higher electrochromic stability than the polymer, derived from the class II diamine (N,N'-bis(4-aminophenyl)-N,N'di(4-methoxyphenyl)-4,4'-biphenyldiamine).^{11,41} However, there is no report of the electronic coupling between the different redox states on their electrochemical stability. Our study shows that polymers with more electroactive nitrogen centers exhibit longer wavelength absorption in the NIR region at the first oxidation stage. Longer wavelength absorption in the NIR region means a weaker electronic coupling between the different redox states. The weak electronic coupling is attributed to the fact that a charge of the cation radical can be dispersed by resonance. As a result, the polymers containing more electroactive nitrogen centers have weaker electronic coupling between the different redox centers. However, our study shows that the polymers with weaker electronic coupling exhibit better electrochemical stability. Consequently, the key to determining the stability of the EC materials classes II and III is the electron resonance delocalization over all the redox centers, rather than the electronic coupling between the different redox centers.

Conclusion

A series of novel PAs 5 were successfully prepared from the newly synthesized diamine monomer 4 with various dicarboxylic acids *via* phosphorylation polyamidation reaction. **5a** exhibited excellent electrochromic characteristics, including multiple color changes (from colorless to yellow, dark green, blue-green, and blue), fast response speed (10/2.4 s at 1404 nm at the first electrochromic process), high contrast of optical transmittance change (ΔT (%) = 57.9% at 1404 nm at the first oxidation stage), and exceptional electrochromic stability. At the first oxidation stage, the PA 5a exhibited the highest electrochromic stability (only 8.8% and 9.9% decay in its CE at 1404 nm and 440 nm after 24 000 and 20 000 switching cycles, respectively) compared to all other TPA-based polymers to date. It is discovered for the first time that polymers containing more electroactive nitrogen centers exhibit longer wavelength absorption in the NIR region at the first oxidation stage. Longer wavelength absorption in the NIR region means a weaker electronic coupling between the different redox states. The weak electronic coupling is attributed to the fact that a charge of the cation radical can be dispersed by resonance. As a result, polymers containing more electroactive nitrogen centers exhibit longer wavelength absorption in the NIR region. This absorption shift results from the electron delocalization from a neutral TPA center to the TPA cation radical center, enhancing electrochromic stability. This research distinctly illustrated that incorporating multiple electroactive nitrogen centers into the polymer chain significantly amplifies the electrochromic stability of the polymer. Notably, the stability of each cation radical center on the TPA-based polymer depends on the electron-donating or electron-withdrawing effect of substituents and the resonance effect of the electron delocalized over the electroactive nitrogen centers. Our described concept confirms that the key to determining the electrochemical stability of materials is the resonance by the electrons delocalized over all the redox centers, rather than the electronic coupling between the different redox centers.

Experimental

Materials

In this work, CaH_2 was added into NMP and dimethyl sulfoxide (DMSO) for dehydration, and then it was distilled *in vacuo* prior to use. Calcium chloride was dried under a vacuum at 200 °C for 10 hours. Dry 4 Å molecular sieves were added to pyridine and triphenyl phosphite (TPP) for water removal. Tetrabutylammonium perchlorate (TBAP) was recrystallized by ethyl acetate, and then dried *in vacuo* before use. *N*-(4-Aminophenyl)-*N*'-(4-nitrophenyl)-1,4-phenylenediamine, **P1**, and **P2** were synthesized according to a previous method.^{11,34,42} All other reagents were used as received from commercial sources.

Synthesis of *N*,*N*-bis(4-methoxyphenyl)-*N*'-(4-methoxyphenyl)-*N*'-(4-[4'-nitrophenyl-4"-methoxyphenylamino)phenyl]-*p*phenylenediamine (1)

A 100 mL three-neck flask was charged with 3.0 g (9.4 mmol) of N-(4-aminophenyl)-N'-(4-nitrophenyl)-1,4-phenylenediamine, 11 g (47 mmol) of 4-iodoanisole, 2.5 g of copper powder, 60 g of K₂CO₃, 3 grams of 18-crown-6-ether, and 75 mL of *o*-dichlorobenzene. The mixture was heated under reflux in a nitrogen atmosphere for 24 hours. The mixture was then filtered to remove the copper powder, and the filtrate was cooled to precipitate the brown crude





product. The crude product was recrystallized from DMF to afford a yellow powder with a yield of 3.63 g, 52%: mp 222–224 °C. IR(KBr): 3038 (ar. C–H str.), 2945, 2827 (al. C–H str.), 1587 (sym. NO₂ str.), 1311 (asym. NO₂ str.) cm⁻¹. ¹H NMR (DMSO- d_6 , δ_H , ppm): 3.72 (6H, s), 3.74 (3H, s), 3.77 (3H, s), 6.66 (2H, d, J = 8.9 Hz), 6.76 (2H, d, J = 8.9 Hz), 6.82 (2H, d, J = 8.9 Hz), 6.87–6.95 (10H, m), 6.98–7.02 (6H, m), 7.08 (2H, d, J = 8.9 Hz), 7.11 (2H, d, J = 8.9 Hz), 7.23 (2H, d, J = 8.9 Hz). ¹³C NMR (DMSO- d_6 , δ_C , ppm): 55.13, 55.15, 55.27, 114.59, 114.82, 114.99, 115.39, 120.27, 121.14, 125.60, 125.86, 126.02, 127.04, 127.76, 128.57, 136.64, 137.34, 137.70, 139.51, 139.61, 140.28, 144.37, 146.50, 154.02, 155.36, 155.97, 157.57.

Synthesis of *N*,*N*-bis(4-methoxyphenyl)-*N*'-(4-(4'-aminophenyl-4"-methoxyphenylamino)phenyl)-*N*'-(4-methoxyphenyl)-*p*-phenylenediamine (2)

A flask was charged with compound 1 (8.3 g, 11.1 mmol), 20 mL of hydrazine monohydrate, 100 mL of ethanol, 10 mL of tetrahydrofuran, and 0.60 g of 10% palladium on carbon (Pd–C). The mixture was heated under reflux for 48 hours. The mixture was then filtered to remove the Pd–C, and the reaction mixture was poured into methanol. The precipitate was collected by filtration, and the crude product was recrystallized from toluene to afford a light green crystal with a yield of 6.5 g, 82%: mp 249–251 °C. IR(KBr): 3440, 3365 (N–H str.) cm⁻¹. ¹H NMR (Pyridine- d_5 , δ_H , ppm): 3.69 (6H, s), 3.70 (6H, s), 4.96 (2H, s), 6.93–7.00 (10H, m), 7.12–7.30 (8H, m). ¹³C NMR (Pyridine- d_5 , δ_C , ppm): 55.81, 115.51, 115.64, 116.35, 122.56, 124.38, 125.31, 125.99, 126.44, 126.66, 128.12, 129.04, 129.79, 138.53, 142.08, 142.17, 142.35, 142.65, 143.45, 143.83, 145.07, 146.33, 156.04, 156.37. 156.45.

Synthesis of *N*,*N*'-bis(4-methoxyphenyl)-*N*-(4-(bis(4'methoxyphenyl)amino)phenyl)-*N*'-(4-(bis(4'nitrophenyl)amino)phenyl)-*p*-phenylenediamine (3)

A flask was charged with compound 2 (4.1 g, 5.7 mmol), cesium fluoride (2.1 g), 1-fluoro-4-nitrobenzene (2.2 g, 14.2 mmol), and dry DMSO (20.5 mL). The reaction mixture was heated under reflux for 24 hours with stirring under N₂. Then, the reaction mixture was allowed to cool to precipitate the brown crude product. The crude product was collected by filtration, and then recrystallized from NMP to afford red-brown powder with a yield of 3.1 g, 56%: mp 331–333 °C. IR(KBr): 3037 (ar. C–H str.), 2906, 2833 (al. C–H str.), 1579 (sym. NO₂ str.), 1309 (asym. NO₂ str.) cm⁻¹. ¹H NMR (Pyridine- d_5 , $\delta_{\rm H}$, ppm): 3.71 (12H, m), 6.98 (8H, m), 7.03 (2H, d, J = 9.0 Hz), 7.12 (2H, d, J = 9.0 Hz), 7.23–7.31 (16H, m), 7.36 (4H, d, J = 9.0Hz), 8.21 (4H, d, J = 9.0 Hz).

Synthesis of N,N'-bis(4-methoxyphenyl)-N-[4-(bis(4'-amino-phenyl)amino)phenyl]-N'-[4-(bis(4'-methoxyphenyl)amino)-phenyl]-p-phenylenediamine (4)

In a 150 mL three-neck flask, 6.4 g (6.6 mmol) of compound 3, 0.46 g of Pd/C, and 48 mL of NMP were added, and the mixture was stirred under a hydrogen atmosphere at room temperature until the theoretical amount of hydrogen was consumed. The time to reach this stage is about 144 hours. Afterward, Pd/C was

filtered out, and the filtrate was precipitated into methanol. The crude product was collected by filtration, and then recrystallized from *N*,*N*-dimethylformamide (DMF) to afford a light purple powder with a yield of 3.0 g, 50%: mp > 350 °C. IR (KBr): 3446, 3365 (N–H str.) cm⁻¹. ¹H NMR (Pyridine- d_5 , δ_H , ppm): 3.69 (6H, s), 3.70 (6H, s), 4.93 (4H, s), 6.90–6.99 (12H, m), 7.11–7.30 (24H, m). ¹³C NMR (Pyridine- d_5 , δ_C , ppm): 55.90, 115.69, 115.73, 115.76, 116.38, 121.09, 124.78, 125.01, 126.18, 126.60, 126.66, 126.92, 127.88, 128.99, 131.41, 138.97, 140.76, 142.16, 142.31, 142.39, 142.93, 143.31, 144.14, 144.41, 146.05, 146.36, 156.46, 156.50, 156.64.

Polymer synthesis

Using the synthesis of PA **5a** as an example: in a 100 mL threeneck flask, 1.027 grams (1 mmol) of monomer **4**, 0.259 grams (1 mmol) of 4,4'-dicarboxydiphenyl ether, 3.0 mL of NMP, 1.2 mL of TPP, 0.4 mL of pyridine, and 0.15 grams of CaCl₂ were added. The reaction was carried out at 120 °C under a nitrogen atmosphere for 6 hours. The obtained polymer solution was poured into 40 mL of stirred methanol, forming a stringy, fiber-like precipitate. The precipitate was washed several times with hot water, and then vacuum-dried. The obtained PA **5a** was dissolved in DMAc to prepare an 8 wt% solution. The solution was again precipitated in methanol for purification. The intrinsic viscosity of the purified **5a** was measured to be 0.40 dL g⁻¹ using NMP as the solvent. IR(KBr): 1662 (C=O), 3310 cm⁻¹ (N-H str.). ¹H NMR (Pyridine- d_5 , δ_H , ppm): 3.74 (12 H), 7.00–7.31 (36 H), 8.19 (4 H), 8.42 (4H), 11.14 (2 H, NHCO).

Instrumentation

A Bio-Rad 3240-SPC FTIR spectrophotometer was used to record IR spectra (KBr pellets). In a typical experiment, an average of 20 scans per sample was made. ¹H and ¹³C NMR spectra were recorded on Bruker AVIII 500 Fourier transform nuclear magnetic resonance spectrometers using tetramethylsilane (TMS) as the internal standard. The melting points were obtained by a standard capillary melting point apparatus. Inherent viscosities of all polymers were determined at 0.5 g dL^{-1} using an Ubbelohde viscometer. Qualitative solubility was determined using 0.1 g of polymer in 2.0 mL of solvent. A TA instruments differential scanning calorimeter (DSC25xx) and a TA instruments thermogravimetric analyzer (TA Q50) were employed to study the transition data and thermal decomposition temperature of all of the polymers. DSC was conducted under a nitrogen stream at a flow rate of 30 cm³ min⁻¹ and a heating rate of 20 °C min⁻¹. TGA was determined under a nitrogen flow of 50 cm³ min⁻¹. Electrochemistry was performed using a CH instruments 6123e electrochemical analyzer. Cyclic voltammetry (CV) measurements were conducted using polymer film/indium-tin-oxide (ITO) as a working electrode, Ag/ AgCl, KCl (sat) as a reference electrode, and a platinum wire as an auxiliary electrode. Spectroelectrochemical measurements were performed in a cell built from a 1 cm UV-visible cuvette using UV PerkinElmer for Lambda 900 spectrophotometer and UV Hitachi U-4100. The polymer film/ITO was used as a working electrode, platinum as a counter electrode, and

Ag/AgCl as a reference electrode. An orbitrap QE plus mass spectrometry was used to record ESIMS spectra.

Author contributions

Y.-T. C. conceived the idea, designed the experiments, and wrote the manuscript with help and feedback from all authors. Y.-C. C. discussed the results, contributed to the data interpretation, and revised and organized the manuscript. Y.-T. C. and Y.-C. C. also secured funding and provided supervision throughout. Z.-Y. Z., Y.-J. W., and C.-H. L. conducted the experiments and analyzed the results. J.-J. W., P.-L. L., and G.-S. L. revised the manuscript. All the authors have approved the final version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

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