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Electrochromic/electrofluorochromic poly(urea-urethane) bearing oligoaniline and tetraphenylethylene groups: Synthesis, characterization, and H_2O_2 visualized determination



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ABSTRACT

The elegant electroswitchable color/emission properties of electrochromic/electrofluorochromic dual-functional materials motivates the exploration of their new applications. In this work, a new poly (urea-urethane) was synthesized via nucleophilic copolymerization of electroactive oligoaniline derivative, solid-emissive tetraphenylethylene groups, and alkyl isocyanate. The resultant poly (urea-urethane) exhibited good electroactivity and desirable aggregation-induced emission properties. High-performance electrochromic/electrofluorochromic behavior had been disclosed with a high optical contrast ratio of $\Delta T = 50.4\%$, a moderate fluorescence on/off ratio of 10.5, and high coloration efficiency of 503 cm²/C at 768 nm. A reflective/emissive dual-mode display device had also been manufactured based on the resultant poly (urea-urethane) and charge-balancing V₂O₅, exhibiting a reversible color change and tunable fluorescence rownersion upon the electric stimulus. Furthermore, this polymer showed an interesting color/fluorescence response to H₂O₂, due to the linkage mechanism between its redox states and optical properties. The spray-coated poly (urea-urethane) test strips were employed in visualized dual-determination of H₂O₂ with gradual color change from gray to dark green, along with an obvious fluorescence change from light blue to dark, which displays easy operation and rapid detection.

1. Introduction

Electrochromic/electrofluorochromic (EC/EFC) dual-functional materials have attracted great attention and interest from researchers because of their elegant electroswitchable color/emission feature [1-3]. Thereinto, the polymeric materials exhibit the tremendous advantage of flexible molecular design and engineering, tunable photoelectric properties, as well as facile large-scale processability [4-6]. Hence, a series of EC/EFC dual-functional polymers have been prepared through multifarious synthetic strategies. For example, several novel functional monomers integrated propeller structural triphenylamine and high-efficiency fluorophore have been designed to prepare EC/EFC dual-functional polymers, yielding a rational color/emission switching behavior under electric stimuli [7–10]. The oligoanilines have also been utilized as electroactive units to construct EC/EFC polymeric systems, due to their low redox potentials and reversible electroactivity. The resultant polymers exhibit improved electroswitchable color/emission behavior with low energy consumption and well electrochemical durability [11–13]. To eliminate the aggregation-caused quenching effect, some high solid fluorescence-efficiency tetraphenylethylene (TPE) derivatives have been involved in the dual-functional polymeric architecture [14–20]. As is expected, high-performance EC/EFC properties with approving fluorescence on/off ratio are revealed from these resultant TPE-based materials. Moreover, a few fluorescent quantum dots (CdS dots, carbon dots) were adopted to manufacture polymer composites, which show high fluorescence contrast, fast response time, and new functions such as light-induced coloration, electrochemiluminescence, and photocurrent responsiveness [21–23].

By means of multifarious synthetic tactics, the improvement of EC/ EFC performance has received a relatively matured development. However, the application exploit of these EC/EFC polymers is still an infant. Only a few practicality explorations have been revealed, such as anti-counterfeiting inks [24], reflective/emissive dual-mode displays [25], energy storage level color/fluorescence dual-indicating supercapacitor [26], smart sensors for cyanide anions and cancer cell surface glycoprotein [27,28]. Nevertheless, more effort should be devoted to the

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further application expansion and deep practical exploration of EC/EFC dual-functional polymers.

In this paper, a novel poly (urea-urethane) (PUU) bearing electroactive oligoaniline and AIE-active TPE groups via nucleophilic copolymerization reaction. The EC and EFC performance of the resultant PUU was disclosed through the electrochemical workstation coupled with a UV–vis spectrometer and/or fluorescence spectrometer. In addition, an improvised test strip featuring EC/EFC was manufactured to achieve sensitive monitoring of H_2O_2 . The visualized color/fluorescence dualdetermination of H_2O_2 was accomplished as a result of the redox reaction (between oligoaniline and H_2O_2) and the energy transfer (between oligoaniline and TPE).

2. Experimental section

2.1. Materials

Benzophenone, bis(4-hydroxyphenyl)methanone, titanium tetrachloride (TiCl₄), zinc powder (Zn), hexamethylene diisocyanate (HMDI) were purchased from Aladdin. Hydrogen peroxide (H₂O₂, 30% mass fraction) were obtained from Sinopharm Chemical Reagent Co., Ltd. Potassium carbonate (K₂CO₃), hydrazine monohydrate (N₂H₄·H₂O), polymethyl methacrylate (PMMA), propylene carbonate (PC), *N*,*N'*dimethylformamide (DMF), lithium perchlorate (LiClO₄), dichloromethane (DCM) and tetrahydrofuran (THF) were purchased from Energy Chemical. Other reagents and solvents were employed directly as received from commercial sources. The indium tin oxide glass (ITO, 10 Ω /cm²) was obtained from Zhuhai Kaivo Optoelectronic Technology Co., Ltd.

2.2. Synthetic procedure

2.2.1. Synthesis of 4,4'-(2,2-diphenylethene-1,1-diyl)diphenol (DEDO)

DEDO was synthesized by a common McMurry approach [29]. A mixture of benzophenone (4.00 g, 21.97 mmol), bis(4-hydroxyphenyl) methanone (4.70 g, 21.97 mmol), Zn power (5.70 g, 88 mmol), and 150 mL anhydrous THF was mixed into a two-necked flask, and cooled down to -78 °C. Then drop-by-drop addition of 9.7 mL TiCl₄ (87.8 mmol) into the above mixture was performed under nitrogen atmosphere. The solution was kept at -78 °C under constant stirring for 30 min and further warmed to room temperature (RT) for another 8 h. It was continued to reflux at 70 °C for an additional 15 h. After cooling down, the reaction was quenched by the addition of a saturated K₂CO₃ solution. The mixtures were then extracted with DCM to remove any soluble hydrocarbons, followed by washing with 0.1 M HCl solution and drving with Na₂SO₄. After the solvent was removed by rotary evaporation, the raw product was purified by column chromatography (SiO₂, DCM/petroleum ether, V/V = 1:3-1:5) to render DEDO as pale yellow solid (6.80 g, 85% yield). FTIR (KBr, cm⁻¹): 1607, 1594, 1505, 1441 (-C=C- stretch in the aromatic region), 3311 (-OH stretch). ¹H NMR (400 MHz, DMSO-*d*₆): δ 9.30 (s, 2H, –OH), 7.14–7.05 (m, 6H), 6.95–6.90 (m, 4H), 6.73 (d, J = 8.6 Hz, 4H), 6.48 (d, J = 8.6 Hz, 4H). ¹³C NMR (101 MHz, DMSO-d₆): δ 156.34, 144.65, 141.07, 138.11, 134.56, 132.51, 131.24, 128.23, 126.44, 115.03. HRMS(ESI): m/z: calcd for $[M+H]^+ C_{26}H_{21}O_2$: 365.1536, found: 365.1531. $\Phi F = 28.25\%$. Tm (m.p. by DSC): 195 °C.

2.2.2. Synthesis of 2,6-bis(4-aminophenoxy)-N-(4-(phenylamino)phenyl) benzamide (TA-NH2)

TA-NH2 was synthesized by a series of oxidative coupling reaction, amidation reaction, and nucleophilic substitution according to the established method [30]. All the characterization data are presented as follow. FTIR (KBr, cm⁻¹): 3385 (-NH₂ stretch), 1661 (amide group). ¹H NMR (400 MHz, DMSO-*d*₆): δ 10.28 (s, 1H), 7.78 (s, 1H), 7.73 (s, 1H), 7.65 (s, 1H), 7.58 (d, *J* = 8.9 Hz, 2H), 7.16 (dd, *J* = 10.4, 5.0 Hz, 3H), 6.98 (ddd, *J* = 16.5, 7.8, 4.8 Hz, 13H), 6.89–6.84 (m, 4H), 6.70 (t, *J* =

7.3 Hz, 1H), 6.64–6.58 (m, 4H), 6.34 (d, J = 8.4 Hz, 2H), 5.03 (s, 4H). ¹³C NMR (101 MHz, DMSO- d_6): δ 162.08, 157.18, 145.93, 145.93, 145.70, 145.65, 141.00, 138.92, 137.74, 136.41, 135.06, 131.41, 129.90, 121.51, 120.84, 120.65, 119.85, 119.34, 118.44, 118.09, 117.80, 115.87, 114.94, 114.79, 109.06. HRMS (ESI): m/z: calcd for [M – H]⁺ C₄₃H₃₆N₆O₃: 683.2765, found: 683.2769. Tm (m.p. by DSC): 156 °C.

2.2.3. Synthesis of PUU

DEDO (219 mg, 0.6 mmol), TA-NH2 (618 mg, 1.2 mmol), HMDI (301 mg, 1.8 mmol), and 6 mL of DMF were added in a dry roundbottom flask under N₂ atmosphere. The random copolymerization was carried out at 60 °C for 36 h, followed by precipitation successively from ethanol and DCM solution, yielding 1.02 g of PUU for light gray powder with 90% yield. ¹H NMR (400 MHz, DMSO-*d*₆): δ 9.40, 9.35 (–CONH–), 8.47, 8.34 (–NHCONH–), 7.78, 7.71 (–NH– in the TA-NH2), 7.51–6.41 (mH, Ar–H), 6.13, 5.75 (–NHCONH–), 4.02–3.62 (mH, –CH₂-), 3.10–2.89 (mH, –CH₂-), 2.76–2.65 (mH, –CH₂-). FTIR (KBr, cm⁻¹): 3426 ($\nu_{\rm N-H}$), 2927 ($\nu_{\rm C-H}$ of aryl groups), 1651 ($\nu_{\rm C}$ =0), 1514, and 1442 ($\nu_{\rm C}$ =C of benzenoid rings), 1098 ($\nu_{\rm C-N}$). Gel permeation chromatography (GPC) date: Mw: 130800, polydispersity index: 2.10.

2.3. Fabrication of PUU/ITO electrode

The ITO substrates were cut into a square shape with a dimension of $3 \times 3 \text{ cm}^2$ or $1 \times 5 \text{ cm}^2$ for the electrochemical measurements (sheet resistance = 10 Ω/cm^2), which were ultrasonically cleaned with toluene, acetone, alcohol, and ultrapure water for 30 min, respectively. After dried with N₂ flow, the ITO substrates were performed to hydrophilization using Plasma Cleaner under O₂ flow. Finally, the PUU/ITO electrodes were manufactured through the drop-coating method using 100 µL 3 mg/mL PUU DMF solution and following dried at 50 °C under vacuum. The size of the PUU capacity was set at 1 cm² (area) × 400 nm (thickness) measured by a profilometer.

2.4. Manufacture of PUU test strips

A typical procedure to fabricate test strips based on PUU is stated as follows. The qualitative filter paper was cut with a dimension of 1×5 cm². Then the top of the filter paper strip (1×1 cm² area) was spray-coated with PUU through a high-pressure spray gun using 5 mg/mL PUU DMF solution. The spraying time was fixed at 5 s. The resultant test strips would be dried with an N_2 flow and then sealed storage for the following testing analyses of H₂O₂.

2.5. The H_2O_2 visualized determination with PUU test strips

The as-fabricated PUU test strips were immersed into the H_2O_2 solution (pH = 1, adjusted by HCl solution) for 30 s and dried under the air atmosphere for another 30 s. The change of color and fluorescence was collected by the spectrum instruments as well as a digital camera.

2.6. Instrumentation

¹H NMR and ¹³C NMR spectra of the synthetic molecules were received on a Bruker Avance NEO 400 system (400 MHz) using deuterated dimethyl sulfoxide (DMSO-*d*₆). All the chemical shifts were presented in ppm using tetramethylsilane as the internal standard. BRUKER VECTOR 22 Spectrometer was used to gather the Fourier-transform infrared spectra (FTIR) in the range of 4000–400 cm⁻¹. High-resolution mass spectra (HRMS) signs were collected on the Bruker Agilent1290-micrOTOF Q II. The thermal stability of PUU was measured by thermogravimetric analysis (TGA) on PerkinElmer PYRIS 1 TGA in the temperature range of 100–800 °C with a rate of 10 °C/min under N₂ flow. Differential scanning calorimetric (DSC) analysis was carried out on DSC821e at a scanning rate of 10 °C/min using 50 mL/min nitrogen

flow for the melting point test. The transmittance and/or absorption spectrum of PUU were monitored using UV–vis spectra on a UV-3101 PC spectrometer (SHIMADZU). Photoluminescence (PL) spectra were collected on an F97Pro fluorospectro photometer (Shanghai Lengguang Co. Ltd., Shanghai, China). Fluorescence quantum yields (Φ F, tested by using a calibrated integrating sphere) were determined using an Edinburgh FLS920fluorescence spectrophotometer. The data of CIE *L**a*b* were obtained from a high-quality portable colorimeter (Shenzhen 3 nhCo., Ltd., Shenzhen, China). The cyclic voltammetry (CV) and electrochemical impendence spectroscopy (EIS) for PUU was collected on a CHI 660E Electrochemical Workstation (CH Instruments, USA) using a three-electrode electrochemical cell, which was constituted with an Ag/ AgCl reference electrode, a platinum counter electrode, and a PUU/ITO working electrode.

3. Results and discussion

3.1. Synthesis and structure characterization

As shown in Scheme 1, the AIE-active DEDO was synthesized through McMurry coupling reaction catalyzed by $Zn-TiCl_4$, which was used as a general tactic to prepare AIE compounds. Scheme 1 also displays the synthesis of novel poly (urea-urethane) via nucleophilic copolymerization of DEDO, TA-NH2, and HMDI. In this smart electro-optical polymeric architecture, the TPE-derived DEDO unit is held accountable for the membrane-state emission, and tetraaniline is utilized as an electro-control unit attributed to its low redox potentials and excellent reversibility. To suppress the charge transfer effect, an

aliphatic linkage has also been involved in the polymeric structure.

The ¹H NMR and ¹³C NMR spectra of the as-synthesized monomers (DEDO and TA-NH2) are presented in Fig. 1. The chemical shift at 9.3 ppm is assigned to the hydroxy groups of DEDO. The aromatic signals of DEDO can be found from 6.47 ppm to 7.14 ppm. The characteristic signals of amino groups of TA-NH2 appear at 10.28, 7.78, 7.73, 7.65, and 4.13 ppm, and terminal amino groups at 5.03 ppm. In the ¹³C NMR spectra, all the chemical shifts and splits of carbon groups could verify their molecular structure well, respectively. Moreover, the FTIR spectra were also utilized to characterize the molecular structure of the monomers. Fig. 2a shows the characteristic vibration of -OH stretch at 3311 cm⁻¹, and the skeleton vibration of the aromatic ring at 1607, 1594, 1505, and 1441 cm⁻¹ for the DEDO monomer. In the FT-IR curve of TA-NH2, the peak at 3385 cm^{-1} and 1661 cm^{-1} can be assigned to the stretching vibration of -NH2 and amide groups. In addition, these structures of DEDO and TA-NH2 were further accurately confirmed by high-resolution mass spectrometry (HRMS) data.

The polymeric structure of the as-prepared PUU was carefully investigated through FT-IR spectrum, ¹H NMR spectrum, and GPC measurement. The FTIR spectrum in Fig. 2a shows the characteristic absorption around 3426 cm⁻¹, corresponding to the N–H stretching vibration, and around 2927 cm⁻¹ due to the C–H stretching vibrations of aryl groups. The vibration around 1651 cm⁻¹ is attributed to the stretching vibration of carbonyl groups. The stretching vibration of C=C groups in the benzene rings is observed at 1514 and 1442 cm⁻¹. The characteristic stretching vibration of C–N appears at 1098 cm⁻¹. Fig. 2b illustrates the ¹H NMR spectrum of the as-prepared PUU. The peaks of 9.40, 9.35 ppm according to the –CONH–, the peaks of 8.47, 8.34, 6.13,



Scheme 1. Synthetic procedure for AIE-active DEDO and PUU.



Fig. 1. (a) ¹H NMR spectra and (b) ¹³C NMR spectra of DEDO; (c) ¹H NMR spectra and (d) ¹³C NMR spectra of TA-NH2.



Fig. 2. (a) FTIR spectra of DEDO, TA-NH2, and PUU. (b) ¹H NMR spectra of PUU. (c) TGA curve of the PUU under N₂ atmosphere.

5.75 ppm were matched to –NHCONH– in carbamide, the signs of 7.78, 7.71 ppm were assigned to –NH– in the TA unit. Furthermore, the PUU displays a general number-average molecular weight of 130800 with an acceptable polydispersity index of 2.10.

The excellent solubility is beneficial to the processibility of the polymeric materials towards large-scale production in the application.

The obtained PUU exhibits good solubility in polar solvents of DMF, DMSO, NMP, and DMAc, due to its large pendant groups and flexible aliphatic segments. Furthermore, the thermostability of PUU was evaluated by TGA. The resulting curve in Fig. 2c reveals that there is no weight loss before 225 °C. The 5% degradation is observed at the temperature of 289 °C, associated with the gradual decomposition of the



Fig. 3. (a) UV-vis absorption and PL spectra of PUU DMF solution and PUU film. (b) FL spectra of PUU in DMF-water mixture solution with diverse solvent ratio (inset: the images of fluorescence variation in different proportion solutions).

polymeric main chain. The overall thermal stability of PUU is quite satisfactory in the actual application scenario in the future.

3.2. Photophysical properties

Photophysical properties of PUU solution and PUU film were studied by UV-vis absorption and PL spectra as shown in Fig. 3a. The PUU absorbs the UV light with intense absorption maxima at $\lambda_{abs} = 295$ nm and 332 nm for its solution and film states, respectively, which were assigned to the $\pi \rightarrow \pi^*$ transition of the aromatic zone in AIEgens and TA-NH2. The obvious 37 nm red-shifted for the PUU film should be attributed to tight π - π packing in the solid aggregation state. Moreover, the PUU film is a highly fluorescent material showing intense emission in the blue region at $\lambda_{PL} = 436$ nm, whereas almost no fluorescence emission is observed in its solution state. The absolute fluorescence quantum yield of PUU film was measured to be 22.5%. It is obvious that this semblable AIE performance of PUU should be ascribed to the DODE groups. Hence the AIE behavior of PUU was further investigated by mixing H₂O as a poor solvent into the soluble DMF solution. The diverse blue light emission of the resulting PUU DMF-H₂O mixed solution with various proportions was observed with naked eyes. As increasing water content, the PUU aggregated to varying extent in the mixed system. A concentration-dependent blue light emission behavior was observed for PUU with the excitation light of 365 nm in Fig. 3b. The maximum fluorescent around $\lambda_{PL} = 436$ nm was enhanced with higher H₂O content. The respective photographs of enhanced blue emission were recorded as the inset in Fig. 3b. The distinct AIE phenomenon could be explained by the restriction of the intramolecular rotations mechanism proposed by professor Tang [31]. The flexible intramolecular rotations of TPE-analog units in the solution state dissipate the excited-state energy via the non-radiatively decay channel, while the restriction of free rotations in the aggregate state efficiently refrains the dissipation path, leading to the illustrious fluorescence emission. The intrinsic strong fluorescence of AIE polymer would ensure high fluorescence on/off ratio in the EFC process of PUU film.

3.3. Electrochemical properties

The reversibility and stability test of the PUU/ITO electrode was evaluated by cyclic voltammetry firstly, which was carried out in a three-electrode cell with PUU/ITO working electrode, Ag/AgCl reference electrode, and platinum wire counter electrode, respectively. The polyaniline and its derivatives usually display two pairs of redox peaks during the CV cycle, which indicates a typical two-step continuous two-electron redox transition from leucoemeraldine base (LEB) to emeraldine base (EB), and from the EB to pernigraniline base (PNB) [32]. However, the resultant PUU exhibited only one pair of redox peaks at 0.51/0.25 V as shown in Fig. 4a. It would be speculated as an incorporated redox process containing LEB/EB and EB/PNB, indicating an

integrated four-electron molecular transition of tetraaniline segments [33]. This simplified redox process of PUU material should be attributed to its low content of electroactive tetraaniline segments and fast scanning speed. Moreover, the CV curves remain stable after 200 cycles, benefiting from the high stability of PUU and good anchoring strength with the ITO substrate during the electrochemical measurements. Then the electrochemical activity of PUU was evaluated at different scanning speeds from 10 to 100 mV/s (Fig. 4b). The peak currents increased concomitantly with the elevated scanning rates, and a quasi-linear relationship between the peak current and the square root of the sweep rate further proves that a slow diffusion-controlled process dominates the electrochemical behavior. ESI measurements were applied to the PUU/ITO electrode for the conductivity test. The Nyquist curve was fitted by the Randles type equivalent circuit model to assess the electrical conductivity as shown in Fig. 4c. Charge transfer resistance (R_{ct}) estimated from the semicircle diameter in Nyquist plots was about 78 Ω and 110 Ω corresponding to the applied voltages of 1.0 V and 0 V, respectively, indicating that the voltage-driven PUU/ITO electrode facilitates counterion diffusion in the electrolyte.

3.4. Electrochromic performance

The spectroelectrochemical process was carried out to investigate the optical modulation and color switch upon the driven voltage. The PUU/ITO electrode was used as a working electrode in the spectroelectrochemical cell. Reversible and reliable color-skip was studied by sequential transmittance variation with incremental potential from 0 V to 1.0 V with a retention time of 100 s. There is an overall dropping of transmittance in the visible light band from 380 to 800 nm as shown in Fig. 5a, along with an apparent improvement in the UV- region from 300 nm to 380 nm. To elucidate valence electron transitions, the corresponding absorbance variation was also obtained by the classic Lamber-Beer law as follows:

$$A = \lg I_0 / I_t = -\lg T = \varepsilon bc \tag{1}$$

where A represents absorbance, I₀ represents the intensity of incident light, I_t represents the intensity of transmitted light, T is the transmittance, ε is the molar absorption coefficient, b is the optical path and c is the concentration. The resultant absorbance variation was plotted in Fig. 5b. The absorption peak around 350 nm should be ascribed to π - π * transition in the benzoid rings. While the absorption in the range of 400–800 nm could be assigned to the transitions between polaron and π/π^* . During this process, the PUU/ITO electrode switched from neutral light yellow (0 V, $L^* = 26.38$, $a^* = -0.33$, $b^* = 0.49$), to semi-oxidized blue (0.6 V, $L^* = 19.07$, $a^* = 2011$, $b^* = -0.36$), and finally to full oxidized dark blue (1.0 V, $L^* = 18.02$, $a^* = 3.10$, $b^* = 0.04$), respectively (Fig. 5c). The rapid transformation of two oxidation doped states in oligoaniline segments under an applied electric field facilitates the heterochromatic changes well.



Fig. 4. (a) CV curves of the PUU/ITO electrode through the driving voltage from 0 V to 1.0 V, with the scanning speed of 100 mV/s (b) CV curves of the PUU/ITO electrode with the gradient increasing scanning rate, the inset shows a linear correlation on the peak current of the redox with the square root of the scan rate. (c) EIS of the PUU film with different voltages of 0 V and 1.0 V.



Fig. 5. (a) Transmittance spectra and (b) absorbance spectra of PUU film under the applied potentials from 0 to 1 V in 0.1 M HCl solution. (c) Inset shows the color photographs of PUU/ITO electrode at different potentials. (d) The cycling stability of transmittance changes of PUU/ITO electrode in spectrochronoamperometry measurements. (e) The representative transmittance switching at 489 nm and 768 nm of PUU/ITO electrode under a step-voltage of 0 and 1.0 V. (f) Optical density vs charge density curves of PUU/ITO electrode.

The optical contrast and switching behavior of PUU/ITO were studied in the spectroelectrochemical cell by the chronoamperometry technology, repeatedly switching between the applied potentials of 0 V and 1.0 V with the retention time of 15 s, monitoring the optical response at specified wavelengths (Fig. 5d). The optical contrast is calculated from a relatively larger spectral change at 489 nm around 34% (Δ T1: changing from 75.8% to 41.8%) and at 768 nm around 50.4% (Δ T2: changing from 82.5% to 32.1%) between its bleaching and coloring states. The responsiveness for the coloring/bleaching switching was calculated to be 9.6 s/9.8 s and 8.2 s/7.8 s, respectively, as shown in Fig. 5d, which was determined from the response time of 90% transmittance fluctuation at 489 nm and 768 nm. The periodic contrast response is shrunk markedly compared to that in prolonged voltage field under square wave voltammetry, mainly attributed to its hasty residence time in which the electron transfer or doping cannot reach saturation. Subsequently, the cycling performance of spectrum fluctuation for PUU film was presented in Fig. 5e. Applying the alternative potentials of 0 V and 1.0 V with the residence time of 15 s, the PUU/ITO electrode exhibits acceptable cycling performance after 200 cycles. It still retains 80.3% and 84.7% optical contrast at the respective wavelengths, indicating the well electrochemical reversibility and stability of PUU film. The strong hydrogen bond interaction between urethano/urea groups and hydroxyl groups on ITO substrate, coupled with agile and reversible redox nature in oligoaniline segments would enhance the charge transfer rate in the interface effectively, which is favorable for the improvement of electrochromic performance.

In addition, coloration efficiency (CE) is a key parameter, defining the charge utilization during the optical contrast change and thus expressing the charge efficiency of EC materials widely. CE can be determined according to the following eq (2):

$$CE = \Delta OD/\Delta Q = \log(T_b/T_c)/\Delta Q$$
 .2

where ΔQ represents the transmissive charge density of the active region of PUU/ITO, which can be calculated by corresponding I-t integral curve from chronoamperometry experiment. T_b and T_c are the transmittance values of bleached and colored states at a specified wavelength for a square signal voltage. The curves of Δ OD vs charge density at 489 nm and 768 nm were presented in Fig. 5f. The CE value of the polymer PUU obtained from the slope of the quasi-linear curve was about 322 and 503 $\rm cm^2/C$ at 489 nm and 768 nm, indicating a higher electron utilization efficiency for the electroactive PUU compared to numerous classic EC polymeric materials [9–13,22,23,34–36].

3.5. Electrofluorochromic performance

Considering the light-emitting performance of classical AIEgens in aggregation state as well as the fluorescence quenching effect of oxidized oligoaniline segment, we would study the EFC properties of PUU integrated above two functions in the molecular design. It is expected extremely that the higher brightness AIEgens and electroactive oligoaniline segments could also assemble a subtle EFC system. Above all, the EFC performance of PUU was investigated by monitoring the fluorescence fluctuation through these continuously driven voltages. The PUU film gives bright blue emission, centered at 438 nm derived from the localized emission of TPE unites in the neutral state as shown in Fig. 6a, with a moderate fluorescence quantum yield of 22.5%. As the applied voltage increases from 0.0 to 1.0 V with a retention time of 100 s, the emission of PUU film decreases gradually, almost resulting in 97% fluorescence quenching (at 1.0 V) compared with its original emission state at 0.0 V. The energy transfer between the quinone structures of the oxidized oligoaniline segments and the excited state of the AIE-active groups would be accountable for the effective fluorescence quenching essence. The PL intensity could restore to its initial state when the applied potential was changed to 0 V. The fluorescence switching contrast ratio was calculated at about 41.7, which is better than previous reports [11-13,22,23,26]. The large fluorescence on/off contrast of PUU film could be ascribed to the effective solid-state emission of AIEgens and high-efficiency electro-modulation of oligoaniline segments, as well as restrained charge transfer effect through a nonconjugated aliphatic chain structure. Furthermore, spectrochronoamperometry was carried out to investigate the detail of EFC behavior for PUU. The fluorescence-emission changes centered at 438 nm were detected through alternative square-wave voltages of 0 and 1.0 V, with a retention time of 15 s. The on/off response speed was calculated around 9.1/9.2 s marked at 90% conversion of fluorescence intensity, shown in magnified EFC switching curves in Fig. 6b. The fluorescence switching



Fig. 6. (a) Fluorescence emission of PUU film under diverse potentials from 0.0 to 1.0 V. (b) Magnified EFC switching cycles and switching times of PUU/ITO electrode. (c) Fluorescent switching stability of PUU film monitored at 438 nm under alternative potentials of 0 and 1.0 V. (d) The optical images of EC/EFC dual-mode device under daylight and UV light.

contrast ratio at the alternative voltages of 0 and 1.0 V declines to 10.5, ascribed to its short residence time in spectrochronoamperometry measurements. After 200 cycles, the PL switching process maintains an 87% modulation range of the original state, which demonstrates the quite good switching durability of EFC performance in Fig. 6c.

Compared with other EC/EFC polymers bearing tetraphenylethylene groups (Table 1), the resultant PUU demonstrates advanced electrooptic behavior with lower onset oxidation potential, high coloration efficiency, moderate EC contrast, and good electrochemical durability, which greatly promote the application of the intelligent materials in the optoelectronics filed.

Given the higher fluorescence on/off contrast ratio, good switching durability, and low switching potentials of its EFC performance, as well as good EC properties, a simple EC/EFC dual-mode device was fabricated by PUU film as shown in Fig. 6d. The components of the gel electrolyte include PMMA, PC, and lithium perchlorate with a mass ratio of 5:10:1. An electrophoretic deposited V_2O_5/ITO electrode was employed as a counter electrode for charge balance during the electrochemical process. The as-assembled device reveals moderate CE of 265 cm² C⁻¹ at 768 nm, an acceptable switching time of 10 s, a large optical contrast of 90% in the visible region (489 nm and 768 nm), and a fluorescence contrast ratio of 9.5. The optical image of reflective and emissive mode was displayed in Fig. 6d. Thanks to the outstanding dualmode electro-optical feature, the prepared PUU material reveals great application potential in smart chemosensors, intelligent displays, and encrypted information devices.

3.6. H_2O_2 visualized determination

H₂O₂ is an important signaling molecule in many diseases and is an

Table	1
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The electro-optic properties of the PUU and reported polymers in the literatures.

Polymer	Ox potential	Cycli-cality	EC		EFC		Ref.	
	E _{onset} (V)		Contrast (%)	T_b/T_c (s)	$CE (cm^2C^{-1})$	on/off time (s)	on/off contrast	
PA-TPE ^a	0.62	100	_	6.7/1.2	127	64.7/4.9	417	[37]
PI5a ^b	0.31	100	87.9	2.04/1.45	-	8.46/0.9	-	[20]
ProDOT-TPE ^c	1.0	10	36	1.5/4.0	-	-	64	[14]
TPA-CN-TPE ^d	1.6	300	-	-	-	7.1	42.1	[15]
TPEOTPA-PA ^e	0.6	200	39	2.6/0.8	385	3.1/1.1	82	[38]
PA7 ^f	0.35	300		1.8/1.1		0.4/2.9	-	[19]
PUU	0.2	200	50.4	8.2/7.8	503	9.1/9.2	41.7	This work

^a An electro-optic polyamide containing diphenylamine-tetraphenylethylene moiety.

^b A polyamides containing tetraphenylethylene unit and triphenylamine.

^c An alternating polymer bearing tetraphenylethylene and 3,3-bis((2-ethylhexyloxy)methyl)-3,4-dihydro-2H-thieno [3,4-b], [1,4]-dioxepine.

^d An aromatic polyamide with tetraphenylethene and triphenylamine moieties.

^e An electro-optic polymer with tetraphenylethylene and triphenylamine units.

^f A polymer containing tetraphenylethylene and tetraphenyl-p-phenylenediamine units.

enzyme-catalyzed outcome [39]. Many enzymatic reactions, such as xanthine and xanthine oxidase, will produce H₂O₂ in metabolism. Up to now, many effective methods for determining H₂O₂ have been developed, among them, the colorimetric and fluorescent methods are more practical owing to their fast responsiveness and simple operation [40-43]. Whereas, the general method focuses on detection with the aid of spectroscopic instruments in the solution state, so that the practicality of visualization is ignored, and the results are susceptible to unexpected factors of concentration of background, the polarity of the solvent, etc. Herein, the fluorescence and colorimetric dual-mode visualization method in form of membrane assay of H2O2 in our design may effectively improve the test repeatability, remove the interference from the background, which makes the detections more accurate and portable. To elaborately investigate the dual-signal sensing of H₂O₂, the as-fabricated PUU-based test strips were studied by means of spectro-analysis firstly. The gradient increase of H₂O₂ content can cause a regular response of both the UV-vis absorption spectra and the PL emission spectra as shown in Fig. 7a and b. With the increase of H₂O₂ concentration from 0 mM to 20 mM, PUU was oxidized correspondingly along with the stepped incremental of the absorption at 405 nm, 489 nm, 768 nm, and gradually attenuate at 325 nm (Fig. 7a). Meanwhile, the appearance of the PUU test strips altered from light gray to dark blue (Fig. 7d). The color for different PUU test strips after the treatment of different H₂O₂ concentrations was quantified using the CIELAB colorspace, whose values were collected and shown in Table 2. The extensive color index changes further prove the reliability of color indication rigorously for H₂O₂ test strips. Besides, the fluorescence intensity decreased gradually with the increase of H_2O_2 concentration (Fig. 7b), ascribed to the fast charge transfer effect between oxidized oligoaniline segments and luminous AIEgens. The PL intensity for the PUU test strip and the H₂O₂ concentration showed a quasi-linear relationship ranging from 0 to 1 mM H₂O₂, which indicates that the portable test strips possessed

excellent fluorescent indicator credentials for the quantitative detection of H_2O_2 (Fig. 7c). The appearance photos of the PUU test strips were captured with the camera instantly, changed continuously from light gray to light blue and dark blue at the maximum concentration of 20 mM H_2O_2 . The blue fluorescence of these PUU test strips was weakening evidently under radiation by UV lamp, which intuitively demonstrated the application prospect of the test strips for H_2O_2 dual-mode detection (Fig. 7d).

4. Conclusions

We have synthesized a novel electroswitchable color/emission dualfunctional electrochromic/electrofluorochromic poly (urea-urethane) bearing AIE-active tetraphenylethylene unit and electroactive oligoaniline derivative. The approving AIE effect, high fluorescence contrast of 41.7, and good electrochemical durability in the EFC process, as well as the desirable electrochromic performance with outstanding CE of 503 cm^2/C , moderate switching speed, and a large optical contrast of 50.4%, demonstrate that PUU was an excellent bifunctional EC/EFC material. The assembled dual-functional device based on PUU and V2O5 also demonstrated a subtle color/emission switching function. Moreover, the PUU test strips exhibit outstanding color/fluorescence dual-mode determination of H₂O₂ by the appearance changing from light gray to dark blue gradient, along with fluorescence changing from light blue to faint. Easy operation, low cost, and reliably visual distinguish could impart this novel polymer to bright application prospects in H₂O₂ fast determination. The dual-sign color/fluorescence test strips would endow novel insights in the convenient and sensitive biological analysis fields.



Fig. 7. (a) UV–vis absorption spectra and (b) PL emission spectra changes of the PUU test strips with different H_2O_2 concentrations. (c) The curve of H_2O_2 concentration vs fluorescence intensity of the PUU test strips. (d) The optical image change of the PUU test strips after treating with different concentrations of H_2O_2 (0–20 mM) under daylight and UV radiation.

Table 2

Colorimetry of these PUU test strips via the oxidation of H_2O_2 with different concentrations in CIELAB space.

	0 μΜ	200 µM	400 µM	600 µM	800 µM	1 mM	2 mM	5 mM	10 mM	20 mM
L*	$26.01 \\ -0.69 \\ -0.23$	18.99	13.82	17.56	16.64	18.06	17.84	18.64	15.67	13.15
a*		3.76	7.19	3.92	3.79	2.47	2.78	2.16	5.69	5.82
b*		0.05	1.58	0.18	0.53	0.07	0.18	-0.13	0.83	2.63

CRediT author statement

Yingchao Zhang: Investigation, Methodology, Writing – original draft. Yunfei Xie: Investigation, Methodology, Formal analysis. Mingjuan Zhou: Investigation, Formal analysis. Erik B. Berda: Writing – review & editing, Formal analysis. Danming Chao: Conceptualization, Writing – review & editing, Supervision, Project administration.

Declaration of competing interest

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

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