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Colorless Triphenylamine-Based Aliphatic Thermoset Epoxy for Multicolored and Near-Infrared Electrochromic Applications

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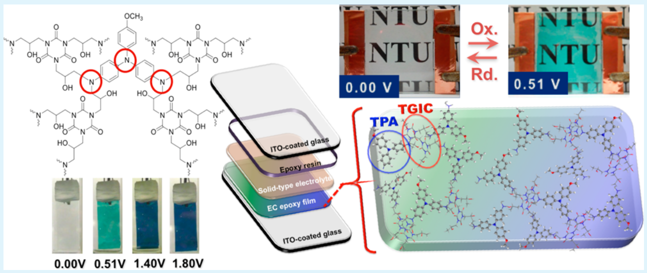

ABSTRACT: In this study, two novel colorless thermoset epoxy resins with anodically electrochromism were prepared from the thermal curing of two triphenylamine-based diamine monomers, 4,4′-diamino-4″-methoxytriphenylamine (**1**) and *N*,*N*′-bis(4-aminophenyl)-*N*,*N*′-di(4-methoxylphenyl)-1,4-phenylenediamine (**2**) with aliphatic epoxy triglycidyl isocyanurate, respectively. The resulting thermoset epoxy resins showed excellent softening temperature (T_s, 270 and 280 °C) due to the rigid structure and highly crosslinking density. In addition, novel colorless epoxy resin films revealed good reversible electrochemical oxidation and interesting multi-electrochromic behavior with high contrast ratio both in visible and near-infrared regions. The aliphatic thermoset epoxy resins also exhibited high transparency in visible region as colorless and great potential for practical electrochromic applications.

KEYWORDS: *thermoset epoxy, electrochromism, triphenylamine, near-infrared, triglycidyl isocyanurate, multicolored*

INTRODUCTION

Electrochromism is broadly defined as the phenomenon revealed by materials with reversible color change when an electrical current or potential is applied, in other words, it produces new or different visible region absorptions in accompaniment with an electro-transfer or redox reaction in which it either gains or loses an electron; it undergoes reduction or oxidation. Moreover, where the switching of redox stages produces different colors changing, this material is defined as electrochromic (EC).[1] The EC behavior has been known for a long time and utilized for many kinds of applications, such as E-paper, smart window, optical switching devices, and camouflage materials in the visible range (e.g., 400–800 nm),[2−5] and data storage, optical communication, thermal control (heat gain or loss) in spacecraft and buildings in the near infrared region (NIR; e.g., 800–2000 nm).[6−8] In addition, the EC materials could be classified into five distinct families including metal oxides such as iridium dioxide (IrO_2) or tungsten trioxide (WO_3),[9] coordination complexes such as prussian blue and phthalocyanines,[10,11] small organic molecules like viologens,[12] organic conjugated polymers,[13,14] and aryl-amine-based polymers which are generally colorless unless they undergo some formations of charge-transfer interaction with an electron-deficient acceptor species. In 2005, our groups initiated some high-performance polymers (e.g., aromatic polyimides and polyamides) using the triphenylamine (TPA) moieties as an hole-transporting and EC functional unit. We also investigated whether the introduction of electron donor at the para-position of phenyl groups on the electrochemically active positions of the TPA unit will contribute to stable TPA cationic radicals and lowered oxidation potential, which resulted in a significantly enhanced electrochemical and EC stability.[15−20]

Epoxy resin is a commercial available material for many applications, such as coatings, adhesives, and composite materials with properties of toughness, low shrinkage, excellent adhesion, and corrosion resistance.[21] The epoxy groups usually react with amines, anhydrides, phenols, mercaptans, isocyanates, and acids as hardeners to produce thermoset epoxy resins with amine, ester, or ether linkages. Among these hardeners, amines are most commonly used in curing epoxy resins. However, curing thermoset epoxy resins generally uses not only hardeners but also accelerators. Moreover, epoxy resins usually are applied as flame retardant microelectronic materials by utilizing halogen or phosphorus-containing epoxy resins and curing agents.[22,23] Considering the environmental issue, TPA groups could be expected to impart flame retardant behaviors to the epoxy materials because of high aromatic content, and these systems could be seen as “green” because they are halogen-free and phosphorus-free.[24,25]

Thus, in this contribution, we synthesized two new TPA-based aliphatic thermoset epoxy resins from two mature diamines with aliphatic epoxy via curing reaction. These TPA-containing diamines could not only be the hardeners of epoxy resins without adding any other accelerators, but also preserve the favorable thermal stability due to high aromatic content in the system. Furthermore, comparing with their corresponding polyamides,[26,27] the incorporation of **TGIC** with electron-

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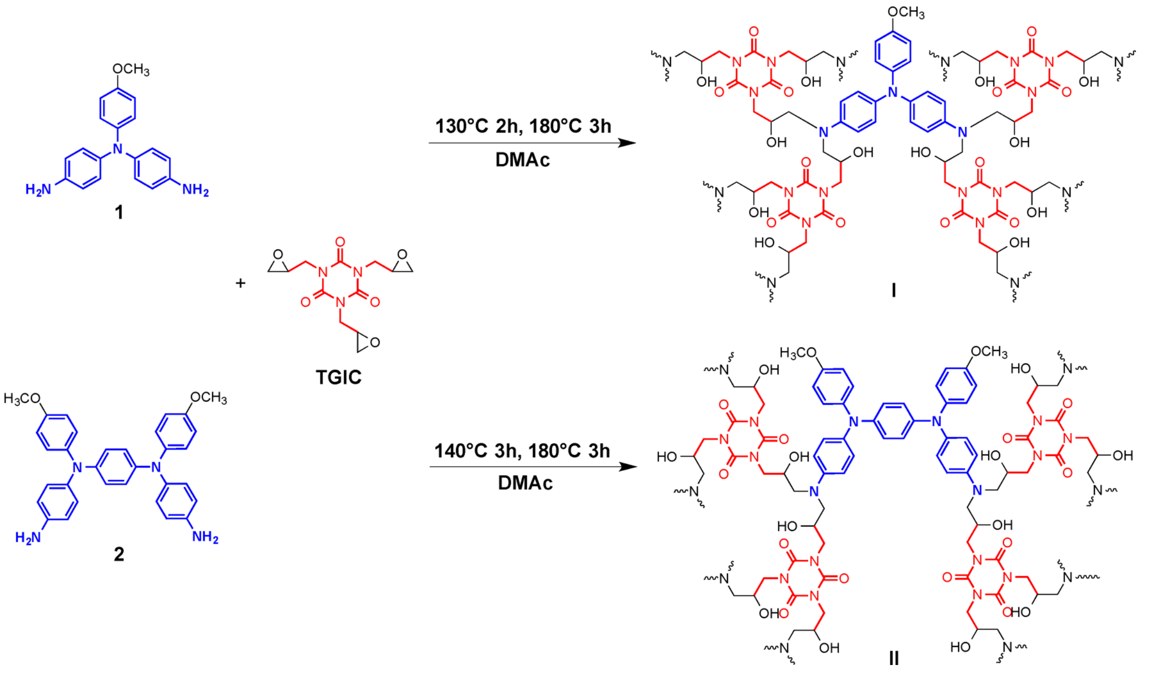
Scheme 1. Synthetic Route to EC Thermoset Epoxy Resins



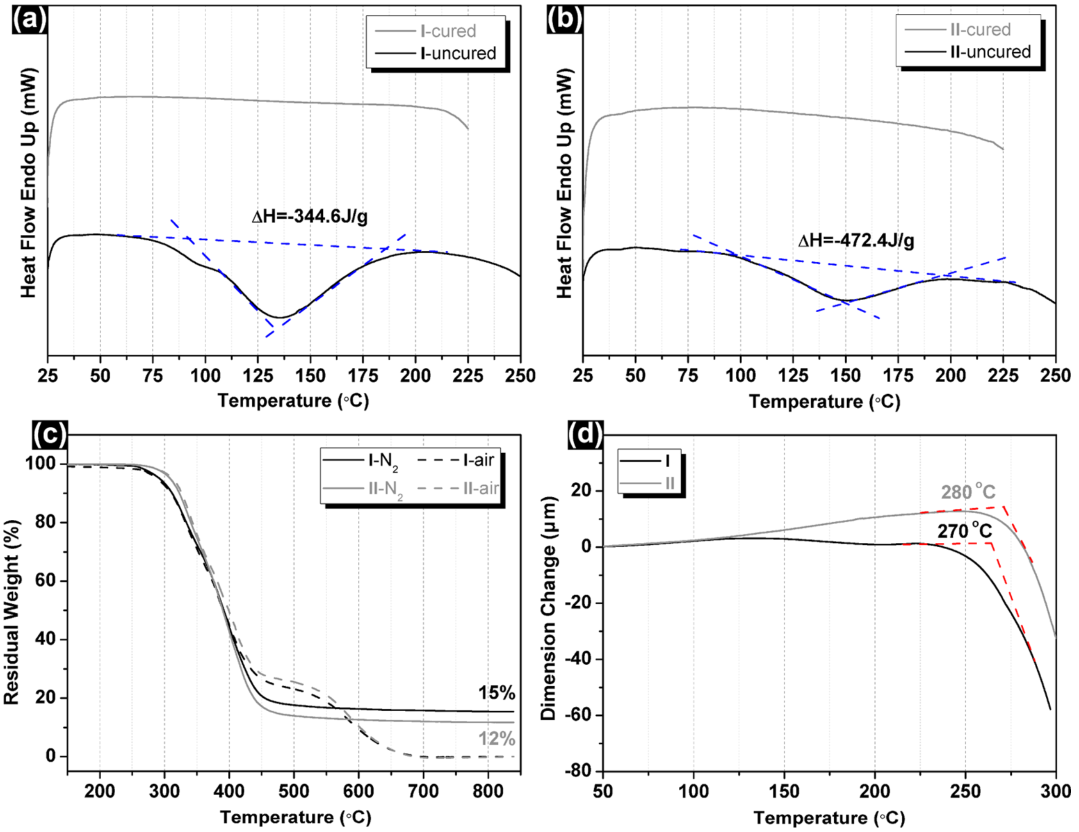


Figure 1. (a, b) DSC curves of cured and uncured epoxy resins, (c) TGA thermograms, and (d) TMA curves of thermoset epoxy resins.

donating dialkyl moieties into amino groups of TPA derivatives are expected to effectively increase the oxidative stages and reduce the oxidative potential of the resulting thermoset epoxy resins. Therefore, we anticipated that the prepared EC thermoset epoxy materials could have high transparency, excellent thermal properties, low oxidative potential, good electrochemical stability, and high optical transmittance contrast (Δ%*T*) in both visible and NIR ranges.

■ RESULTS AND DISCUSSION

Preparation and Basic Characterization of Thermoset Epoxy Resins. The new epoxy materials **I** and **II** were synthesized by the curing reaction of TPA-based diamines, 4,4′-

diamino-4″-methoxytriphenylamine (**1**)[26] and *N,N*′-bis(4-aminophenyl)-*N,N*′-di(4-methoxylphenyl)-1,4-phenylenediamine (**2**),[27] with triglycidyl isocyanurate (**TGIC**), respectively, in *N,N*-dimethylacetamide (DMAc) (Scheme 1). As shown in Figure 1, these epoxy resins before and after curing reactions were identified by the DSC. After curing processes, the exothermic peak disappeared in DSC measurement implying the completed curing reaction.

Table 1. Thermal Properties of Epoxy I and II

code	T_s (°C)[a]	T_d^5 (°C)[b]		T_d^{10} (°C)[b]		R_{w850} (%)[c]	LOI[d]
		N_2	air	N_2	air		
I	270	295	290	315	310	15	24
II	280	310	315	325	330	12	22

[a] Softening temperature measured by TMA with a constant applied load of 100 mN at a heating rate of 5 °C min^{-1} by penetration mode. [b] Temperature at which 5 and 10% weight loss occurred, respectively, recorded by TGA at a heating rate of 20 °C min^{-1} and a gas rate of 30 cm^3 min^{-1}. [c] Residual weight percentage at 850 °C in nitrogen. [d] LOI = limiting oxygen index = (17.5 + 0.4(char yield)) at 850 °C.

The thermal behaviors of thermoset epoxy resins were examined by TGA and TMA, and the results were summarized in Table 1. The TGA diagrams of thermoset epoxy **I** and **II** are shown in Figure 1c. All the epoxy resins revealed good thermal stability with no remarkable weight loss up to 290 °C in nitrogen. In addition, the high softening temperatures (T_s) of 270 and 280 °C for epoxy **I** and **II**, respectively, were measured by TMA and could be attributed to the rigid structure of **TGIC** and high crosslinking density after thermosetting processes (Figure 1d).

Electrochemical Properties. The redox behavior of the epoxy resins were evaluated by cyclic voltammetry (CV) conducted by the cast film on an indium−tin oxide (ITO) coated glass slide as working electrode in anhydrous acetonitrile (CH_3CN), using 0.1 M of tetrabutylammonium perchlorate (TBAP) as a supporting electrolyte under a nitrogen atmosphere. Figure 2 depicted the typical CV curves of **I** and **II** for comparison; there are two reversible oxidation redox couples both for epoxy **I** and **II**. Furthermore, differential pulse voltammograms show clearly that there are two splitting oxidation potentials for epoxy **II** (as shown in Figure 2c), suggesting effective charge delocalization during the formation of the mixed-valence cation **II**$^{3+}$ and long-distance electron communication between the bridged diamines moieties. Because of the high solvent resistance and good adhesion between the cross-linked thin film and ITO substrate, both epoxy **I** and **II** exhibited excellent electrochemical stability and reversible CV behaviors by continuous 750 cyclic and 1000 cyclic scans at first oxidation stages, respectively (Figure 2). In addition, these novel epoxy resins reveal much lower oxidative potentials comparing with their corresponding polyamides,[26,27] and the electrochemical data were summarized in Table 2. During the oxidation switching of epoxy **I** thin film, the film color changed from colorless to green, blue-green, and then

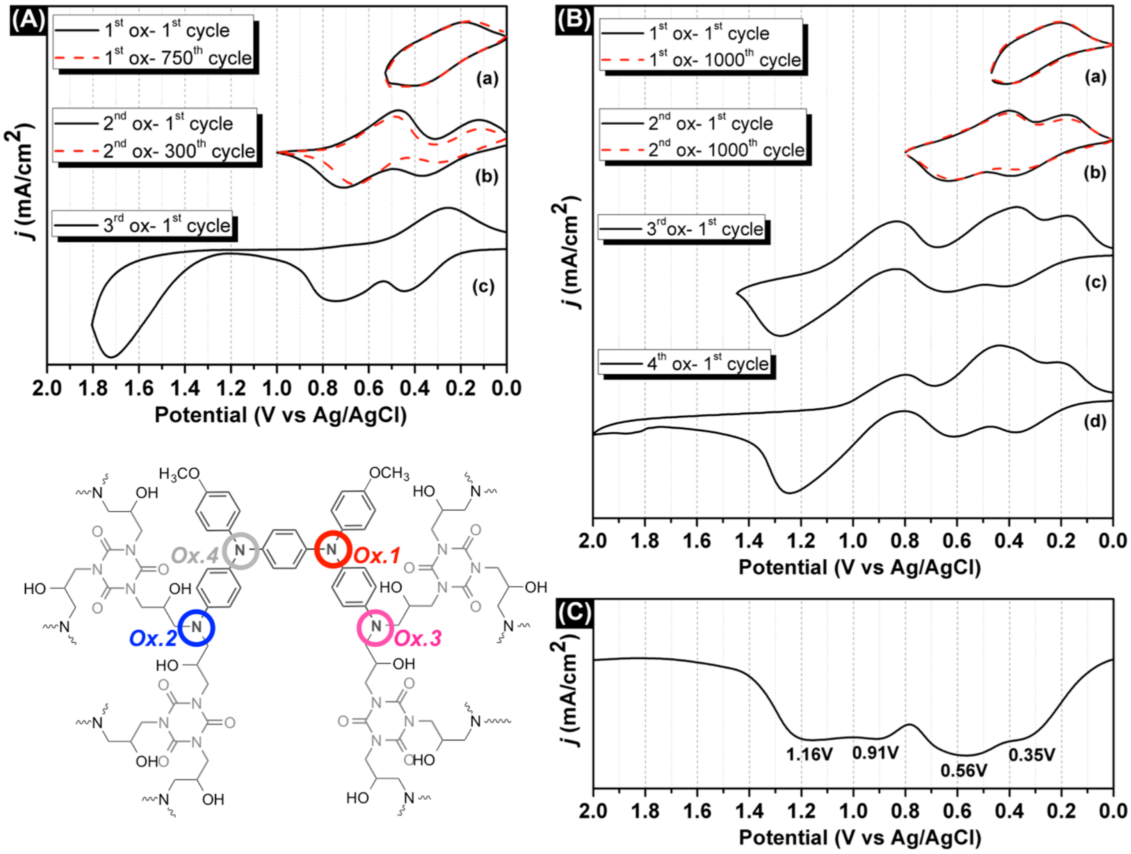


Figure 2. Cyclic voltammetric diagrams of epoxy (A) **I** (135 ± 15 nm in thickness), (B) **II** (170 ± 20 nm in thickness) films for each oxidation stages over cyclic scans at a scan rate of 50 mV/s, and (C) differential pulse voltammograms of epoxy **II** film onto an indium−tin oxide (ITO)-coated glass substrate in 0.1 M TBAP/CH_3CN with the possible electro-oxidation order for the amino centers. Scan rate, 5 mV/s; pulse amplitude, 50 mV; pulse width, 50 ms; pulse period, 0.2 s.

Table 2. Electrochemical Properties of Epoxy I and II

	thin films		oxidation potential (V)[c]				
code	$\lambda_{400\ \mathrm{nm}}$ (%)[a]	λ_0 (nm)[b]	E_{onset}	$E_{1/2}$ (ox1)	$E_{1/2}$ (ox2)	$E_{\mathrm{p(ox3)}}$	$E_{\mathrm{p(ox4)}}$
I	92.2	318	0.19	0.30	0.58	1.74	
II	88.6	320	0.18	0.30	0.51	0.91[d]	1.16[d]

[a] Transmittance of UV−vis at the wavelength of 400 nm. [b] The cutoff wavelength (λ_0) from the UV−vis transmission spectra of epoxy thin films (thickness of ~150 nm). [c] From cyclic voltammograms versus Ag/AgCl in CH_3CN. [d] The data were confirmed by DPV.

blue. On the other hand, the color of **II** thin film changed from colorless to light green, blue, dark blue, and then blue-black. Meanwhile, these two thermoset epoxy resins do show multi-electrochromic behavior with increased oxidative stages as opposed to their corresponding polyamides.[26,27]

Spectroelectrochemical Properties. Spectroelectrochemical experiments were used to manifest the optical properties of the EC films. For the investigations, the thermoset epoxy resin films were cast on an ITO-coated glass, and an electrochemical cell was assembled from an ultraviolet (UV)−visible cuvette. The cell was placed in the optical path of light beam in a UV-vis spectrophotometer, which allowed us to acquire absorption spectra upon various applied potential in a 0.1 M TBAP/CH_3CN solution. The results of TPAs/**TGIC** films were presented in Figure 3, and the UV−vis absorbance curves were correlated to electrode potentials. The colorless epoxy **I** film revealed obvious absorption at 312 nm corresponding to the $\pi-\pi^*$ transition of aromatic rings at the neutral state (0 V) shown in the Figure 3a. Upon oxidation (increasing electrode potential from 0 to 0.51 V), the intensity of absorption peak at 312 nm gradually decreased, where new peaks at 382 nm and 647 nm, and a broad band with maximum absorption wavelength at 1022 nm in the NIR range gradually enhanced in intensity. The spectral change in visible-light region can be attributed to the formation of a monocation radical of TPA unit corresponding to $\mathbf{I}^{+}$. In addition, the broad absorption in NIR range was due to IV-CT associated with electron transfer from active neutral nitrogen center to the cation radical nitrogen atom of TPA moiety, which is consistent with the behavior defined by Robin and Day.[28] The reversibility of first oxidation is 98.6 % based on the intensity of absorbance at 312 nm. When the potential was increased to 1.4 V corresponding to $\mathbf{I}^{2+}$, a new peak at around 840 nm appeared, which might be attributed to the formation of dications from these tertiary amino groups thus lowered the IV-CT absorbance. The second oxidation reversibility is 98.0 %. When the applied potentials increased to the third oxidation state corresponding to $\mathbf{I}^{3+}$, the NIR wavelength further decreased and the third oxidation reversibility is 65.1 %. For epoxy **II** shown in Figure 3b, the colorless epoxy **II** film also exhibited strong characteristic absorption at 314 nm in the visible range. When the applied potential was increased from 0 to 0.48 V corresponding to $\mathbf{II}^{+}$, the intensity of the absorption at 314 nm decreased gradually, whereas the intensity at 768 nm and 1122 nm increased. The absorption at 1122 nm in NIR region attributed to IV-CT characteristic was the formation of a monocation radical of the TPA unit in epoxy **II** central moiety, similar as the spectroelectrochemistry of epoxy **I** film. As the applied potential keep increasing to 0.92 V, the nitrogen of aliphatic carbon−nitrogen bond was oxidized and also enhanced the IV-CT behavior at wavelength of 1098 nm, while the absorption band around 1100 nm of monocation radical gradually decreased and a new broad band centered at around 647 nm increased with increasing the potential to 1.1 V. The slight decreased NIR band could be attributed to the formation of dication at the other nitrogen of aliphatic carbon−nitrogen bond. As the potential was even higher to 1.4 V corresponding to $\mathbf{II}^{4+}$, the NIR region absorbance decreased obviously just similar as the phenomenon of $\mathbf{I}^{3+}$. The reversibility of epoxy **II** at the first, second, third and fourth oxidation stages are 99.8, 99.8, 96.1, and 96.1%, respectively. In addition, the transmittance of UV−vis spectra of epoxy **I** and **II** (indicated as dashed line in Figure 3) not only showed 92.2 and 88.6% at 400 nm, respectively, but also revealed quite low cutoff wavelength in the UV region. Therefore, the EC thermoset epoxy resins could be claimed as “colorless” because they are almost transparent in the visible region.

We further fabricated single-layer EC cell for preliminary evaluation (Figure 4). As a typical example, an EC cell prepared by epoxy **I** was fabricated, and the epoxy film was colorless at neutral state. When the applied voltage was increased to 0.51 V,

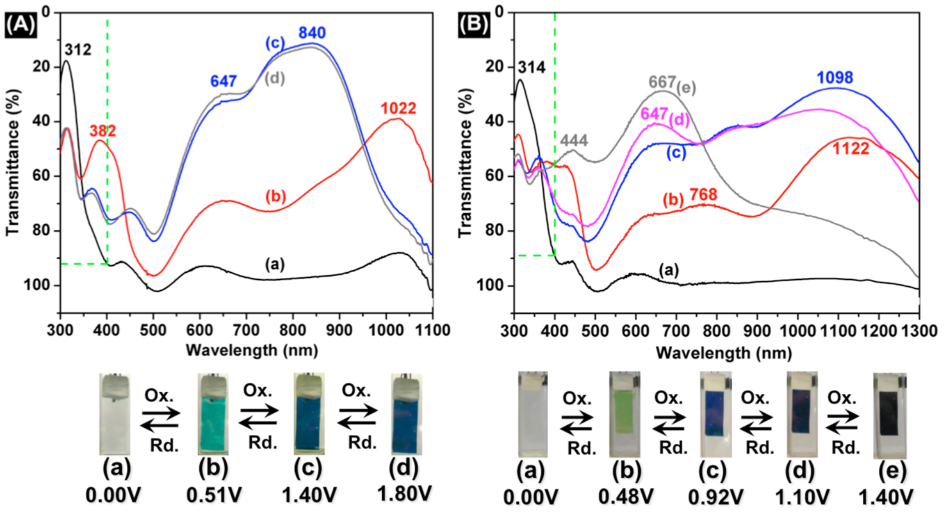


Figure 3. EC behavior of aliphatic thermoset epoxy (A) **I** (135±15 nm in thickness) and (B) **II** (170±20 nm in thickness) on the ITO-coated glass substrate in 0.1 M TBAP/CH_3CN at various applied potentials (V vs. Ag/AgCl). Transmittances at 400 nm are indicated by dashed lines.

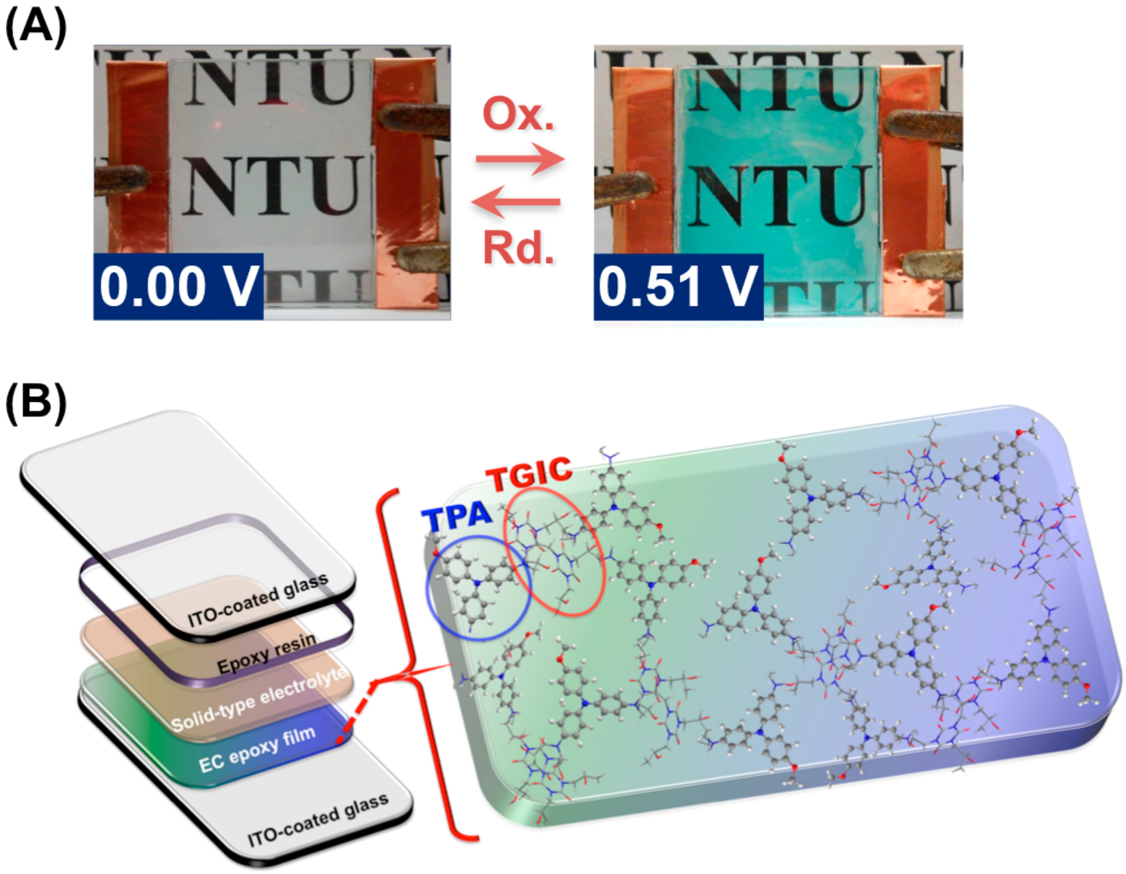


Figure 4. (A) Photographs of single-layer ITO-coated glass EC device, using epoxy **I** as active layer. (B) Schematic diagram of epoxy **I** EC device sandwich cell.

the color changed from colorless to green at first oxidative stage, as same as the behavior observed in the above spectroelectrochemical investigations. The epoxy EC film then turned back to original colorless state when the potential was set back at 0.0 V. We believe that the optimization would further enhance the device performance and explore the potential for application of these EC thermoset epoxy resins.

CONCLUSIONS

Two novel aliphatic thermoset epoxy resins with anodically EC characteristic were successfully prepared from the thermal curing reaction of two TPA-based diamine monomers with aliphatic epoxy triglycidyl isocyanurate. In addition to the good thermal properties (T_s, 270 and 280 °C) based on its rigid structure and highly crosslinking density, the novel EC TPA-based epoxy materials exhibit good electrochemical stability and interesting multi-electrochromic behavior with highly optical contrast both in visible and NIR ranges. Moreover, these TPA-based thermoset epoxy materials could be claimed as "colorless" since they are almost transparent in visible region with transmittance up to 92.2 % at 400 nm. Furthermore, these novel epoxy resins reveal much lower oxidative potentials as opposed to their corresponding polyamides, which can effectively decrease the energy required for practical EC applications.

EXPERIMENTAL SECTION

Materials. 4,4′-Diamino-4″-methoxytriphenylamine (**1**) and *N*,*N*′-bis(4-aminophenyl)- *N*,*N*′-di(4-methoxyl-phenyl)-1,4-phenylenediamine (**2**) were prepared according to our previous reports.[26,27] Triglycidyl isocyanurate (**TGIC**) is a commercial epoxy with molecular weight of 297.27 g/mol and used as received. Tetrabutylammonium perchlorate (TBAP) (Acros) was recrystallized twice by ethyl acetate in nitrogen and then dried in vacuo prior to use. All the other reagents were used as received from commercial sources.

Thermoset Epoxy Thick Films Synthesis. The preparation of thermoset epoxy **I** was utilized as an example to depict the synthetic route to the thermoset epoxy thick films. A solution of the pre-epoxy polymer was synthesized by dissolving 0.462 g (1.513 mmol; 1 equiv) of the **1** and 1.224 g (4.035 mmol; 2 equiv) of the **TGIC** in 1 mL of DMAc. The homogeneous solution was heated to 80 °C under nitrogen for 2 h. Next, dropping the solution into four molds which were made by release papers and heating in conventional oven under nitrogen atmosphere at 120 °C for 12 h to remove most of the solvent; then the semi-dried thick films were further dried in vacuo at 40 °C for 3 h, 130 °C for 2 h, and then 180 °C for 3 h. The obtained thick films were about 790 ± 60 μm (thickness) and used for thermal analysis.

Thermoset Epoxy Thin Films Synthesis. The preparation of epoxy **I** was utilized as an example to depict the synthetic route to the thermoset epoxy thin films. A solution of the pre-epoxy polymer was synthesized by dissolving 0.061 g (0.201 mmol; 1 equiv.) of the **1** and 0.163 g (0.536 mmol; 2 equiv.) of the **TGIC** in 1.5 mL of DMAc. The homogeneous solution was heated to 80 °C under nitrogen atmosphere for 2 h. After reacting, the solution was spin-coated onto ITO glass and cured under the program of 130 °C for 2 h, and then 180 °C for 3 h in vacuo. The obtained thin films were about 135±15 nm (thickness) and used for electrochemical and spectroelectrochemical tests.

Fabrication of the EC Device. EC epoxy thin films were prepared by spin-coating onto an ITO-coated glass (25 × 25 × 0.7 mm, 50 Ω/square). The pre-epoxy polymers were spin-coating onto an active area (about 20 × 25 mm^2) then dried and cured in vacuum. A gel electrolyte based on PMMA (M_w: 120,000) and $LiClO_4$ was plasticized with propylene carbonate to form a conductive and highly transparent gel. PMMA (3 g) and $LiClO_4$ (0.3 g) were dissolved in dry acetonitrile (15 g) as a supporting electrolyte, propylene carbonate (5 g) was added as plasticizer. The gel electrolyte was then spread on the thermoset epoxy resin-coated side of the electrode, and the electrodes were sandwiched. Finally, a commercial epoxy resin was used to seal the device.

Measurements. DSC analyses were performed on a PerkinElmer Pyris 1 DSC at a scan rate of 10 °C/min, isothermal scanning was set at a scan rate of 30 °C/min to the certain temperature and then kept at the temperature in flowing nitrogen (20 cm^3/min). Thermogravimetric analyses (TGA) were conducted with a PerkinElmer Pyris 1 TGA. Experiments were carried out on approximately 6−8 mg film samples heated in flowing nitrogen or air (flow rate = 20 cm^3/min) at a heating rate of 20 °C/min. Thermal Mechanical Analyzer (TMA) was conducted with a TA Instruments TMA Q400. The TMA experiments were measured at a scan rate of 5 °C/min with a penetration probe under an applied constant load of 100 mN. Electrochemistry was performed with a CH Instruments 612C electrochemical analyzer. Voltammograms were presented with the positive potential pointing to the left and with increasing anodic currents pointing downwards. Cyclic voltammetry (CV) was conducted with the use of a three-electrode cell in which ITO (the area of thermoset epoxy resin thin film was about 2.0 cm × 0.8 cm) was used as a working electrode. A platinum wire was used as an auxiliary electrode. All cell potentials were taken by using a homemade Ag/AgCl, KCl (sat.) reference electrode. Spectroelectrochemical experiments were carried out in a cell built from a 1 cm commercial UV−visible cuvette using Hewlett-Packard 8453 UV-Visible diode array and Hitachi U-4100 UV−vis−NIR spectrophotometer. The ITO-coated glass slide was used as the working electrode, a platinum wire as the counter electrode, and a Ag/AgCl cell as the reference electrode. The thickness of the thermoset epoxy resin thin films was measured by alpha-step profilometer (Kosaka Lab., Surfcorder ET3000, Japan).

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Author Contributions

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Notes

The authors declare no competing financial interest.

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