

Supporting Information

Intelligent Biomimetic Chameleon Skin with Excellent Self-Healing and Electrochromic Properties

Rongzong Zheng, Yi Wang, Chunyang Jia*, Zhongquan Wan, Junsheng Luo,

Haseeb Ashraf Malik, Xiaolong Weng, Jianliang Xie, Longjiang Deng

State Key Laboratory of Electronic Thin Films and Integrated Devices, National Engineering Research Center of Electromagnetic Radiation Control Materials, School of Electronic Science and Engineering, University of Electronic Science and Technology of China,

Chengdu 610054, PR China.

*E-mail: cyjia@uestc.edu.cn

Experimental

Materials and Reagents

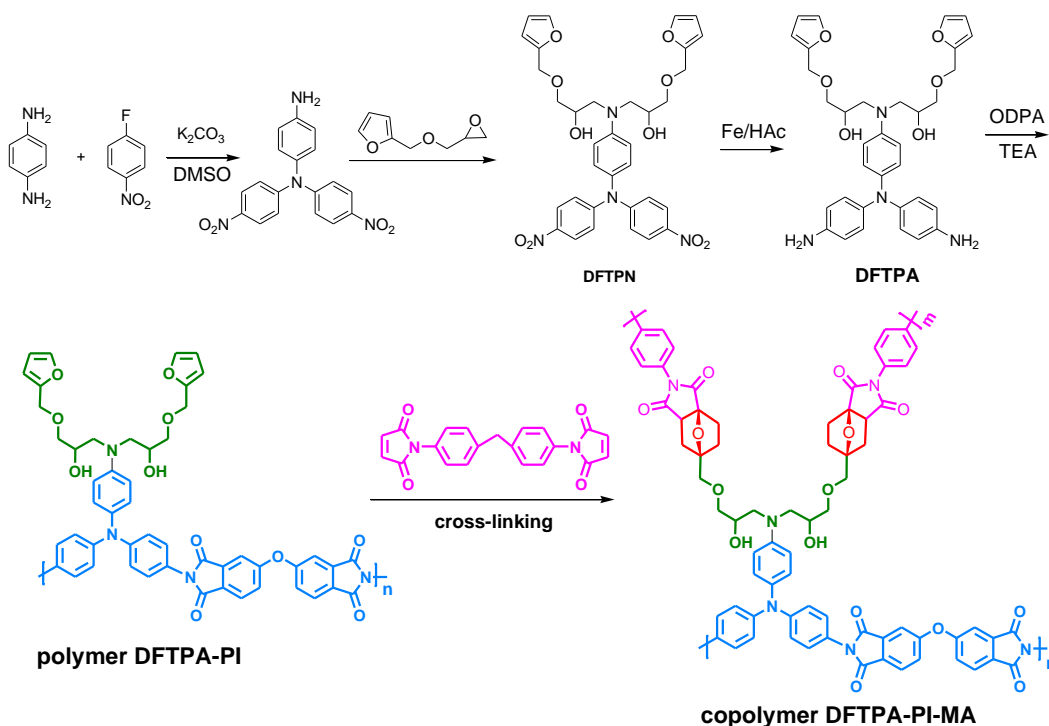
The ITO ($15\ \Omega/\square$, commercial purchased) was cut into pieces with size of $0.8\times 4\text{ cm}^2$, then sequentially ultrasonic washed with acetone, ethanol, deionized water for 15 mins, respectively. Finally, the clean ITO glass substrates were submerged in ethanol for use. LiClO_4 in acetonitrile (CH_3CN) solution ($0.1\text{ mol}\cdot\text{L}^{-1}$) was employed as electrolyte in the tests. All reagents and solvents were purchased from commercial sources and used without any further purification. Ag conductive fabric ($\leq 0.5\ \Omega/\square$) was commercial purchased from Guangzhou Jiujin Leather Material Co., Ltd.

Synthesis

The synthetic route for copolymer DFTPA-PI-MA is shown as Scheme S1. *N,N*-bis(4-nitrophenyl)benzene-1,4-diamine was synthesized according to literature,¹ and furfuryl glycidyl ether (FGE) was further introduced to obtain 1-amine-bis(furfuryl glycidyl ether)-*N,N*-bis(4-nitrophenyl)benzene (DFTPN). DFTPN was reduced and polymerized with 4,4'-oxydiphthalic anhydride (ODPA) to obtain poly[1-amine-bis(furfuryl glycidyl ether)-*N,N*-bis(4-nitrophenyl)benzene -4,4'-

dimaleimidophenylmethane)] imide (DFTPA-PI), and then poly-[[1-amine-bis(furfuryl glycidyl ether)-*N,N*-bis (4-nitrophenyl)benzene] -(4,4'-dimaleimidophenylmethane)-*g*-bismaleimide} (DFTPA-PI-MA) was synthesized by DA cross-link reaction with MA. The specific synthetic process is described as below:

Scheme S1 The synthetic route of copolymer DFTPA-PI-MA.



The energy levels of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the monomer DFTPA-PI were also calculated to be -4.34 eV and -2.71 eV, respectively (**Figure S1**). Its band gap (E_g) is 1.63 eV, which was small value for the TPA-based polymers,^{12, 28-29} the main reason may be the fact that the TPA unit was replaced with electron-rich substituent group. So the redox reactions of the copolymer were more easily and the redox voltages were relatively low, which is good for improving the electrochemical stability of the copolymer film.

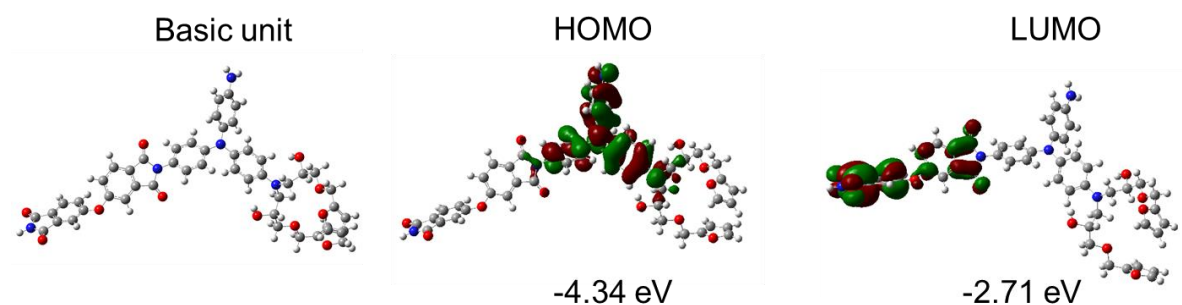
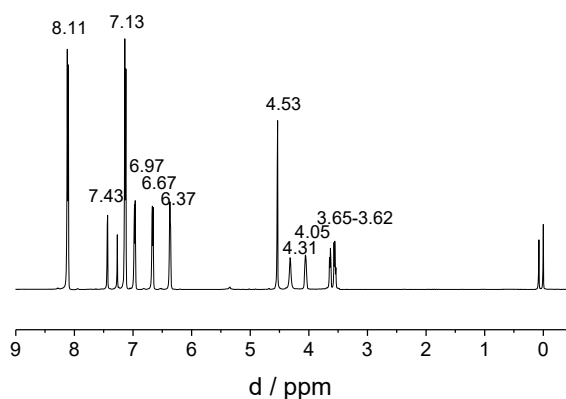


Figure S1 The optimized geometries and frontier molecular orbitals of DFTPA-PI

Synthesis of DFTPN: Furfuryl glycidyl ether (FGE) (1.25 g, 8.1 mmol) was heated up to 50°C in a flask and stirred without any solvent under nitrogen protection, *N,N*-bis(4-nitrophenyl)benzene-1,4-diamine (1.4 g, 4 mmol) and 0.1 g NaOH as the catalyst were added to the flask, then the mixture was stirred at 90°C for 6 h. Upon cooling, the crude product was eluted through a silica-gel column with dichloromethane to obtain the brownish red solid 2.3 g (87%). ^1H NMR (400 MHz, CDCl_3) δ : 8.11(d, $J=7.2$ Hz, 4H), 7.43(d, $J=6.8$ Hz, 2H), 7.13(d, $J=7.2$ Hz, 4H), 6.97(d, $J=3.2$ Hz, 2H), 6.67(d, $J=7.2$ Hz, 2H), 6.37-6.34(m, 4H), 4.53(s, 4H), 4.31(d, $J=2.4$ Hz, 4H), 4.05(d, $J=2.4$ Hz, 2H), 3.65-3.62(m, 4H). FT-IR (KBr) $\tilde{\nu}$: 3379, 2926, 2854, 1576, 1511, 1415, 1264, 1150, 1079, 822. MS-TOF (m/z): calcd for $(\text{C}_{34}\text{H}_{34}\text{N}_4\text{O}_{10})$: 658.2275, found 658.2278.



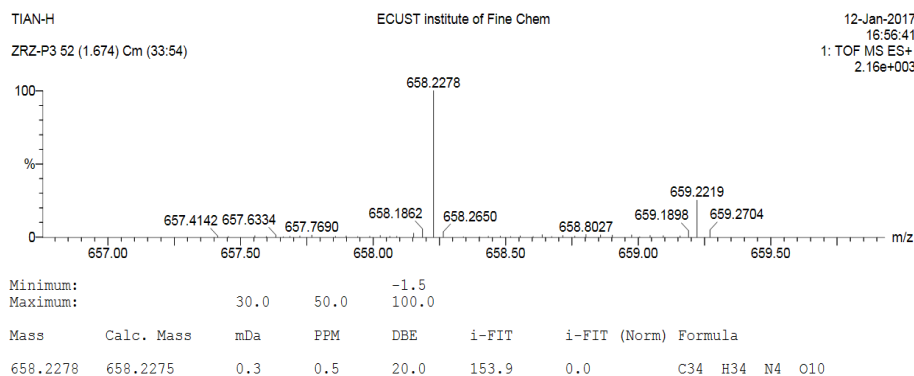


Figure S2 ^1H NMR and MS of DFTPN

Synthesis of DFTPA-PI: 10 mL glacial acetic acid and zero valent iron (5 g) was stirred in a flask at 60°C under nitrogen protection for 0.5 h, DFTPN (1.3 g, 2 mmol) in 100 mL dichloromethane solution was added and fiercely stirred for 12 h. The organic solution was washed three times with 0.5 M aqueous sodium hydroxide and water, filtrated with diatomite and dried with anhydrous Na_2SO_4 . The obtained solution was evaporated under vacuum to give a pale-yellow solid DFTPA, then the solid was dried under vacuum at 80°C for 24 h.

DFTPA (0.6 g, 1 mmol) and 3 mL dry dimethylacetamide (DMAc) were stirred in a flask under nitrogen protection, anhydrous ODPA (0.31 g, 1 mmol) was separately added in three times, then the mixture was stirred at room temperature for 24 h. 2 mL dry triethylamine was added into the reaction and kept 80°C for 12 h. Upon cooling, the mixture was poured into methanol (100 mL) to give a precipitate, and collected by suction filtration and dried to obtain the brown-yellow solid.² ^1H NMR (400MHz, D_6 -DMSO) δ : 8.24(d, J =8.8 Hz, 2H-Ph), 7.74(d, J =2.4 Hz, 2H-Ph), 7.58-7.67(m, 4H-Ar), 7.19-7.23(m, 4H-Ar), 6.21-6.47(m, 12H-Ar), 4.48 (s, 4H), 4.40-4.45(m, 6H), 3.35-3.45(m, 4H). FT-IR (KBr) $\tilde{\nu}$: 3403, 2992, 1709, 1585, 1507, 1474, 1360, 1265, 1225, 1150, 1086, 920, 821, 751, 599. The weight-average of the polyimide DFTPA-PI was observed as the polystyrene standards, M_n was 53.2 kDa, PDI (M_w/M_n) was 2.14.

Preparation of DFTPA-PI-MA: 0.45 g DFTPA-PI and 0.16 g MA were dissolved in 5 mL DMAc, the mixture was stirred at 110°C for 4 h. After reaction, the solvent DMAc was evaporated under vacuum to obtain a brown-yellow copolymer. ^1H NMR (400MHz, D_6 -DMSO) δ : 8.25(d, J =8.8 Hz, H-Ph), 7.74(d, J =2.8 Hz, H-Ph), 7.60-7.64(m, H-Ar),

7.12-7.32(m, *H-Ar*), 6.39-6.68(m, *H-Ar*), 4.73(s, *CH₂-Furan*), 4.37-4.42(m), 3.64-3.97(m), 3.35-3.39(m), 2.50-3.03(m, *H-DA group*). FT-IR (KBr) $\tilde{\nu}$: 3414, 2362, 2292, 1709, 1593, 1510, 1474, 1386, 1264, 1225, 1191, 1150, 1061, 969, 740, 601.

Characterization

The infrared spectrum was observed by FT-IR (8400s, SHI-MADZU), high resolution mass spectra (HRMS) data were determined with FTICR-APEX instrument, nuclear magnetic resonance (NMR) spectra were measured on Brücker AM 400 NMR instrument. All the structural characterization results were consistent with the target compounds.

The electrochemical processes of copolymer DFTPA-PI-MA film, coated on the ITO glass substrate was analyzed by the cyclic voltammetry (CV) on CHI660C electrochemical workstation in electrolyte solution by the three-electrode, the reference electrode was Ag/AgCl in saturated, Pt sheet as the counter electrode, copolymer DFTPA-PI-MA coated onto ITO glass substrate as the work electrode, using 0.1 mol·L⁻¹ LiClO₄ in CH₃CN solution as electrolyte.

Optical property and kinetic feature of the copolymer DFTPA-PI-MA film was observed by spectrophotometer (UV-2250, SHI-MADZU) and CHI660 electrochemical workstation. Electrochemical measurements were performed using a home-made three-electrode cell with a platinum wire as the counter electrode, Ag stick as the reference electrode, the copolymer DFTPA-PI-MA film coated on ITO glass substrate as work electrode, using 0.1 mol·L⁻¹ LiClO₄ in CH₃CN solution as electrolyte. A situ colorimeter (SP60, X-Rite) was used to test chromaticity of the polymer film, which was switched to different states by amperometric *i-t* method on the electrochemical workstation before tests. Each states of the film were tested at least three times to access average values.

The surface morphology of the DFTPA-PI-MA film before and after electrochromic circulations was measured by scanning electron microscope (SEM, JEOL, JSM-7600F). Thermogravimetric analysis (TGA) was conducted with a WRT-1D (Beijing). Experiments were carried out on approximately 3-5 mg of samples heated in flowing of nitrogen (flow rate 35 cm³ min⁻¹). Differential scanning calorimetry (DSC) analyses

were performed on Q200 (TA, USA) at a heating rate of 10 °C min⁻¹ in flowing of nitrogen (flow rate 50 cm³ min⁻¹). Mechanical tensile strength was tested by the electronic universal material testing machine (ITW-5967, USA).

The FT-IR spectrum of copolymer DFTPA-PI-MA showed difference with DFTPA and DFTPA-PI, as shown in Figure S3. The peaks at 1709 and 1191 cm⁻¹ in the spectrum was ascribed to stretching vibrations of C=O bond as well as asymmetric and symmetric stretching vibrations of C-C bond, which were specific to the D-A adduct group.³ Meanwhile, the peak at 1147 was ascribed to the furan ring, and the intensity of DFTPA-PI-MA was much lower than that of DFTPA-PI, which was due to the furan ring was consumed by MA. All the evidence showed that the DFTPA-PI-MA was synthesized successfully.

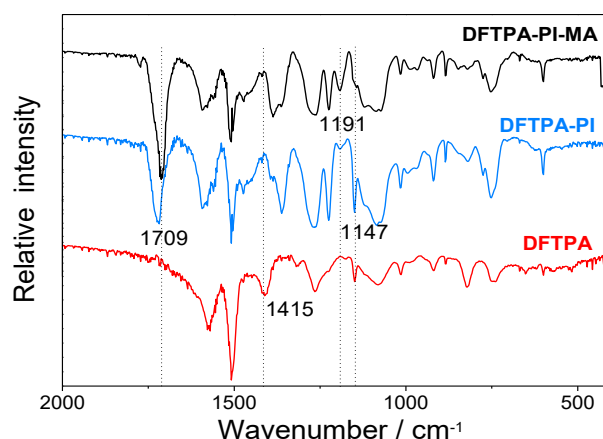


Figure S3 FT-IR spectra of DFTPA-PI-MA, DFTPA-PI, DFTPA.

Equilibrium swelling experiments⁴ were employed to determine the cross-link density of the resultant copolymer DFTPA-PI-MA, three weighted pieces of copolymer samples were immersed in the toluene at room temperature to achieve their swollen equilibrium. Then, the swollen copolymer DFTPA-PI-MA were blotted with tissue paper to remove the excess of the toluene and immediately weighted. Finally, the swollen copolymer DFTPA-PI-MA samples were dried at 60°C until constant weight was obtained. The cross-link density was determined from the Flory-Rehner⁵ equation (1):

$$-[\ln(1-\Phi_r) + \Phi_r + \chi\Phi_r^2] = V_{0n} (\Phi_r^{1/3} - \Phi_r/2) \quad (1)$$

The average mean molecular weight was also calculated from the equation 2:

$$\bar{M}_c = -\rho_2 V_0 \Phi_r^{1/3} / [\ln(1-\Phi_r) + \Phi_r + \chi \Phi_r^2] \quad (2)$$

where Φ_r is the volume fraction of copolymer DFTPA-PI-MA in the swollen mass. V_0 is the molar volume of the toluene (106.2 cm^3) and n is the number of active network chain segments per unit of volume (cross-link density). χ is the Flory-Huggins polymer-solvent interaction term, which is 0.44 for toluene. The Φ_r was obtained according to Bala *et al.*⁶ and the equation 3:

$$\Phi_r = (m_2/\rho_2) / [m_2/\rho_2 + (m_1-m_2)/\rho_1] \quad (3)$$

where m_1 and m_2 are the mass of swollen copolymer DFTPA-PI-MA before and after dried, respectively. ρ_1 and ρ_2 are the densities of toluene ($\rho_1 = 0.865 \text{ g/cm}^3$) and copolymer DFTPA-PI-MA ($\rho_2 = 1.341 \text{ g/cm}^3$), respectively. The \bar{M}_c and n were calculated as 520.3 and 0.04 mol/cm^3 , respectively. The results indicate that the most FGE group was cross-linked with the MA group.

To evaluate the thermodynamic stability of polymer DFTPA-PI, MA and copolymer DFTPA-PI-MA, DSC and TGA curves were shown in Figure S4. The DSC curve of MA showed two sharp endothermic peaks, while the TGA curve had no obvious weight loss below 450°C , so the peaks located at 160 and 170°C in DSC curve could be ascribed to the fusion and crystal transfer. The DSC curve of DFTPA-PI has two peaks, the endothermic peak located at $210\sim 270^\circ\text{C}$ was ascribed to the fusion, while the broad exothermic peak in the range of 305 to 395°C can be ascribed to the decomposition of FGE groups in the structure of DFTPA-PI. TGA curve of the DATPF-PI was shown in Figure S4a: the first stage at 240 to 390°C with 31.2% weight loss is due to the decomposed the FGE group of DFTPA-PI, and the second stage at 410 to 610°C with 54.7% weight loss can be ascribed to the decomposition of the PI chains. The DSC curve of copolymer DFTPA-PI-MA had two endothermic peaks and one exothermic peak: the broad endothermic peaks in the range of 100 to 170°C was due to the breakage of DA bonds in DFTPA-PI-MA, the second endothermic peak, as same as polymer DFTPA-PI, was also observed as the fusion, and the exothermic peak ranged from 290 to 320°C was ascribed to the copolymer decomposition. TGA curve of copolymer DFTPA-PI-MA (Figure S4B) shows that the copolymer was decomposed in three stages: the first stage at 291.4 to 406.6°C with 27.6% of weight loss represented

the decomposition of FGE groups, the second stage with the weight loss of 31.7% was observed at 406.6 to 568.2°C as the breakage of MA and PI chains, the last stage in the range of 568.2 to 892.7°C is PI chain decomposed with about 30.9% weight loss. The final residual weight was about 9.8% after the calcinations at 900°C. All the DSC and TGA curves showed that copolymer DFTPA-PI-MA had excellent thermodynamic stability, and can be used for the self-healing materials with great reliability and safety even at 110°C.

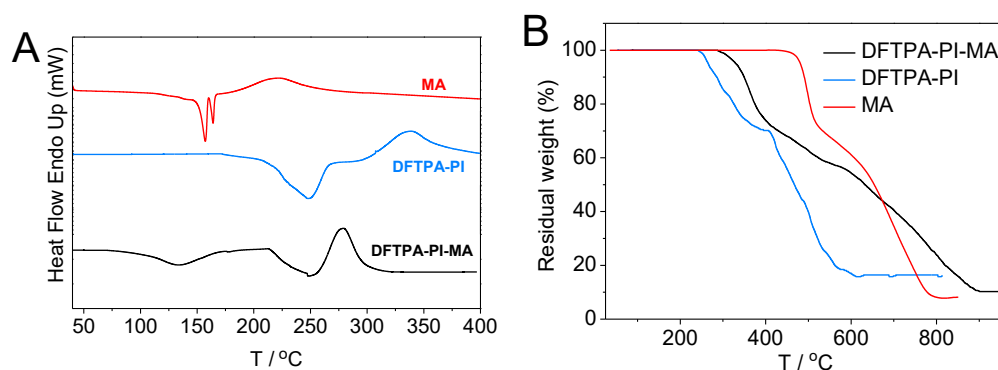
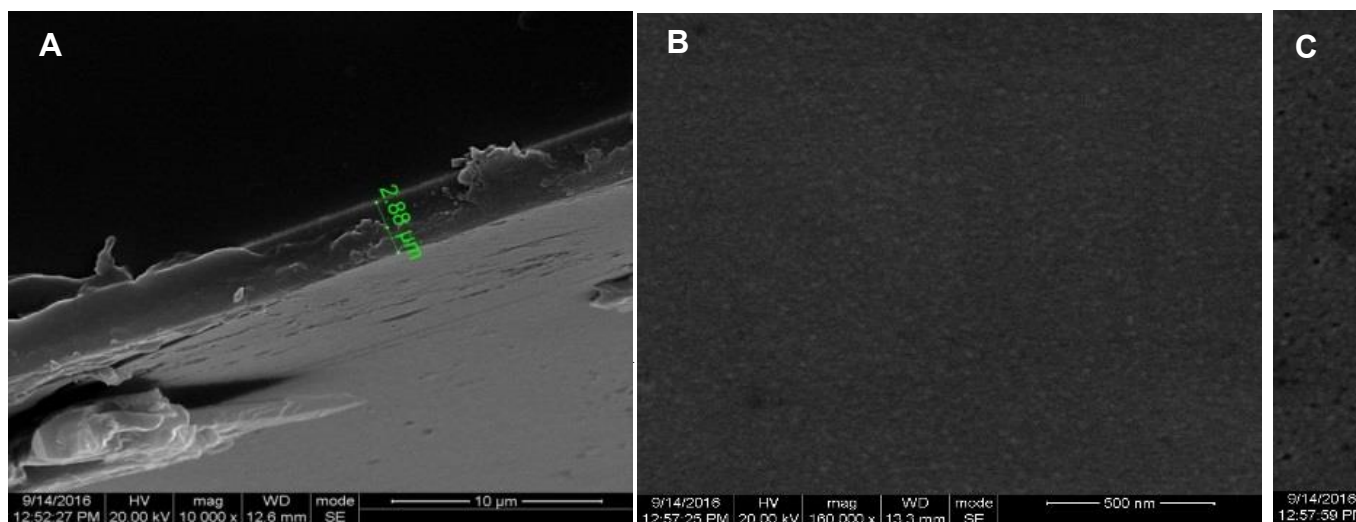


Figure S4 Thermodynamic analysis of DFTPA-PI-MA, DFTPA-PI, MA.

(A) DCS curves. (B) TGA curves.



The copolymer DFTPA-PI-MA solution (35 μL , 50 mg/mL) was dropped onto a clean ITO glass substrate ($0.8 \times 2 \text{ cm}^2$), and spread into a homogeneous copolymer DFTPA-PI-MA film (about 3~5 μm , Figure S5A) using a plastic scraper. The morphology of copolymer DFTPA-PI-MA film was investigated by SEM. It was observed that the surface was relatively smooth and uniform before the CV test (Figure S5B), while different sizes of holes appeared on the surface after several CV test (Figure S5C). It may be attributed to that the Li^+ ions repeatedly inserted/ extracted the film, which resulted in the formation of holes.



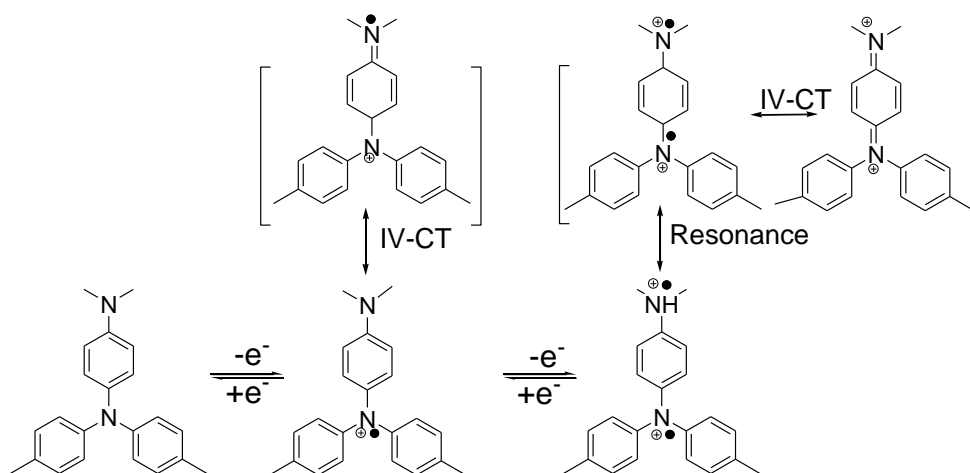
(A) the cross-sectional SEM image, the surface of the film before (B) and after (C) cyclic voltammetry circles.

The colors of DFTPA-PI-MA film were valued by the colorimetric analysis. To defined the color regularly, the chromaticity instrument was used to test the L^* (luminance), a^* (hue), b^* (saturation) parameters of copolymer DFTPA-PI-MA film and the corresponding film images under different voltages is shown in the Table S1, respectively.

Table S1 Color parameters and optical images of DFTPA-PI-MA film

Voltage (V)	L^*	a^*	b^*	Color	Picture
0	61.49	-1.12	38.85	Light brown-yellow	
1.1	41.13	-5.49	18.07	Olive green	

Scheme S2 Postulated redox behavior of copolymer DFTPA-PI-MA.



The preparation process of copolymer DFTPA-PI-MA film was described in Figure S6. Copolymer DFTPA-PI-MA solution (3 mL, 50 mg/mL) was dropped onto a teflon substrate ($5 \times 5 \text{ cm}^2$), the solution was rolled using a plastic scraper and dried at 80°C for 6 h under vacuum to evaporate DMAc solvent. The copolymer film was peeled off using a blunt forcep to obtain a free-standing and flexible film.

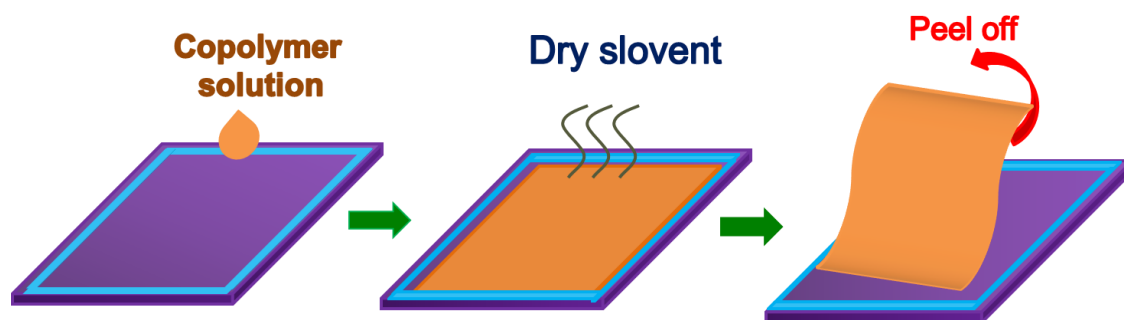


Figure S6 The schematic diagram of the copolymer film preparation.

Copolymer DFTPA-PI-MA film was coated on the flexible silver conductive substrate to obtain the electrochromic fabric, and the method of the copolymer film was shown in Figure S7A. The same copolymer DFTPA-PI-MA solution (1.25 mL) was also dropped over a teflon substrate ($4 \times 5 \text{ cm}^2$), and then the majority of solvent evaporated leading to the viscous solution. The concentrated copolymer DFTPA-PI-MA solution was coated on a silver conductive fabric to evaporate the rest of solvent. By this method, the copolymer can be attached closely with the fabric. The back of the electrochromic fabric was cleaned by the cotton swabs with solvent DMAc.

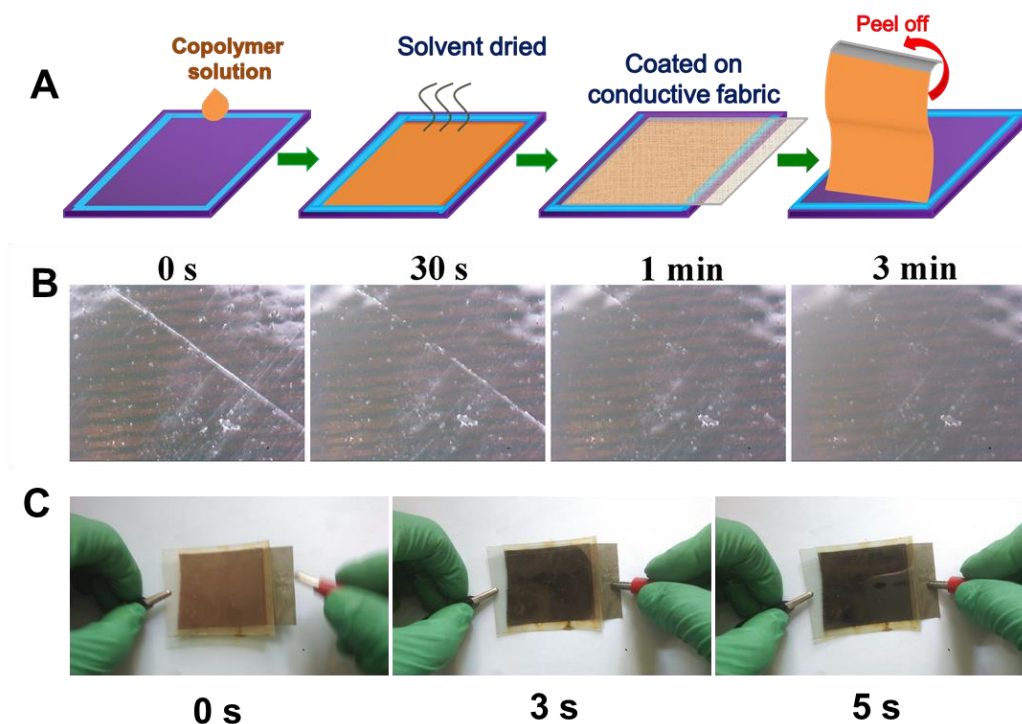


Figure S7 (A) The schematic preparation procedure of the electrochromic fabric, (B) the self-healing of the electrochromic fabric, (C) the flexible electrochromic skin switching colors process

under 1.2 V.

The self-healing of the electrochromic fabric was also investigated, as shown in Figure S7B. The copolymer film was scratched by a razor blade (about 20 μm), and the healing process at 110°C was observed by optical microscopy. The scratched region started to heal in the first 30 s, and gradually healed and blurred after 1 min, then completely healed after 3 minutes. The self-healing process was similar to the healing of copolymer film coated on ITO glass substrate. The electrochromic skin switched the colors between faint yellow and olive green under 0 V, 1.2 V with different states, respectively. The electrochromic skin became faint green about 3 s and then switched to olive green about 5 s under the voltage of 1.2 V (Figure S7C), and return to faint yellow at the voltage of 0 V with the bleach time about 20 s.

Notes and references

1. Chang, C. W.; Liou, G.S.; Hsiao, S. H. Highly stable anodic green electrochromic aromatic polyamides: synthesis and electrochromic properties. *J. Mater. Chem.* **2007**, 17, 1007–1015.
2. Cheng, S. H.; Hsiao, S. H.; Su, T. H.; Liou, G. S. Novel aromatic poly (amine-imide) s bearing a pendent triphenylamine group: synthesis, thermal, photophysical, electrochemical, and electrochromic characteristics. *Macromolecules* **2005**, 38, 307–316.
3. Dolci, E.; Michaud, G.; Simon, F.; Boutevin, B.; Fouquay, S.; Caillol, S. Remendable thermosetting polymers for isocyanate-free adhesives: a preliminary study. *Polym. Chem.* **2015**, 6, 7851–7861.
4. Nie, Y. J.; Huang, G. S.; Qu, L. L.; Zhang, P.; Weng, G. S.; Wu, J. R. Cure kinetics and morphology of natural rubber reinforced by the in situ polymerization of zinc dimethacrylate. *J. Appl. Polym. Sci.* **2010**, 115, 99–106.
5. Flory, P. J. Statistical mechanics of swelling of network structures. *J. Chem. Phys.* **1950**, 18, 108–111.
6. Bala, P.; Samantaray, B. K.; Srivastava, S. K.; Nando, G. B. Organomodified montmorillonite as filler in natural and synthetic rubber. *J. Appl. Polym. Sci.* **2004**, 92, 3583–3592.